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Photochemistry Of Aromatic Thiones And Of Compartmentalized Ketones

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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS RÉCU
PHOTOCHEMISTRY OF AROMATIC THIONES AND OF
COMPARTMENTALIZED KETONES

by

Jorge F. Miranda

Department of Chemistry

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Ontario
March 1985

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ABSTRACT

This thesis is concerned with three main topics. The first of them refers to some mechanistic aspects of the photocyclization of phenyl 1-naphthyl thione (PNT) and related thiones. It was found that for PNT the disappearance quantum yield increases mildly with electron-withdrawing substituents in the para position of the phenyl ring. The transients generated by laser flash photolysis of the thiones are assigned to their triplet states. The triplet of PNT is quenched by oxygen with a rate constant of $2.8 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$.

By monitoring the triplet tetracene generated by energy transfer from PNT excited by a 337 nm-laser, the intersystem crossing quantum yield of the thione could be estimated. The values thus obtained were 0.71 for PNT and 0.65 for phenyl 6-chryseryl thione. It is concluded that the main reason for the disappearance quantum yield being low is not the reversion of an intermediate, but its inefficient formation owing to competing photophysical processes.

Absorption spectroscopy of nitrite esters and carbonyl functions, and $^{13}$C chemical shifts of the oxo-carbon, in substituted dodecanoate micelles appear to indicate the presence of a polar environment in the neighbourhood of the substituent.

Photolysis of 5-nonanone in an urea inclusion compound leads to the formation of Norrish Type II products. The product distribution is different from that formed by irradiation in solution. The cyclization to fragmentation ratio was higher for irradiations in the urea inclusion compound than in solution. One cyclobutanol was formed in the urea inclusion compound, the other was almost entirely absent.
ACKNOWLEDGEMENTS

I am grateful to my supervisor Dr. Paul de Mayo for his guidance, insight, support, patience, and his inspiring commitment to science. I feel very privileged to have come to know a man of his calibre.

I am also grateful to Dr. J.C. Scaiano for making it possible for me to spend an enjoyable term in his laboratory, where the laser flash photolysis and the urea inclusion compounds experiments were performed. I have appreciated his friendship and his ability to make things look attainable. Without their contribution this work could not have been performed.

I acknowledge those who recorded spectra for me: the technical staff at UNO and NRC (MS, GC/MS, $^{13}$C and 100 MHz NMR spectra); Dr. A.P. Roth (SEM); Dr. D. Griller (EPR); Dr. H.L. Casal (Raman). The latter's initiative and continuous interest in the u.i.c. project is appreciated.

I am thankful to Dr. A.C. Weedon for his help during the preparation of compounds, and to Dr. S.K. Hux for valuable encouragement in times of need. J.E. Hux kindly proofread part of this thesis.

I have greatly enjoyed meeting many persons from Canada and various parts of the world during my time in London.
TABLE OF CONTENTS

CERTIFICATE OF EXAMINATION .................................................. II
ABSTRACT .................................................................................. III
ACKNOWLEDGEMENTS .................................................................. IV
TABLE OF CONTENTS ................................................................. V
LIST OF TABLES ........................................................................ XIII
LIST OF FIGURES ........................................................................ XV
LIST OF PHOTOGRAPHIC PLATES ................................................ XVIII

Part I - Photocyclization of diaryl thiones

CHAPTER 1 - INTRODUCTION TO THE PHOTOPHYSICS
AND PHOTOCHEMISTRY OF THIONES ....................................... 1

1.1 Photophysics of thiones ......................................................... 1

1.1.1 Absorption ....................................................................... 2

1.1.2 Decay dynamic of excited thiones .................................... 3

1.1.2.1 The second excited singlet state .................................. 3

1.1.2.2 The first excited triplet state ....................................... 4

1.1.2.3 The first excited singlet state ....................................... 4

1.2 Photochemistry of thiones .................................................... 5

1.2.1 Photocycloadditions ....................................................... 6

1.2.2 Hydrogen abstraction ..................................................... 8

1.2.3 Intramolecular hydrogen abstraction ............................... 9

1.2.4 Photooxidation of thiones by molecular oxygen ............... 11

1.2.5 Conclusions ................................................................. 12

1.3 The photochemical pericyclic cyclization of some polycyclic
aromatic thiones .................................................................. 12
CHAPTER 3 - DISCUSSION OF THE MECHANISM OF PHENYL 1-NAPHTHYL THIONE PHOTOCYCLIZATION

3.1 Possible mechanisms
3.2 The insertion mechanism
  3.2.1 Case 1: negligible reversion of the insertion intermediate
  3.2.2 Case 2b: predominant reversion of the insertion intermediate
  3.2.3 A comparison of case 1 and case 2b
  3.2.4 Consideration of charge transfer states being involved
  3.2.5 Considerations concerning conformations and rotations
3.3 Conclusions

CHAPTER 4 - EXPERIMENTAL OF PART I

4.1 General procedures
4.2 Preparation of para substituted aromatic ketones
4.3 Preparation of para substituted aromatic thiones
4.4 Photocyclization products
4.5 Disappearance quantum yields
4.6 Attempts to observe fluorescence from aromatic thiones
4.7 Laser flash photolysis experiments
4.8 Quenching of the transient of PNT by oxygen
4.9 Intersystem crossing experiments using laser flash photolysis
4.10 Preparation of trans-1,1,4-triphenylbutadiene
Part II - Studies of microenvironments

CHAPTER 5 - INTRODUCTION TO THE PROBLEM OF WATER-HYDROCARBON

CONTACT IN MICELLES ........................................... 89

5.1 Introduction to the subject ................................... 89

5.2 Reports on water-hydrocarbon contact in micelles ............ 91

5.2.1 Reports claiming limited water-hydrocarbon contact ......... 91

5.2.2 Reports claiming extensive water-hydrocarbon contact ..... 95

5.2.2.1 Studies using no probes .................................. 96

5.2.2.2 Studies using intrinsic probes ............................ 98

5.2.2.3 Studies using extrinsic probes ........................... 100

5.3 Difficulties with the use of spectroscopic probes ............. 102

5.4 Models of micellar structure ................................... 107

CHAPTER 6 - RESULTS RELATED TO THE PROBLEM OF WATER-HYDROCARBON

CONTACT IN MICELLES ........................................... 111

6.1 Electronic absorption properties of nitrites ................... 111

6.1.1 Electronic absorption properties of simple nitrites in solvents ........................................... 111

6.1.2 Absorption spectra of simple nitrites in micellar solutions of potassium dodecanoate ....................... 115

6.1.3 Electronic absorption properties of the nitrito substituted potassium dodecanoates ....................... 115

6.1.4 Concentration effect on the absorption properties of nitrito substituted potassium dodecanoates ....................... 117

6.1.5 Other observations concerning alkyl nitrites ................ 118
6.2 Electronic absorption properties of oxo-compounds

6.2.1 Electronic absorption properties of oxo-substituted
dodecanoeic systems and some simple carbonyl compounds

6.2.2 Concentration dependence of the electronic absorption
of oxododecanoates in water

6.2.3 Electronic absorption properties of some carbonyl
containing molecules solubilized in micellar systems

6.3 Carbon-13 chemical shifts of oxo-carbons in micellar
systems

6.4 Proton spin-lattice relaxation rates of potassium
7-oxododecanoate and of potassium 10-oxododecanoate in
deuterium oxide

6.5 Partition of tert-butoxy radicals in micellar solutions

6.6 Lifetimes of some ketone transients in micellar solutions
and quenching of long chain aliphatic ketone triplets by
biphenyl

CHAPTER 7 - DISCUSSION ON THE PROBLEM OF WATER-HYDROCARBON

CONTACT IN MICELLES

7.1 Justification for the use of electronic absorption of nitrites
as polarity probes

7.2 Conclusions from the electronic absorption of nitrites
experiments

7.3 Justification for the use of electronic absorption of carbonyls
as polarity probes

7.4 Conclusions from the electronic absorption of carbonyls
experiments
7.5 Justification for the use of carbon-13 chemical shifts of carbonyls as polarity probes .................................................. 146

7.6 Conclusions from oxo-carbon chemical shift experiments ............ 151

7.7 Discussion on the proton spin-lattice relaxation rates of potassium 7-oxo- and 10-oxo-dodecanoates ..................................... 152

7.8 Partition of tert-butoxy radicals in micellar systems ..................... 153

7.9 Concluding remarks ................................................................ 156

CHAPTER 8 - PHOTODECOMPOSITION OF ALKAMONES IN UREA INCLUSION COMPOUNDS ................................................................. 158

8.1 Introduction ........................................................................... 158

8.2 Results and discussion ........................................................... 160

  8.2.1 Characterization of 5-nanonone/uic ..................................... 162

  8.2.2 Results of photolysis of 5-nanonone/uic ............................... 168

  8.2.2.1 Characterization of photoproducts .................................... 168

  8.2.2.2 Relative yields from 5-nanonone irradiations .................... 177

  8.2.2.3 Determination of the configuration of cyclobutahols ........... 178

  8.2.3 Explanation of the photolysis results .................................. 182

  8.2.4 Some results with 2-undecanone/uic .................................... 184

CHAPTER 9 - EXPERIMENTAL OF PART II ......................................... 190

9.1 Experimental of micellar studies ............................................ 190

  9.1.1 Materials and methods for micellar studies .......................... 190

  9.1.2 Experimental of nitrites .................................................... 190

    9.1.2.1 Preparation of nitrito dodecanoates in micellar potassium dodecanoate ......................................................... 190

    9.1.2.2 Preparation of aqueous nitrito-dodecanoate solutions ....... 191
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1.2.3 Preparation of simple nitriles</td>
<td>191</td>
</tr>
<tr>
<td>9.1.3 Experimental of ketones</td>
<td>192</td>
</tr>
<tr>
<td>9.1.3.1 Preparation of oxo- and hydroxy-dodecanoates and related</td>
<td>192</td>
</tr>
<tr>
<td>compounds</td>
<td></td>
</tr>
<tr>
<td>9.1.3.2 Determination of the critical micelle concentration of</td>
<td>193</td>
</tr>
<tr>
<td>potassium 7-oxododecanoate</td>
<td></td>
</tr>
<tr>
<td>9.1.3.3 Proton spin-lattice relaxation times of potassium 7-oxododecanoate</td>
<td>194</td>
</tr>
<tr>
<td>potassium 10-oxododecanoate in deuterium oxide</td>
<td></td>
</tr>
<tr>
<td>9.1.4 Experimental of di-tert-butyl peroxide</td>
<td>194</td>
</tr>
<tr>
<td>9.1.4.1 Materials</td>
<td>194</td>
</tr>
<tr>
<td>9.1.4.2 Analysis</td>
<td>195</td>
</tr>
<tr>
<td>9.1.4.3 Irradiation of di-tert-butyl peroxide in different media</td>
<td>195</td>
</tr>
<tr>
<td>9.1.4.4 Irradiation of di-tert-butyl peroxide at different concentrations</td>
<td>196</td>
</tr>
<tr>
<td>of sodium dodecyl sulphate</td>
<td></td>
</tr>
<tr>
<td>9.2 Experimental of urea inclusion compounds</td>
<td>196</td>
</tr>
<tr>
<td>9.2.1 Materials</td>
<td>196</td>
</tr>
<tr>
<td>9.2.2 Experimental of 5-nonanone urea inclusion compound</td>
<td>197</td>
</tr>
<tr>
<td>9.2.2.1 Preparation of 5-nonanone urea inclusion compound</td>
<td>197</td>
</tr>
<tr>
<td>9.2.2.2 Scanning electron micrographs</td>
<td>198</td>
</tr>
<tr>
<td>9.2.2.3 Raman spectra</td>
<td>198</td>
</tr>
<tr>
<td>9.2.2.4 Emission from 5-nonanone urea inclusion compound</td>
<td>198</td>
</tr>
<tr>
<td>9.2.2.5 Irradiations of 5-nonanone urea inclusion compound</td>
<td>199</td>
</tr>
<tr>
<td>9.2.2.6 Analysis and characterization of the irradiation products from</td>
<td>199</td>
</tr>
<tr>
<td>5-nonanone urea inclusion compound</td>
<td></td>
</tr>
</tbody>
</table>
9.2.2.7 Laser flash photolysis experiments ..................... 200
9.2.2.8 Electron paramagnetic resonance spectra .............. 200
9.2.3 Experimental of 2-undecanone urea inclusion compound .... 200
9.2.3.1 Preparation of 2-undecanone urea inclusion compound ... 200
9.2.3.2 Irradiation of 2-undecanone urea inclusion compound .... 201
9.2.4 Irradiations of aliphatic ketones in solution .......... 201
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Disappearance quantum yields of para-substituted phenyl 1-naphthyl thione</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>Substituents effects on the disappearance quantum yields of para-substituted phenyl 1-naphthyl thione following $S_1$ irradiation</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>$\rho$ values from disappearance quantum yields of para-substituted phenyl 1-naphthyl thione</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>Effect of viscosity or temperature on phenyl 1-naphthyl thione photocyclization</td>
<td>21</td>
</tr>
<tr>
<td>5</td>
<td>Attempts to observe intermolecular reaction of aromatic thiones with substrates having free peri positions</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
<td>Transient decays of thiones at low temperature</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>Concentration dependence of phenyl 1-naphthyl thione transient decay</td>
<td>44</td>
</tr>
<tr>
<td>8</td>
<td>Quenching of phenyl 1-naphthyl thione transient by oxygen</td>
<td>45</td>
</tr>
<tr>
<td>9</td>
<td>Aromatic thiones intersystem crossing, and quenching by tetracene</td>
<td>59</td>
</tr>
<tr>
<td>10</td>
<td>Electronic absorption properties of potassium 6-nitrito-dodecanoate</td>
<td>117</td>
</tr>
<tr>
<td>11</td>
<td>Electronic absorption properties of potassium 12-nitrito-dodecanoate</td>
<td>117</td>
</tr>
<tr>
<td>12</td>
<td>Electronic absorption properties of potassium 6-oxo-dodecanoate</td>
<td>120</td>
</tr>
<tr>
<td>13</td>
<td>Electronic absorption properties of potassium 10-oxo-</td>
<td></td>
</tr>
</tbody>
</table>
dodecanoate

14 Electronic absorption properties of potassium 7-oxo-
   dodecanoate 121

15 Electronic absorption properties of 4-heptanone in different
   media 124

16 Electronic absorption properties of oxo-compounds in alcohols
   and micelles 124

17 Chemical shift of the oxo-carbon of 6-oxododecanoic acid in
   solvents and aqueous mixtures 126

18 Chemical shifts of the oxo-carbon of some substituted
   potassium dodecanoates at different concentration in water 126

19 Spin-lattice relaxation times of potassium 7-oxododecanoate 133

20 Spin-lattice relaxation times of potassium 10-oxododecanoate 134

21 Irradiation of di-tert-butyl peroxide in hydrogen donating
   micellar systems and other aliphatic liquids 136

22 Irradiation of di-tert-butyl peroxide at different
   concentrations of sodium dodecyl sulphate 137

23 Transient lifetimes of some carbonyl compounds in micellar
   systems 140

24 Values of $k_q$ for the quenching of some aliphatic ketone
   transients by biphenyl 140
<table>
<thead>
<tr>
<th>Fig.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenyl 1-naphthyl thione transient decay at 415 nm in benzene at 25°</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>Phenyl 1-naphthyl thione transient absorption spectrum in benzene at 24°</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>Phenyl 6-chrys enyl thione transient absorption spectrum in benzene at 20°</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>Phenyl 3-fluoranth enyl thione transient absorption spectrum in benzene at 24°</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>Phenyl 1-pyrenyl thione transient absorption spectrum in benzene at 25°</td>
<td>29</td>
</tr>
<tr>
<td>6</td>
<td>Phenyl 1-pyrenyl thione transient decay at 500 nm in benzene at 25°</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>Phenyl 1-naphthyl ketone transient absorption spectrum in methanol at 25°</td>
<td>31</td>
</tr>
<tr>
<td>8</td>
<td>Phenyl 6-chrysenyl ketone transient absorption spectrum in benzene at 25°</td>
<td>32</td>
</tr>
<tr>
<td>9</td>
<td>Phenyl 1-pyrenyl ketone transient absorption spectrum in isooctane at 27°</td>
<td>33</td>
</tr>
<tr>
<td>10</td>
<td>Phenyl 3-fluoranth enyl ketone transient absorption spectrum in isooctane at 23°</td>
<td>34</td>
</tr>
<tr>
<td>11</td>
<td>Para-methoxyphenyl 1-naphthyl ketone transient absorption spectrum in methanol at 22°</td>
<td>35</td>
</tr>
<tr>
<td>12</td>
<td>Para-fluorophényl 1-naphthyl ketone transient absorption spectrum in benzene at 25°</td>
<td>36</td>
</tr>
</tbody>
</table>
Para-chlorophenyl 1-naphthyl ketone transient absorption spectrum in benzene at 25°

Para-methylphenyl 1-naphthyl ketone transient absorption spectrum in benzene at 25°

Phenyl-9,10-dimethyl-2-anthracenyl ketone transient absorption spectrum in benzene at 25°

Phenyl 1-naphthyl thione transient absorption spectrum in methanol at -48°

Para-methoxyphenyl 1-naphthyl thione transient decay at 415 nm, in methanol at -45°

Para-methoxyphenyl 1-naphthyl thione transient absorption spectrum in methanol at -46°

Quenching of phenyl 1-naphthyl thione transient by oxygen, in benzene at room temperature

Absorption spectra of phenyl 1-naphthyl thione, butyrophenone and stock solution of tetracene, in benzene at room temperature

to 24 Triplet tetracene absorption from sensitization

Triplet tetracene top absorbance at 470 nm sensitized by various donors versus tetracene concentration

Absorption spectrum of 4-heptyl nitrite in cyclohexane

Absorption spectra of 6-nitritododecanoic systems in solvents and micellar solutions

Absorption spectra of 12-nitritododecanoate in dodecanoate solution and in solvents
LIST OF PHOTOGRAPHIC PLATES

<table>
<thead>
<tr>
<th>Plate</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Scanning electron micrographs of a 5-nonanone/uic sample</td>
<td>164</td>
</tr>
<tr>
<td>2</td>
<td>Top view photograph of the hexagonal and tetragonal crystals obtained by slow crystallization from methanol of a partially photolyzed 5-nonanone/uic sample</td>
<td>166</td>
</tr>
</tbody>
</table>

***

APPENDIX 1. TRANSIENTS OF SOME TETRAMETHYLCYCLOBUTANES FOLLOWING LASER PHOTOLYSIS ........................................... 202

APPENDIX 2. CARBON-13 CHEMICAL SHIFTS OF SOME OXO-DODECANOIC SYSTEMS ............................................................... 219

APPENDIX 3. FORMULAE RELATING COMPOSITION WITH MOLAR OR MASS RATIO OF UREA IN NONANONE/UREA INCLUSION COMPOUNDS .... 220

APPENDIX 4. EPR OF IRRADIATED 5-NONANONE/UREA INCLUSION COMPOUND .............................................................................. 221

REFERENCES ........................................................................................................................................................................ 223

VITA ...................................................................................................................................................................................... 237
CHAPTER 1 - INTRODUCTION TO THE PHOTOPHYSICS AND PHOTOCHEMISTRY OF THIONES

Considering the great importance that the carbonyl group has had in the development of mechanistic photochemistry, it seemed obvious that there was a need to study the photochemistry of thiones. Despite the fact that the latter are usually reactive, considerable attention has been given to the photophysical and photochemical properties of molecules containing the thiocarbonyl functional group. The effort to study them has proved to be fruitful. Thus, on one hand some photoreactions were found which resemble photoreactions of ketones. On the other hand some photophysical and photochemical properties were found to be considerably different.

One of the reactions which has no analog in ketone photochemistry, is the peri-cyclization of some polycyclic aromatic thiones. The state of knowledge with regards this reaction will be described later; the aim of the first part of this thesis was to make some contribution to the understanding of the mechanism of this photoreaction. However before describing this specific reaction, a short review of the photophysical and photochemical properties of thiones will be given. The emphasis will be almost exclusively on the larger thiones and the examples wherever possible will be taken from the aromatic thiones.

1.1 Photophysics of thiones

Spectroscopic and photophysical properties are important for the understanding of the transitions and states involved before and during a photochemical reaction.
1.1.1 Absorption

In general the absorption spectra of thiones show a long-wavelength absorption band due to a $S_0 \rightarrow S_1$ transition.\textsuperscript{2} For aromatic thiones this has $\lambda_{\text{max}} = 600 \text{ nm}$ and $\epsilon_{\text{max}} = 100 \text{ M}^{-1} \text{ cm}^{-1}$; it has been assigned to an $n\pi^*$ transition. The spin forbidden transition $S_0 \rightarrow T_1$ may also be observed for some thiones at even lower energies and with lower intensity ($\epsilon \approx 8 \text{ M}^{-1} \text{ cm}^{-1}$) which may appear as a shoulder on the more intense $S_0 \rightarrow S_1$ transition.

The $S_0 \rightarrow S_1$ transition, which is responsible for the colour of the thiones, is blue shifted in polar solvents. The band is poorly resolved at room temperature and may overlap the weaker $S_0 \rightarrow T_1$ transition. The resolution improves at low temperature and a vibrational progression of $\approx 1000 \text{ cm}^{-1}$ is observed, close to the frequency of the C=S stretching vibration.\textsuperscript{3} The $S_0 \rightarrow S_1$ transition is forbidden by symmetry; this band system is considered to gain intensity through an $n-\pi$ orbital mixing mechanism or via symmetry-breaking vibrations.\textsuperscript{4-7}

The $S_0 \rightarrow S_2$ band appears at considerably higher energies\textsuperscript{*} than the $S_0 \rightarrow S_1$ band. The $S_0 \rightarrow S_2$ absorption is of high intensity and has been assigned to a $1(\pi\pi^*)$ transition. For thiobenzophenone in ethanol it was found $\lambda_{\text{max}} = 316.5 \text{ nm}$ and $\epsilon = 15800 \text{ M}^{-1} \text{ cm}^{-1}$.\textsuperscript{8-9} Electron donating substituents in substituted benzophenones produce shifts to shorter and longer wavelength of the $n\pi^*$ and $\pi\pi^*$ bands respectively.\textsuperscript{10-11} The $\pi\pi^*$ band is partially resolved into two bands if only one of the rings bears a substituent in the para position.\textsuperscript{10-11} Of these two, the band shifted to longer wavelength is considered to involve predominantly the substituted ring; the other can likewise be shifted to longer wavelengths if
the second ring is also substituted by electron withdrawing substituents in the para position.

1.1.2 Decay dynamics of excited thiones

It can be observed from the transitions mentioned above that the energy separation between $S_2$ and $S_1$ is large; a factor that has great influence on the photophysical properties of these thiones. Thus, as far as radiative transitions are concerned, it was observed that for large thiones emission appears to occur only from $S_2$ (fluorescence) and from $T_1$ (phosphorescence).

1.1.2.1 Second excited singlet ($S_2$)

Several larger thiones were found to fluoresce from their second excited state with a quantum yield of around 0.01-0.001. This may be due to the large energy gap between the first and second excited singlet states $\Delta E(S_2-S_1)$. For azulene and its derivatives it was observed that the smaller the energy gap the smaller the fluorescence quantum yield. This was taken to imply that the non-radiative rates became faster, the Franck-Condon factor being larger.

For xanthione in 3-methylpentane, use of the measured fluorescence quantum yield from $S_2$ (0.0051) and the $k_{rad}$ of $1.05 \times 10^8\ s^{-1}$ for the radiative rate constant, calculated from absorption, led to a rate constant, for the non-radiative decay ($k_{nr}$) from $S_2$, of $2 \times 10^{10}\ s^{-1}$. Aralkyl-thiones had longer fluorescence lifetimes, typically $\tau_f = 0.4\ ns$ and fluorescence quantum yields $\Phi_f = 0.05; k_{rad} = 1.1 \times 10^7\ s^{-1}$ and $k_{nr} = 3 \times 10^9\ s^{-1}$. It appears that the internal conversion $S_2 \rightarrow S_1$ is the most important deactivation pathway for $S_2$, although the intersystem crossing ( isc) to
a $T_n$ state is not easy to rule out completely.$^3,13$

1.1.2.2 **First excited triplet** ($T_1$)

The other state from which thiones were found to emit was the lowest triplet ($n\pi^*$). At room temperature the phosphorescence quantum yields of some aromatic thiones were $\Phi_p = 0.023$ or less.$^{15}$ The $\Phi_p$ increased at low temperature, e.g. $\Phi_p = 0.11$ for xanthione in 3-methylpentane at 77 K.$^4$ At least for xanthione the main unimolecular deactivation pathway of $T_1$ was found to be the isc from $T_1$ to $S_0$ with a rate constant of $\approx 2 \times 10^4 \text{ s}^{-1}$ at 77 K.$^{13}$

In fluid solution a near diffusion controlled quenching of the triplet thione by ground state thione occurred.$^{16-17}$ The self-quenching was attributed in the case of xanthione to the formation and radiationless decay of a triplet exciplex.

1.1.2.3 **First excited singlet** ($S_1$)

No fluorescence has been observed from the $S_1$ state of large aliphatic or aromatic thiones. Rapid deactivation by intersystem crossing to the $T_1$ state is likely taking place, as suggested by the high quantum yields of isc, which approaches unity. The various estimations of the quantum yield of intersystem crossing $\Phi_{ST}$ were as follows:

a) Adamantanethione when irradiated into the $S_0 \rightarrow S_1$ band added to olefins to give a thietane. Under the same conditions of thione and olefin concentration the direct irradiation produced the thietane with the same quantum yield, within experimental error, as the sensitized irradiation using as triplet sensitizer benzophenone and Michler's ketone which have $\Phi_{ST} = 1$. It was concluded that direct irradiation produced triplet adamantanethione with $\Phi_{ST} = 1.2^{21-23}$
b) Xanthione in 3-methylpentane at 77 K emits following $S_0^+S_1$ excitation with a measured emission lifetime of $(43 \pm 5) \mu$s. In reasonable agreement, a value of $50 \mu$s was calculated from the oscillator strength of its $S_0^+T_1$ transition, the $\Phi_p = 0.11$ and the assumption of $\Phi_{ST} = 1.4$. This agreement led to the conclusion that the isc from $S_1$ is the only significant deactivation pathway from that state. $^3$

c) Thioureaone phosphorescence was observed at 77 K following excitation into the 0-0 bands of $S_1$ and $T_1$. The intensity of phosphorescence was proportional to the molar extinction coefficient of these 0-0 bands, implying $\Phi_{ST} = 1.5$.

d) The same method was used for xanthone at 295 K. $^6$ Here again the coincidence of the phosphorescence excitation spectrum, including the $T_1^+S_0$ band, with the absorption spectrum, suggested $\Phi_{ST} = 1$.

e) A similar method, based on successive selective excitations into the $S_0^+S_1$ and $S_0^+T_1$ bands and the measurement of the resultant phosphorescence ratio, was used for a few more thiones. The results, reported to have $\pm 15\%$ of instrumental error, are reproduced in the following table.

<table>
<thead>
<tr>
<th>THIONE</th>
<th>$\Phi_{ST}$</th>
<th>SOLVENT</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="thione" /></td>
<td>0.72</td>
<td>3-methylpentane (3-MP)</td>
</tr>
<tr>
<td><img src="image" alt="thione" /></td>
<td>0.70; 0.74; 0.79</td>
<td>3-MP, 1-Cl- and 1-Br-butane</td>
</tr>
<tr>
<td><img src="image" alt="thione" /></td>
<td>0.95</td>
<td>3-methylpentane</td>
</tr>
</tbody>
</table>
These $\Phi_{ST}$ were calculated from the relationship

$$\frac{I_p}{I_0} \ rac{\epsilon}{\epsilon'} = \Phi_{ST}$$

where prime stands for the $S_0 \rightarrow T_1$ irradiation case.\textsuperscript{19}

The intersystem crossing rate of xanthone in 3-methylpentane was estimated to be $>10^{11}$ s$^{-1}$.\textsuperscript{13,20}

1.2 Photochemistry of thiones

1.2.1 Photocycloadditions

Thiobenzophenone was found to react with olefins when irradiated by light. The wavelength of excitation and the type of substituents (electron withdrawing or releasing) influenced the course of the reaction. With electron-deficient olefins the reaction following irradiation into the $S_2$ band of thiobenzophenone yielded thietanes.\textsuperscript{21-23} The reaction of thiobenzophenone with cyanoethylene was studied in detail.

\[
\begin{align*}
\text{Ph} = S & \quad \xrightarrow{-70^\circ \pi\pi^*} \quad \text{Ph} = S \quad \xrightarrow{20^\circ \pi\pi^*} \\
\text{Ph} + \text{CN} & \quad \xrightarrow{\pi\pi^*} \quad \text{Ph} \quad \text{Ph} + \text{CN} \quad \text{Ph} \quad \text{Ph} + \text{CN}
\end{align*}
\]

The reaction from the $\pi\pi^*$ band at $-70^\circ$ gave the 1,3-dithiane which at room temperature decomposed quantitatively to the thietane. The reaction was regiospecific with acrylonitrile but there was a lack of regiospecificity with crotononitrile. It was also stereospecific, as demonstrated during the addition of 1,2-dicyano or 1,2-dichloroethylene.

Irradiation into the $\pi\pi^*$ led to different results (see previous
The triplet $n\pi^*$ was the reactive state, as suggested by the quenching by cyclooctatetraene and other triplet quenchers.

Two other aromatic thiones, thioxanthione and xanthione were also found to add to electron-deficient olefins. The reaction was stereospecific from $T_1.2^{4}$

Electron-rich olefins also underwent cycloaddition to excited thio-benzophenone$^{27-31}$ (scheme below). Based on the fact that the quantum yield was invariant with wavelength and that cis-trans isomerization was observed in the recovered olefin it was concluded that $T_1$ was the reactive state. The reactions were regiospecific but nonstereospecific.

Aliphatic thiones (scheme below) also underwent photocycloaddition

$X = CN, OEt$

$X = CN$
to both electron-rich and electron-deficient olefins upon $S_1$ or $S_2$ irradiation. For adamantane thione it was found that $S_2$ and $T_1$ were the reactive states upon irradiation at short and long wavelength, respectively. The reaction from $T_1$ was nonstereospecific but regiospecific and occurred with much lower quantum yield. The reaction from $S_2$ in turn was stereospecific but nonregiospecific.

Dimerization of adamantane thione was always observed to give 1,3-dithiane. The quantum yields for dimerization were very different, around $10^{-4}$ from $T_1$ and $= 0.2$ from $S_2$, for a 0.2 M solution.

A general reaction which was observed to occur only on $S_2$ irradiation was the addition to the nitrile function. The reaction proceeded with several thiones, aliphatic and aromatic, as well as with several nitriles.

$$
\begin{align*}
\text{S} + \text{RCN} &\rightarrow \text{S}_2 \rightarrow \left[ \begin{array}{c}
\text{S} \\
\text{N}
\end{array} \right] \\
&\rightarrow \text{SNR}
\end{align*}
$$

1.2.2 Hydrogen abstraction

Excited thiobenzophenone reacted with ethanol, 2-propanol and other alcohols as follows:\n
$$
\begin{align*}
\text{Ph}_2\text{C}=\text{S} \xrightarrow{hv} &\text{Ph}_2\text{HSCHSCHPh}_2 + \text{Ph}_2\text{CHSH} + \text{Ph}_2\text{CH}_2 + \\
&\text{(68\%)} \quad \text{(16\%)} \\
&\text{Ph}_2\text{CHSCHPh}_2 + \text{Ph}_2\text{CH(SS)CPh}_2
\end{align*}
$$

The same mixture was said to be obtained following irradiation into $S_2$ or $S_1$, but the disappearance was slower from the n$\pi^*$ state. The reaction in cyclohexane was extremely slow from $S_1$ but faster from $S_2$. It was also shown that photoreduction by the n$\pi^*$ state of aromatic thiones required that the C-H bond be weakened for example by oxygen.
substitution or the introduction of unsaturation.\(^2\)

The photoreduction of adamantanethione in cyclohexane was studied in detail.\(^{35-36}\)

\[
\text{ adamantanethione } \xrightarrow{254 \text{ nm}} \text{ 1,3-dithietane} + \text{ 2-adamantyldisulphide}
\]

1,3-dithietane and 2-adamantyldisulphide were also formed. Mechanistic studies indicated that the insertion products were formed in part by hydrogen abstraction and radical recombination inside the solvent cage.\(^{36}\) About half of the radical-pairs combined to form insertion products; the other half disproportionated to starting material. Escape was only a minor process. A rate constant of \(1.3 \times 10^8 \text{ M}^{-1} \text{s}^{-1}\) was found for the hydrogen abstraction by the S\(_2\) of adamantanethione from cyclohexane.

In contrast, irradiation of adamantanethione in cyclohexane at \(\lambda > 500\) nm gave only 1,3-dithiane.\(^{18}\) However, when the irradiation was done in the presence of the good hydrogen donor, 2-adamantanethiol, the product formed was \(\text{bis-}(2\text{-adamantyl})\text{disulphide}\). The reactive state was T\(_1\). The quantum yield was high (1 - 4). Electron paramagnetic resonance (EPR) spin trapping by t-butylnitroxide and deuterium labelling studies showed the involvement of a radical chain mechanism.\(^{37}\)

1.2.3 Intramolecular hydrogen abstraction

Several examples of intramolecular hydrogen abstraction have been reported. For example, o-benzylthiobenzophenone was not photoreduced at long wavelength to the mercaptan and disulphide even when the solvent was ethanol, a hydrogen donating solvent. This 'photostability' was due
to intramolecular hydrogen abstraction.

\[
\begin{array}{c}
\text{Ph} \\ \text{Ph}
\end{array} \overset{589 \text{nm}}{\Delta} \rightarrow
\begin{array}{c}
\text{Ph} \\ \text{H}
\end{array} \rightarrow
\begin{array}{c}
\text{MeOD} \\ \text{MeOH}
\end{array} \rightarrow
\begin{array}{c}
\text{Ph} \\ \text{H}
\end{array} \overset{\Delta}{\rightarrow}
\begin{array}{c}
\text{Ph} \\ \text{D}
\end{array}
\]

Many aralkyl thiones when irradiated into the \( S_2 \) band gave the corresponding cyclopentylthiols,\textsuperscript{39} with a quantum yield of the order of \( 10^{-2} \).

\[
\begin{array}{c}
\text{Ph} \\ \text{S}
\end{array} \rightarrow
\begin{array}{c}
\text{Ph} \\ \text{S}
\end{array}
\]

From \( S_1 \), in turn, the disappearance quantum yield was only \( 10^{-5} \), which excluded \( S_1 \) as the reactive state upon \( S_2 \) irradiation. Triplets were also excluded as reactive states for the \( \delta \)-hydrogen abstraction, since the abstraction was not quenched by over 2 \( M \) piperylene (triplet energy \( E_T = 243 \text{ kJ mol}^{-1} \) and was not sensitized by some triplet donors with triplet energies between 285 kJ mol\(^{-1}\) and 234 kJ mol\(^{-1}\). Furthermore the reaction was quenched by biacetyl (by singlet energy transfer). The lifetime obtained from quenching of product formation by biacetyl was \( \approx 0.17 \text{ ns} \), comparable with the measured fluorescence decay lifetime \( = 0.3 \text{ ns} \).\textsuperscript{41} It was concluded therefore that \( S_2 \) was the reactive state.

The overall unimolecular rate constant for formation of cyclopentyl thiol was of the order of \( 10^8 \text{ s}^{-1} \).\textsuperscript{42}

\( \varepsilon \) and \( \gamma \) insertion was observed when the \( \delta \) position was blocked by oxygen.\textsuperscript{40}
Other thiones underwent β-hydrogen abstraction.\(^\text{43}\)

\[
\begin{align*}
\text{Ph} & \quad \begin{array}{c} \text{X} \end{array} \quad \xrightarrow{\text{S}_2 \text{ or } S_1} \quad \begin{array}{c} \text{Ph} \end{array} \quad \begin{array}{c} \text{SH} \end{array} \quad \begin{array}{c} \text{X} \end{array}
\end{align*}
\]

where \(X = \text{Ph}, \text{CH}_3\text{S}\) and \(1\)-naphthyl.

Cyclopropyl thiols were also produced by photolysis of bridged systems,\(^{44-45}\) e.g.

\[
\begin{align*}
\text{R} & \quad \begin{array}{c} \text{S} \end{array} \quad \xrightarrow{\Delta} \quad \begin{array}{c} \text{SH} \end{array} \quad + \quad \begin{array}{c} \text{R} \end{array} \quad \begin{array}{c} \text{SH} \end{array} \quad + \quad \begin{array}{c} \text{R} \end{array} \quad \begin{array}{c} \text{S}^{-} \end{array} \quad + \quad \begin{array}{c} \text{R} \end{array} \quad \begin{array}{c} \text{SH} \end{array}
\end{align*}
\]

\[\text{R} = (\text{CH}_2)_n \text{CH}_3 \quad n = 1-3\]

1.2.4 \textbf{Photooxidation of thiones by molecular oxygen}

Oxidation by air and light was the first reported reaction of thiones.\(^{46}\) The products, isolated later, were the corresponding ketone and sulphine. With aromatic thiones the ketone was obtained in high yield. The disappearance quantum yields were high (0.2 to 0.5, at an initial thione concentration of 0.006 M). Singlet oxygen was postulated to be generated and to react with the thione during photolysis, and the following simplified mechanism was proposed and discussed.\(^{47-50}\)

\[
\begin{align*}
\{\text{C=S}\} & \quad \xrightarrow{h\nu} \quad \text{3}(\{\text{C=S}\}) \\
\text{3}(\{\text{C=S}\}) + \text{3}_2 & \quad \xrightarrow{} \quad \{\text{C=S} + \text{1}_2\} \\
\{\text{C=S} + \text{1}_2\} & \quad \xrightarrow{} \quad \{\text{C=O} + \text{SO}_2\} \quad \text{(or } \{\text{C=S=O}\})
\end{align*}
\]

This view was supported by two kinds of observations. Firstly, the photooxidation was quenched in the presence of well-known singlet oxygen quenchers like 2,3-dimethyl 2-butene (with the corresponding formation
of allylic hydroperoxide. Secondly, the oxidation was also produced by singlet oxygen generated by dye sensitization or by thermal decomposition of triphenylphosphite ozonide. Oxidation was also achieved by ozonolysis of the thiones.

1.2.5 Conclusions

Wavelength dependent photochemistry is a common feature of thione photochemistry. The second singlet (S₂) and/or the first triplet (T₁) are typically the reactive states.

Reactions from T₁ are usually nonstereospecific and regiospecific. Quenching of T₁ by ground-state thione is also able to trap the intermediates formed.

The S₂ state reactions lead to formal insertion into a C-H bond, both inter- and intramolecularly. Reactions are nonregiospecific but stereospecific.

1.3 The photochemical peri-cyclization of some polycyclic aromatic thiones

1.3.1 Introduction

It can be said from the review of the photophysics and photochemistry of large thiones that the states from which emission or chemical reaction take place are the S₂ and T₁.

There is however one documented case of participation of the S₁ state of a thione in a photochemical reaction.¹

1.3.2 Review

It has been found by de Mayo et al. that a number of polycyclic aromatic thiones in which there was a free peri position, cyclized on
excitation into the $S_1$ band. An example is the reaction that follows.

\[
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic} \\
\text{Cyclic}
\end{array}
\xrightarrow{>500\text{nm}}
\begin{array}{c}
\text{S} \quad \text{H} \\
\text{Ph} \\
\text{Cyclic}
\end{array}
\]

By an analogous photoreaction the following products were formed.

\[
\begin{array}{c}
\text{S} \quad \text{H} \\
\text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{H} \\
\text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{H} \\
\text{Ph} \\
\text{Cyclic}
\end{array}
\]

Although having a free peri position, the aromatic thiones below did not photocyclize.

\[
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\end{array}
\end{array}
\]

Two thiones in which the thiocarbonyl group was remote from the peri position did not undergo photocyclization.

\[
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\quad
\begin{array}{c}
\text{S} \quad \text{Ph} \\
\text{Cyclic}
\end{array}
\]

The absorption spectra at room temperature and at 77 K, as well as the emission spectra at 77 K for all these thiones were also reported. For those thiones which presented detectable emission, the emitting state was assigned to be the lowest excited triplet state, $^3(n\pi^*)$, based on the spectral position and similarity to the emission from other
thiones. Only in the case of phenyl 2-naphthyl thione were both the emission and the lifetime of emission at 77 K reported. This thione, following excitation at 390 or 550 nm in EPA at 77 K, showed emission between 670 nm and 850 nm (emission maximum at $14.4 \times 10^{3}$ cm$^{-1}$) with a lifetime of 66 $\mu$s. The emission of the other thiones at 77 K was weaker and occurred at slightly lower energies. In particular phenyl 1-naphthyl thione presented emission at 77 K from which a triplet energy of 164 kJ mol$^{-1}$ was derived.

The mechanism was investigated in some detail in the case of phenyl 1-naphthyl thione (PNT) by the same workers. Their observations can be summarized as follows:

1) The quantum yield of product formation following excitation into $S_1$ was estimated to be $\approx (1.2 - 3) \times 10^{-3}$ depending on the solvent.

2) When the solvent was D$_2$O/MeCN (1:20 by volume), irradiation into $S_1$ caused complete deuteration at the benzylic position of the photocyclized product, based on the absence of the benzylic proton signal in the $^1$H-NMR ($\approx 6.2$ ppm) and on mass spectrometry.

3) Use of perylene or cyclooctatetraene as quencher left the product quantum yield unchanged. In contrast the transient of $\tau = 10^{-7}$ s lifetime, generated by laser flash photolysis and monitored at 550 nm, was quenched by cyclooctatetraene with a $k_q$ of $\approx 2 \times 10^9$ M$^{-1}$ s$^{-1}$ in benzene. This led to the conclusion that the reaction is not from the triplet but from the singlet $S_1$.

4) Small changes in the quantum yield of photocyclization ($\Phi_c$) of PNT were observed as the solvent system was changed.
1.3.3 Subsequent studies of related hydrocarbons photocyclizations

Lapouyade et al. continued the study of photocyclizations but using olefins rather than thiones;\textsuperscript{51-54} they are mentioned here for comparative purposes. Their results can be summarized in the following reaction schemes (rate constants are in s\textsuperscript{-1})

\[
\begin{align*}
\text{a)} & \quad X=Y=H \\
\text{b)} & \quad X=H, \ Y=\text{OME} \\
\text{c)} & \quad X=\text{OME}, \ Y=H \\
\end{align*}
\]

\[
\frac{\phi_{\text{prod}}}{} \text{ in } \text{C}_{6}H_{12} \quad 0.005(0.12) \quad 0.014(0.02) \\
\text{in MeOH} \quad 0.002(0.25) \quad 0.008(0.004) \\
\text{(parenthesis values: 0.22 M Et}_{3}\text{N present)}
\]

\[
\tau_{s} = 2.5 \text{ ns} \quad \phi_{ST}^{TX} = 0 \quad \tau_{X} > 1 \text{ s}
\]
Singlet
- $\tau_f = 4 \text{ ns}$
- $\phi_f = 0.09$
- $k_f = 2.25 \times 10^7$
- $k_{SG} = 1.6 \times 10^8$
- $k_{ST} = 1.3 \times 10^7$
- $\phi_{ST} = 0.05$
- $k_{SX} = 5.2 \times 10^7$
- $\phi_{SX} = 0.21$

Triplet
- $\tau_T = 1.75 \mu s$
- $k_{TG} = 2.4 \times 10^5$
- $k_{TX} = 3.3 \times 10^5$
- $\phi_{TX} = 0.58$

Intermediate
- $\tau_X = 6.1 \text{ ms}$
- $k_{XP} = 1.6 \times 10^2$
- $\phi_{XP} = \dagger$
CHAPTER 2 - RESULTS AND INTERPRETATION OF RESULTS FROM THIONES

2.1 Effect of para substituents

In the first place the influence of substituents in the para position of the thiobenzoyl group on the photocyclization was investigated. This was prompted primarily by the lack of information concerning the type of intermediate involved, i.e. whether it was purely a biradical intermediate or a species with considerable charge transfer.

Therefore, some thiones bearing a substituent in the p-position were prepared. The quantum yields of disappearance of these substituted thiones were then measured (Table 1).

<table>
<thead>
<tr>
<th>R</th>
<th>$10^3$ [Th]/M</th>
<th>$\lambda_{irr}$/nm</th>
<th>$\lambda_{mon}$/nm</th>
<th>$\epsilon_{mon}$/M$^{-1}$cm$^{-1}$</th>
<th>$\phi_{dis}$/10$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>8.46</td>
<td>362</td>
<td>608</td>
<td>151</td>
<td>2.11</td>
</tr>
<tr>
<td>F</td>
<td>8.27</td>
<td>620</td>
<td>620</td>
<td>143</td>
<td>2.05</td>
</tr>
<tr>
<td>F</td>
<td>7.35</td>
<td>362</td>
<td>608</td>
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<tr>
<td>OMe</td>
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<td>620</td>
<td>620</td>
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</tr>
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<td>596</td>
<td>596</td>
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<td>6.71</td>
<td>362</td>
<td>596</td>
<td>149</td>
<td>4.66</td>
</tr>
</tbody>
</table>

$\lambda_{irr}$: center of the irradiation band; $\lambda_{mon}$: monitoring wavelength; $\epsilon_{mon}$: molar extinction coefficient at $\lambda_{mon}$; $[\text{Th}]$: thione concentration in mol/L.
The disappearances were monitored spectrophotometrically at long wavelengths, around = 600 nm, where only the thione absorbed.

From Table 1 it can be seen that the quantum yields do not differ by more than a factor of 6 (or of 4 for long wavelength irradiations).

The quantum yield of disappearance of a given thione is somewhat larger when the excitation is into the $S_2$ instead of the $S_1$ band. The reason for this was not investigated. It was not determined whether the reaction can occur directly from $S_2$ as well or not, primarily due to the difficulty of finding an appropriate quencher for the $S_1$ state. In view of this, primarily the irradiations done directly into $S_1$ will be considered when comparing quantum yields, but all values will be reported.

In Table 2, the disappearance quantum yields of para-substituted

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SUBSTITUENTS EFFECT ON $\Phi_{\text{dis}}$</strong></td>
</tr>
<tr>
<td>of para-substituted PNT following $S_1$ irradiation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R</th>
<th>$\sigma$</th>
<th>$\sigma^+$</th>
<th>$\Phi_{\text{dis}}/10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>.23</td>
<td>.11</td>
<td>2.79</td>
</tr>
<tr>
<td>F</td>
<td>.06</td>
<td>-.07</td>
<td>2.05</td>
</tr>
<tr>
<td>Me+</td>
<td>-.17</td>
<td>-.31</td>
<td>1.90</td>
</tr>
<tr>
<td>MeO</td>
<td>-.27</td>
<td>-.78</td>
<td>0.78</td>
</tr>
</tbody>
</table>

PNT following $S_1$ irradiation are collected. It can be seen there that the disappearance quantum yields are increased by electron-withdrawing substituents and decreased by electron-donating substituents.

A well known way of correlating rate constants $k$ with substituent
parameters $\sigma$ is by the Hammett relationship, i.e. $\log k = \rho \sigma + \text{const.}$, where the slope $\rho$ is a measure of the sensitivity of the reaction to the effects of substituents.

Strictly speaking rate constants (or equilibrium constants) should be used in the Hammett equation. However, since they are not available for this reaction, it is worth trying to make a correlation using $\log \Phi_{\text{dis}}$ instead of $\log k_{\text{dis}}$. The same $\rho$ will be obtained if the disappearance quantum yields are proportional to the rate constant (or combination of rate constants) associated with the disappearance of the thione.

Using the results from Tables 1 and 2 least square fittings to straight lines give the following (Table 3),

<table>
<thead>
<tr>
<th>Irrad. Band</th>
<th>Parameter</th>
<th>$\rho$</th>
<th>corr. coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>$\sigma$</td>
<td>$1.0 \pm 0.3$</td>
<td>0.887</td>
</tr>
<tr>
<td>$S_1^*$</td>
<td>$\sigma^*$</td>
<td>$0.62 \pm 0.07$</td>
<td>0.984</td>
</tr>
<tr>
<td>$S_1S_2$</td>
<td>$\sigma$</td>
<td>$1.0 \pm 0.3$</td>
<td>0.798</td>
</tr>
<tr>
<td>$S_1S_2^*$</td>
<td>$\sigma^*$</td>
<td>$0.67 \pm 0.1$</td>
<td>0.897</td>
</tr>
</tbody>
</table>

The last two rows were included for the sake of completeness, even though as discussed earlier it is best to use only results from direct irradiations into the reactive state $S_1$. The $\rho$ values do not change very much, however, if the values from the $S_2$ irradiations are included, although the correlation becomes poorer.

Considering the values from the $S_1$ irradiations a value of $\rho = 1$ is obtained using $\sigma$ parameters and a value of $\rho = 0.62$ if $\sigma^*$ parameters are
used. The $\rho$ value is positive, consistent with the disappearance reaction being increased by electron-withdrawing substituents.

The correlation improves when $\sigma^+$ constants are used instead of $\sigma$. If this improvement is considered to be significant it may suggest that there is resonance interaction between the substituent and the reaction sites.

The magnitude of $\rho$ is a measure of the sensitivity of a given reaction to the substituent effects. It has a value of 1 for the reaction used as reference, the dissociation of benzoic acid in water. Here for the disappearance of the thione a value of $\rho = 1$ is obtained, based on the use of $\Phi_{\text{dis}}$ and $\sigma$ (or $\rho = 0.62$ if $\sigma^+$ is used). This value is significant yet not large enough to lead to immediate conclusions. To discuss this further one should consider which steps are involved in the disappearance reaction. This will be done later when the mechanism of the reaction is discussed.

2.2 Effect of lowering the temperature

PNT was irradiated in a few solvent systems both at room temperature and at low temperature (see Table 4). The photoreaction can be stopped under certain conditions. As can be observed from the results in Table 4, the effect seems more directly related to the viscosity of the medium than to the temperature itself, e.g. at $-80^\circ$ the reaction proceeds in methylicyclohexane where the medium is still fluid, but it does not occur in triacetin which is rigid at that temperature.
### Table 4

**EFFECT OF VISCOSITY OR TEMPERATURE ON PNT PHOTOCYCLIZATION**

<table>
<thead>
<tr>
<th>PNT</th>
<th>Reaction Conditions</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>26 hr λ &gt; 360 nm \ MCH; room temperature</td>
<td>Bleached</td>
<td></td>
</tr>
<tr>
<td>37 hr λ &gt; 360 nm \ Me-c-Hexane (MCH); -80°</td>
<td>Bleached</td>
<td></td>
</tr>
<tr>
<td>22 hr λ &gt; 360 nm \ Benzene; 60–80°</td>
<td>Bleached</td>
<td></td>
</tr>
<tr>
<td>32 hr λ &gt; 360 nm \ Triacetin; 37°</td>
<td>Bleached</td>
<td></td>
</tr>
<tr>
<td>7 days λ &gt; 360 nm \ Triacetin; -80°</td>
<td>No Reaction</td>
<td></td>
</tr>
<tr>
<td>25 hr λ &gt; 360 nm \ MCH/3-MP (1:1); -196°</td>
<td>No Reaction</td>
<td></td>
</tr>
</tbody>
</table>

### 2.3 Absence of reaction of thiones with other aromatic hydrocarbons

The possibility of intermolecular insertion of the excited thione into the peri position of some aromatic hydrocarbons was considered. Among the aromatic hydrocarbon substrates, naphthalene and chrysene were included, because they were the parent hydrocarbons of two thiones that are known to undergo photocyclization. Halogenated naphthalenes were used because they are liquids at room temperature and do not require added solvent. Also, naphthalene itself was used above its melting point as neat solvent under vacuum.

The thiones were chosen from those that were known not to photocyclize by themselves, since the interest at this point was to test for
intermolecular insertion.

The results show that no overall reaction takes place between the excited thiones and aromatic hydrocarbons (Table 5).

| Phenyl 3-fluoranthenyl thione | $\xrightarrow{1 \text{ M Naphthalene}}$ 20 days | No Reaction |
| Phenyl 3-fluoranthenyl thione  | $\xrightarrow{\text{Naphthalene (neat, melt)}}$ $100^\circ$; 47 hr / Pyrex | No Reaction |
| Thiobenzophenone              | $\xrightarrow{1 \text{ M Naphthalene}}$ 10 days | No Reaction |
| Thiobenzophenone              | $\xrightarrow{0.12 \text{ M Anthracene}}$ 7 days | No Reaction |
| Thiobenzophenone              | $\xrightarrow{0.062 \text{ M Chrysene}}$ 7 days | No Reaction |
| Thiobenzophenone              | $\xrightarrow{1\text{-Chloronaphthalene (neat)}}$ 7 days | No Reaction |
| Thiobenzophenone              | $\xrightarrow{1\text{-Bromonaphthalene (neat)}}$ 7 days | No Reaction |

Conditions (unless otherwise indicated): $\lambda_{irr} > 520$ nm, room temperature, benzene as solvent.

2.4 Transient absorption spectroscopy of aromatic thiones

2.4.1 Transient spectra and decay of thiones at room temperature

The aromatic thiones were studied by laser flash photolysis. Gene-
rally speaking all of them produced transients which presented weak and very broad absorption bands. The absorption by the transients of PMT and other aromatic thiones are reproduced in Figures 2 to 5 and some of the decay curves are reproduced in Figures 1 and 6.

The values found here for the transient decays should be compared with the phosphorescence studies of other aromatic thiones at room and low temperature. Their non-radiative decay constants were found to be of the order of $10^5 \text{s}^{-1}$ for inflexible thiones, which showed phosphorescence even at room temperature, whereas thiones capable of higher amplitude vibrations or group rotation had triplet non-radiative decay constants which were large enough ($> 10^7 \text{s}^{-1}$) to dominate the triplet decay.

Our thiones, capable of group rotation, do not phosphoresce at room temperature, but likely decay non-radiatively with rate constants of $> 10^7 \text{s}^{-1}$, consistent with the above observations. Therefore, based only on the comparison just made, the transients observed here by laser flash photolysis are tentatively assigned to the lowest triplet of the thione. Some more evidence supporting this assignment will be described later.

2.4.2 Transient spectra of related aromatic ketones

The absorption spectra of the transients of the aromatic ketones corresponding to the thiones used in this work and by Lapouyade, are included for comparative purposes in Figures 7 to 15. The transients from these ketones give much more intense signals and their lifetimes are longer than the corresponding thiones. This provides more examples of how much, in going from ketones to the corresponding thiones, the non-radiative decay of the triplets may vary.
2.4.3 Transients and decays of thiones at low temperature

The decay of the transient of PNT (5.6 x 10^{-5} M) in methanol was followed as well at low temperature (≈ 227 K). The results are reproduced in Table 6 and the spectrum is reproduced in Figure 16.

It should be noticed that the lifetime of the transient of PNT becomes longer at lower temperature (Table 6).

<table>
<thead>
<tr>
<th>Thione</th>
<th>Solvent</th>
<th>Temp./K</th>
<th>λ_{mon}/nm</th>
<th>k/s^{-1}</th>
<th>τ/ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNT</td>
<td>Methanol</td>
<td>226.3</td>
<td>415</td>
<td>5.84 x 10^6</td>
<td>171</td>
</tr>
<tr>
<td>PNT</td>
<td>Methanol</td>
<td>227.6</td>
<td>720</td>
<td>5.97 x 10^6</td>
<td>168</td>
</tr>
<tr>
<td>p-MeO-PNT</td>
<td>Methanol</td>
<td>227.8</td>
<td>415</td>
<td>5.16 x 10^6</td>
<td>193</td>
</tr>
<tr>
<td>p-MeO-PNT</td>
<td>Methanol</td>
<td>227.8</td>
<td>720</td>
<td>4.87 x 10^6</td>
<td>205</td>
</tr>
<tr>
<td>p-Me-PNT</td>
<td>Methanol</td>
<td>225.3</td>
<td>415</td>
<td>2.44 x 10^7</td>
<td>41</td>
</tr>
<tr>
<td>p-Me-PNT</td>
<td>Methanol</td>
<td>225.3</td>
<td>720</td>
<td>2.18 x 10^7</td>
<td>46</td>
</tr>
<tr>
<td>Ph-fluoranthenylTh.</td>
<td>Toluene</td>
<td>227.5</td>
<td>500</td>
<td>5.22 x 10^7</td>
<td>19</td>
</tr>
</tbody>
</table>

At low temperature also it can be seen that essentially the same lifetime is obtained for the transient monitored at 415 nm and at 720 nm, suggesting that the same transient is being followed at both wavelengths.

The results for other thiones at low temperature are also included in Table 6. The decay and the transient spectrum for the p-methoxy-PNT are given in Figures 17 and 18.
Fig. 1 Phenyl 1-naphthyl thione transient decay at 415 nm, in benzene at 25°C

Laser: 337.1 nm; 20 shots/point; fluorescence correction mode

Dashed line: first order decay fit

Top OD = 0.0 133 6

First order decay fit

\[ \ln A \text{ vs. time} \]

\[ A = OD(t) - OD(\infty) \]

\[ OD(\infty) = 0.0002 \]

#points (\downarrow): 18

Correlation: 0.99956

\[ \tau = 83.8 \text{ ns} \]

\[ \ln A: -4.37 \pm -5.97 \]
Fig. 2 Phenyl-1-naphthyl thione transient absorption spectrum in benzene at 24°.
Laser: 337.1 nm; range: 100 ns; markers: 6, 26

$\Delta O D \ (\text{vertical display}) = 0.02214$

**Fig. 3** Phenyl 6-chryseryl thione transient absorption spectrum in benzene at 20°
Fig. 4. Phenyl-1-fluorobenzyl thiole transient absorption spectrum in benzene at 24°.

Laser: 337.1 nm; range: 20 ns; markers: 1: 25
ΔOD (vertical display: 0.02499.

ΔOD vs. wavelength
Laser: 337.1 nm; range: 20 ns; markers: 5, 30

ΔOD (+) vertical display: 0.02413; insert: expansion of the 450 - 550 nm region.

Fig. 5 Phenyl 1-pyrenyl thione transient absorption spectrum in benzene at 25°
**Fig. 6** Phenyl 1-oyrenyl thione transient decay at 500 nm, in benzene at 25°C

Laser: 337.1 nm; 30 shots/point; fluorescence correction mode

Dashed line: first order decay fit

Top OD = 0.02268

First order decay fit

\[
\ln A \text{ vs. time}
\]

\[A = OD(t) - OD(\infty)\]

\[OD(\infty) = 0.0016\]

#points (V): 20

correlation: 0.99902

\[t = 5.3 \text{ ns}\]

\[\ln A: -3.85 \pm -5.80\]
**Fig. 7** Phenyl 1-naphthyl ketone transient absorption spectrum in methanol at 25°

Laser: 337.1 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 420 nm

Range: 5μs
X: 1*100
Markers: 23;30
Fig. 8 Phenyl 6-chryseryl ketone transient absorption spectrum in benzene at 25°.

Laser: 337.1 nm; background correction mode.

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm.

Decay at 650 nm

Range: 5 μs
X: 1 x 100
markers: 23, 33
**Fig. 9** Phenyl 1-pyrenyl ketone transient absorption spectrum in isooctane at 27°

Laser: 337.1 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm.
**Fig. 10** Phenyl 3-fluoranthenyl ketone transient absorption spectrum in isooctane at 23°C

Laser: 337.1 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 500 nm

Range: 5μs
X: 1×100
markers: 24;3.1
Fig. 11  Para-methoxyphenyl 1-naphthyl ketone transient absorption spectrum in methanol at 22°.

Laser: 337.1 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 500 nm

Range: 5μs
X: 1+100
Markers: 20; 28
Fig. 12 Para-fluorophenyl 1-naphthyl ketone transient absorption spectrum in benzene at 25°C
Laser: 337.1 nm; background correction mode
ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 550 nm
Range: 2μs
X: 1×100
markers: 30:54
Fig. 13  Para-chlorophenyl 1-naphthyl ketone transient absorption spectrum in benzene at 25°C

Laser: 337.1 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 575 nm

Range: 2μs
X: 1×100
markers: 30;52
**Fig. 14** Para-methylphenyl 1-naphthyl ketone transient absorption spectrum in benzene at 25°C

Laser: 337.1 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 420 nm

Range: 2μs

X: 1*100

Markers: 27, 52
Fig. 15  Phenyl-9,10-dimethyl 2-anthracenyl ketone transient absorption spectrum in benzene at 25°C.

Laser: 337.1 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 460 nm

Range: 5 μs
X: 1×100
markers: 26:71
Fig. 16 Phenyl 1-naphthyl thione transient absorption spectrum in methanol at -48°C.

Laser: 337.1 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Range: 200 ns
X: 1×100
Markers: 32/37
**Fig. 17** Para-methoxyphenyl 1-naphthyl thione transient decay at 415 nm, in methanol at -45°C.

Laser: 337.1 nm; 10 shots/point; fluorescence correction mode

Dashed line: first order decay fit

Top OD = 0.01853

ΔOD

First order decay fit

$\ln A$ vs. time

$A = \text{OD}(t) - \text{OD}(\infty)$

$\text{OD}(\infty) = 0.0005$

#points (\text{V}) = 21

correlation = 0.99494

$\tau = 195 \text{ ns}$

$\ln A: -4.33 + -5.99$
Fig. 18  Para-methoxyphenyl 1-naphthyl thione

transient absorption spectrum in methanol at -46°C

Laser: 337.1 nm, background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 415 nm

Range: 200 ns

X: 100

markers: 29, 37
2.4.4 Concentration dependence of the transient decay

2.4.4.1 Kinetic treatment of the self-quenching

The deactivation of the triplet state thione may occur, in the absence of an external quencher, by unimolecular decay and by quenching by ground state thione. The competition between these two ways of decay may be represented by

\[ \begin{align*}
\dot{3\text{Th}} & = k_0 + k_{sq}[\text{Th}] \\
3\text{Th} + \text{Th} & \rightarrow 3\text{Th} + \text{Th}
\end{align*} \]

The rate of disappearance of $3\text{Th}$ following pulse excitation is given by

\[\frac{d[3\text{Th}]}{dt} = (k_0 + k_{sq}[\text{Th}])[3\text{Th}] = k_{obs}[3\text{Th}]\]

where $k_{obs}$ is the observed rate constant for the decay of $3\text{Th}$. The $k_{obs}$ are equal to the slopes of the integrated form of the above equation, i.e.

\[\ln\frac{3\text{Th}}{3\text{Th}_0} = k_{obs}t = (k_0 + k_{sq}[\text{Th}])t\]

This expression suggests that if there were a significant contribution from the self-quenching process to the observed triplet decay it should be reflected in the dependence of $k_{obs}$ on [Th]. A plot of $k_{obs}$ vs. [Th] should give a straight line with slope equal to $k_{sq}$ and intercept equal to $k_0$ the unimolecular decay constant.

2.4.4.2 Decay rates at different concentrations

The triplet state of several thiones can be quenched by ground state thione. To determine the extent of this self-quenching process, the decay of the transient of PNT was followed by laser flash photolysis
at several concentrations. Absorption problems limited the usable range.

<table>
<thead>
<tr>
<th>[PMT] / 10^{-4} M</th>
<th>k_{obs} / 10^{-7} s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.79</td>
<td>1.10</td>
</tr>
<tr>
<td>1.2</td>
<td>1.02</td>
</tr>
<tr>
<td>1.4</td>
<td>1.19</td>
</tr>
<tr>
<td>1.7</td>
<td>1.10</td>
</tr>
<tr>
<td>3.6</td>
<td>1.00</td>
</tr>
<tr>
<td>10.3</td>
<td>1.48</td>
</tr>
</tbody>
</table>

(In benzene at room temp.; monitoring $\lambda = 415$ nm)

2.4.4.3 Concentration dependence. Discussion

In the concentration range $< 4 \times 10^{-4}$ M the variations in $k_{obs}$ are within experimental error ($< 25\%$). Only at $= 10^{-3}$ is $k_{obs}$ slightly larger. It could be said that for these dilute solutions ($< 4 \times 10^{-4}$ M) the contribution from self-quenching to the decay is very small. This is expected because the lifetime is quite short. Only at higher concentrations of thione should the self-quenching process become significant as compared with the fast unimolecular decay.

Nevertheless, a least square fitting of the above data to a straight line gives intercept $= k_0 = (1.02 \pm 0.06) \times 10^7$ s$^{-1}$ and slope $= k_{sq} = (4 \pm 1) \times 10^9$ M$^{-1}$ s$^{-1}$. These values are comparable to those reported for PMT in cyclohexane, which were $k_0 = (1 \pm 0.1) \times 10^7$ s$^{-1}$ and $k_{sq} = (1.8 \pm 1) \times 10^9$ M$^{-1}$ s$^{-1}$, since in both determinations considerable error was found due to the limited concentration range used.
2.4.5 Quenching of the transient by molecular oxygen

2.4.5.1 Kinetics of triplet quenching by oxygen

Molecular oxygen is expected to quench the triplet state of PNT causing, therefore, a decrease in the observed lifetime of the thione triplet. To analyze quantitatively the effect of oxygen let us consider a simplified mechanism involving a competition between $^3$Th quenching by $O_2$ and $^3$Th deactivation by other means.

$$
\begin{align*}
\text{Th}^* & \xrightarrow{k_d} \text{product (including Th g.s.)} \\
\text{Th}^* + O_2 & \xrightarrow{k_q} \text{quenching of Th}^*
\end{align*}
$$

where $\text{Th}^*$ is the excited thione (triplet)

$k_d$ is the overall rate constant for the deactivation of $\text{Th}^*$ in the absence of $O_2$ (self-quenching included)

$k_q$ is the quenching rate constant by $O_2$

It follows from the above mechanism that

$$
\frac{1}{\tau} = \frac{1}{\tau_0} + k_q [O_2]
$$

where $\tau_0$ and $\tau$ are the lifetimes at the same concentration of thione in the absence and presence of a given $[O_2]$.

A plot of $\tau^{-1}$ versus $[O_2]$ should then be linear.

2.4.5.2 Results of quenching by oxygen.

The experimental results are reproduced in Table 8 and Figure 19.

<table>
<thead>
<tr>
<th>$[O_2] / 10^{-3}$ M</th>
<th>0.00</th>
<th>0.00</th>
<th>1.59</th>
<th>1.59</th>
<th>7.93</th>
<th>7.93</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau^{-1} / 10^7$ s$^{-1}$</td>
<td>1.14$^a$</td>
<td>1.12$^b$</td>
<td>1.49$^a$</td>
<td>1.62$^b$</td>
<td>3.49$^a$</td>
<td>3.22$^b$</td>
</tr>
</tbody>
</table>

a) original samples; b) remeasured after series a)
Fig. 19  Quenching of phenyl 1-naphthyl thione transient by oxygen, in benzene at room temperature.

(Reciprocal of transient lifetime versus molarity of oxygen)
The slope of the straight line gives the quenching rate constant by O₂, \( k_q = (2.8 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \), in benzene at room temperature.

2.4.5.3 Interpretation of quenching by oxygen

The value for the bimolecular quenching rate constant of triplet PNT by molecular oxygen in benzene at room temperature is found to be \( (2.8 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \). Since the ground state of molecular oxygen is a triplet, the quenching of triplet states of other molecules by O₂ is expected to proceed with rate constants smaller than the diffusion controlled rate constant.

The mechanism proposed for quenching of triplet aromatic hydrocarbons by O₂ may be written as follows:

\[
\begin{align*}
5(M^* + O_2)^* & \rightarrow 1M + 3O_2 \\
3(M^* + O_2)^* & \rightarrow 1M + 3O_2 \\
3M^* + 3O_2 & \rightarrow 1(M^* + O_2)^* + 1M + 1O_2^*
\end{align*}
\]

where M represents the organic compound, the asterisk denotes an electronically excited species and the superscript gives the spin multiplicity.

The maximum rate constant expected for O₂ quenching is \( k_q = p k_D \) where \( p = 1/9 \) when only the lowest process above contributes efficiently to the quenching. Porter et al. have found that triplet aromatic hydrocarbons with triplet energies in the range of 120 to 180 kJ mol⁻¹ have \( p = 0.11 \) when \( k_D \) was taken as \( 2.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \), the latter being an average rate constant for the oxygen quenching of singlet states of aromatic hydrocarbons, which likely have \( p = 1 \). Wilkinson et al. take \( k_D \) in benzene as equal to the rate constant for quenching of singlet
anthracene by $O_2$, which was found by Ware to be $3.1 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$. Wilkinson et al. thus obtain $p = 0.09$ for oxygen quenching of triplet benzophenone in benzene.

Using the experimental value found for the bimolecular rate constant of quenching of triplet PNT by oxygen ($2.8 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$) one gets $p = 0.10$ or $p = 0.09$ depending on which value of $k_D$ is chosen. These two values are very close to each other and just slightly lower than $1/9$.

For several aromatic $N$-heterocyclic compounds as well as aromatic amines and other compounds values of $k_q > k_D/9$ were found. Garner and Wilkinson proposed that for compounds where charge-transfer (CT) interactions with $O_2$ were suspected (when the triplet energies were large but the half-wave oxidation potential were low) quenching could occur also via a low-lying CT state (from the $^3(M\cdots O_2)$ encounter complex) allowing a limiting $k_q$ value of $(4/9)k_D$ to be reached.

There is a report also that the phosphorescence of $N$-methylthioacridone appears to be quenched by $O_2$ at very high rates ($k_q = 0.5k_D$).

Huber et al. found a value of $3.5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ for the triplet xanthione quenching by $O_2$ in ethanol.

The rate constant value found here for quenching of transient PNT by $O_2$ was very close to $(1/9)k_D$ found for triplet aromatic hydrocarbons and benzophenone. This, in itself does not require, but is consistent with, the postulate that the species quenched is triplet PNT.

2.5 The intersystem crossing in aromatic thiones

2.5.1 PNT intersystem crossing and triplet quenching by tetracene

It is of considerable importance to estimate the intersystem cros-
\[ \Phi_\ast = \frac{\Phi_{ST} k_q[Q]}{k_q[Q] + k_d + k_{sq}[Th]} \]

The term \( k_q[Q] \) in the denominator could be neglected for the short-lived thiones triplets, since the concentrations of the sparingly soluble tetracene were low. Therefore

\[ \Phi_\ast = \frac{\Phi_{ST} k_q[Q]}{k_d + k_{sq}[Th]} = \Phi_{ST} k_q \tau_{Th}[Q] \]

where \( \tau_{Th} = (k_d + k_{sq}[Th])^{-1} \) is the lifetime of the triplet thione at a given concentration of thione with no other quencher added.

The quantum yield of triplet tetracene is proportional to the top absorbance by the triplet tetracene (TOD) in its decay trace at 470 nm,

\[ \alpha \Phi_\ast = \text{TOD} \]

where \( \alpha \) is a proportionality factor. Consequently for the energy transfer from \( \text{Th} \) to tetracene we obtain a tetracene triplet initial absorption of

\[ \text{TOD} = \alpha \Phi_{ST} k_q \tau_{Th}[Q] \]

Under appropriate conditions a plot of TOD versus \( Q \) should be linear with a slope given by

\[ \text{slope} = \alpha \Phi_{ST} k_q \tau_{Th} \]

To proceed further a standard needs to be used. Butyrophenone is very appropriate for this purpose; besides having a unity quantum yield of intersystem crossing, its triplet lifetime \(^{64-65}\) is close to that of PNT, so that the extent of quenching is comparable for both, and thus the approximation used above is justifiable for butyrophenone also.

For butyrophenone, by an analogous derivation, the slope of the plot TOD versus \( Q \) under similar conditions is given by
butyrophenone (a sensitizer used as standard) can be obtained by inspection of Figure 20. It can be seen that during the experiments the laser light is absorbed mainly by the donors.

The triplet-triplet absorption of tetracene sensitized by some donors are given in Figures 21 to 24. They show that the same transient (triplet-tetracene) is produced by different sensitizers, as expected, and that at least for acetophenone as sensitizer the absorbance of the triplet tetracene increases with the concentration of tetracene (note however that these figures here are not taken exactly under the same conditions: so this observation should be considered only qualitative at this point). This increased absorbance is an indication of an increased importance of the quenching of the sensitizer by tetracene versus other decay modes of the excited sensitizer. These two observations are basic to the method. The equations necessary to treat this quantitatively will be given next. The experimental results, as plots of maximum absorbance by tetracene triplets at 470 nm vs. tetracene concentration, are reproduced in Figure 25.

2.5.2 Quantitative treatment of the quenching process

Let us consider the following reactions for the triplet thione

\[
\begin{align*}
\text{Th} & \longrightarrow \rightarrow 3\text{Th} \\
3\text{Th} & \longrightarrow \text{Deactivation} \quad k_d \\
3\text{Th} + Q & \longrightarrow \text{Th} + 3Q \quad k_q \\
3\text{Th} + \text{Th} & \longrightarrow \text{Th} + \text{Th} \quad k_{sq}
\end{align*}
\]

The quantum yield of formation of triplet tetracene (represented as \(3^Q\) or \(Q^*\)) will be equal to the quantum yield of isc of the \(3\text{Th} (\Phi_{st})\) multiplied by the fraction of \(3\text{Th}\) that are actually quenched by \(Q\), i.e.
Fig. 20. Absorption spectra of (a) phenyl-1-naphthyl thione, (b) butyrophenone and (c) stock solution of tetracene, in benzene at room temperature.
**Fig. 21** Triplet tetracene absorption from sensitization

Acetophenone + 10 µL of tetracene solution

Laser: 337.1 nm; Solvent: benzene at 26°C

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 470 nm

Range: 10μs

X: 1+100

Markers: 33;60
Fig. 22  Triplet tetracene absorption from sensitization

Acetophenone + 250 µl of tetracene solution

Laser: 337.1 nm; Solvent: Benzene at 27°

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 470 nm

Range: 10 µs
X: 1*100
markers: 27;45
Fig. 23  Triplet tetracene absorption from sensitization

Phenyl 1-naphthyl thione + 360 µL of tetracene sln.

Laser: 337.1 nm; background correction mode; Solvent: Benzene at 24°C

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 470 nm

Range: 5µs
X: 1 × 100
markers: 46, 67
Fig. 24 Triplet tetracene absorption from sensitization

Phenyl 6-chrysene thione + 670 µL of tetracene soln.

Laser: 337.1 nm; background correction mode; Solvent: Benzene at 25°C

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 470 nm

Range: 5 µs
X: 1+100
markers: 39, 64
Fig. 25: Triplet tetracene top absorbance at 470 nm sensitized by various donors versus tetracene concentration.
\[
\Phi^* = \frac{k_q(Q)}{k_q(Q) + k_d + k_{sq}(Th)}
\]

The term \(k_q(Q)\) in the denominator could be neglected for the short-lived thiones triplets, since the concentrations of the sparingly soluble tetracene were low. Therefore

\[
\Phi^* = \frac{k_q(Q)}{k_d + k_{sq}(Th)} = \Phi_{ST} k_q \tau_{Th}(Q)
\]

where \(\tau_{Th} = (k_d + k_{sq}(Th))^{-1}\) is the lifetime of the triplet thione at a given concentration of thione with no other quencher added.

The quantum yield of triplet tetracene is proportional to the top absorbance by the triplet tetracene (TOO), i.e.

\[
\alpha \Phi^* = \text{TOO}
\]

where \(\alpha\) is a proportionality factor. Consequently for the energy transfer from \(^3\text{Th}\) to tetracene we obtain a tetracene triplet initial absorption of

\[
\text{TOO} = \alpha \Phi_{ST} k_q \tau_{Th}(Q)
\]

Under appropriate conditions a plot of TOO versus \(Q\) should be linear with a slope given by

\[
\text{slope} = \alpha \Phi_{ST} k_q \tau_{Th}
\]

To proceed further a standard needs to be used. Butyrophenone is very appropriate for this purpose; besides having a unity quantum yield of intersystem crossing, its triplet lifetime\(^{64-65}\) is close to that of PNT, so that the extent of quenching is comparable for both, and thus the approximation used above is justifiable for butyrophenone also.

For butyrophenone, by an analogous derivation, the slope of the plot TOO versus \(Q\) under similar conditions is given by
slope' = \( \alpha \Phi_{ST} k' \tau' \)

where the prime refers to butyrophenone.

From the ratio of the two slopes it follows after rearrangement

\[
\frac{k_q \Phi_{ST}}{k'_q \Phi'_{ST}} = \frac{\text{slope} / \tau}{\text{slope}' / \tau'}
\]

2.5.3. Numerical results

The plots of TOO versus tetracene concentration in benzene at room temperature are reproduced in Figure 25.

Reasonably good straight lines were obtained for FNT, phenyl 6-chrysanyl thione and butyrophenone, the standard. Their corresponding numerical values appear in Table 9. Under the assumption that the rate constants for quenching by tetracene are equal, the \( \Phi_{ST} \) values can be determined. The intersystem crossing quantum yields are high, 0.71 for FNT and 0.65 for phenyl 6-chrysanyl thione.

The values of TOO as a function of tetracene concentration for the quenching of acetophenone triplets by tetracene are also included in Figure 25. For the long-lived acetophenone triplets though, the extent of quenching by tetracene was large, and therefore the approximation of small extent of quenching does not hold for acetophenone in the range of tetracene concentrations used. Acetophenone then cannot be used as a standard here.

The reverse problem was encountered with phenyl 3-fluoranthanyl thione. Its triplet lifetime was too short (9 ns or shorter, since it was comparable to the laser pulse duration). Assuming a 9 ns lifetime, a \( k_q \) of \( 5 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \) (maximum for exothermic quenching of triplets in
benzene at $25^\circ$ and using the Stern-Volmer equation, the extent of quenching by tetracene was expected to be $<0.2\%$ at the most. This seems too small to render meaningful results for this thione.

<table>
<thead>
<tr>
<th>Donor</th>
<th>$\tau$ / $10^{-7}$s</th>
<th>(Slope of TOD vs $Q$) / $10^{2}M^{-1}$</th>
<th>Corr. coeff.</th>
<th>$k_q$</th>
<th>$\Phi_{ST}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyrophenone</td>
<td>1.2</td>
<td>8.8</td>
<td>0.9990</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>PNT</td>
<td>0.90</td>
<td>4.7±0.7</td>
<td>0.9924</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>Phenyl 6-chrysenyl thione</td>
<td>0.99</td>
<td>4.7</td>
<td>0.9989</td>
<td>0.65</td>
<td></td>
</tr>
</tbody>
</table>

Data in benzene at $(25 \pm 1)^\circ$. Irradiations with a 337 nm laser.

Butyrophenone triplet lifetime in benzene at $25^\circ$ from ref. 65.
CHAPTER 3 - DISCUSSION OF THE MECHANISM OF PNT PHOTOCYCLIZATION

3.1 Possible mechanisms

There are a few mechanisms that could a priori be conceived for the PNT photocyclization. First, a concerted mechanism, with the insertion of the sulphur atom to the C-8 carbon occurring simultaneously with the hydrogen-shift to the benzylic position may be considered. Although these three atoms may be quite close, it is however not possible to explain by a concerted mechanism the reported complete deuteration at the benzylic position when the solvent contained D₂O; this observation requires the presence of an intermediate along the reaction pathway.

As for the mechanisms involving an intermediate, a mechanism involving intramolecular hydrogen abstraction could explain the deuterium exchange when D₂O was present. It is, though, thermodynamically impossible to abstract the aromatic peri hydrogen since the corresponding bond dissociation energy is very high.

3.2 The mechanism involving insertion during the primary process

As a starting point for our discussion let us consider first the mechanism proposed by de Mayo et al.¹ (Scheme 1).

![Scheme 1](image-url)
In Scheme 1, \( \text{Th}, \text{1Th}, \text{3Th} \) represent thione (PNT) in its ground, first singlet and triplet state, respectively. \( X \) represents the insertion intermediate and \( C \) represents the cyclized (final) product.

Some small rate constants have been omitted (e.g. for emission).

Using the steady state approximation for \( \text{1Th} \) and \( X \) one gets for the quantum yield of product formation

\[
\Phi_C = \frac{[C]}{[C]} = \left( \frac{k_{SX}}{k_{SX} + k_{ST} + k_{SG}} \right) \left( \frac{k_{XC}}{k_{XC} + k_{XG}} \right) = k_{SX} \tau_s k_{XC} \tau_X = \phi_{SX} \phi_{XC}
\]

where the subscripts for the rate constants and quantum yields indicate the initial and final state. \( \tau_s \) and \( \tau_X \) are the lifetimes of the first singlet and the intermediate, respectively; \( \phi_{SX} \) and \( \phi_{XC} \) are the quantum yield for the formation of the intermediate and for the process \( X \rightarrow C \), respectively.

If the only stable species are the final product \( C \) and starting material \( \text{Th} \) then the quantum yield of disappearance of the thione (\( \Phi_{\text{dis}} \)) should be equal to the quantum yield of product formation (\( \Phi_C \)). This is strictly true for the mechanism in Scheme 1. However \( \Phi_{\text{dis}} \) could become larger than \( \Phi_C \) if the thione disappears by other means. Ignoring this, comparisons will be made of \( \Phi_{\text{dis}} \) taking them as proportional to \( \Phi_C \).

Let us consider first of all the question of the low quantum yield, \( \Phi_C = 10^{-3} \). This means that of all the \( \text{1Th} \) formed by absorption of light only a minute fraction succeeds in giving the final product \( C \). The rest finds some alternative pathway(s) to return to ground state \( \text{Th} \). Two pathways were mentioned as candidates for the energy wasting process, without choosing between them.\(^1\) One was the \( \text{1Th} \rightarrow \text{3Th} \) (isc). The other was reversion of \( X \) to give starting material, \( \text{Th} \).
These possibilities shall now be analyzed further. If one compares the expression for $\Phi_C$ obtained earlier, with the intersystem crossing quantum yield given by the expression below,

$$\Phi_{ST} = \frac{k_{ST}}{k_{ST} + k_{SX} + k_{SG}}$$

one gets, under steady state conditions the following,

$$\Phi_C = \frac{k_{SX} \cdot k_{XC}}{\Phi_{ST} \cdot \left(\frac{k_{XC}}{k_{XC} + k_{XG}}\right)}$$

This expression links the most important constants for the reaction according to Scheme 1. This equation can be rearranged as follows

$$\Phi_C = \frac{\Phi_{ST} \cdot k_{SX}}{k_{ST} \cdot \left(\frac{k_{XC}}{k_{XC} + k_{XG}}\right)} = \Phi_{SX} \cdot \frac{k_{XC}}{k_{XC} + k_{XG}} = \Phi_{SX} \cdot \Phi_{XC} \quad \text{Eq. 1}$$

where $\Phi_{SX}$ is the quantum yield for the formation of intermediate $X$ and $\Phi_{XC}$ is the fraction of intermediates $X$ that gives product $C$. This equation can be used to analyze some kinetic situations that may be operating. Let us mention now the following alternative cases:

**Case 1:** $k_{XG} \ll k_{XC}$. For this limiting case of "negligible reversion of $X"$, is $\Phi_{XC} = 1$ and

$$\Phi_C = \frac{\Phi_{ST} \cdot k_{SX}}{k_{ST} \cdot \Phi_{SX}} = \Phi_{SX}$$

**Case 2:** $k_{XG}$ significant.

a) If $k_{XG}$ and $k_{XC}$ are of the same order of magnitude, i.e. $1 > \Phi_{XC} > 0.1$, the exact form of equation 1 is required.

b) If $k_{XG} \gg k_{XC}$ a limiting case of "predominant reversion of $X"$ occurs, $\Phi_{XC} < 0.1$ and
\[ \Phi_C = \frac{\phi_{ST} k_{SX}}{k_{ST}} \cdot \frac{k_{XC}}{k_{SG}} = \frac{k_{XC}}{k_{SG}} \frac{\phi_{SX}}{k_{SG}} \]

Only when \( k_{XC} \) and \( k_{SG} \) are of the same order of magnitude a description according to case 2a would be required. Otherwise the mechanism will be well represented by one of the two limiting cases 1 or 2b. The discussion therefore will be focused only on these two limiting cases.

In what follows an attempt will be made to correlate the experimental observations with what would be predicted from cases 1 and 2b, and with what might be considered relevant information from other systems.

3.2.1 Case 1. Negligible reversion of the insertion intermediate

\[ \Phi_{dis} = \Phi_C = \phi_{ST} \frac{k_{SX}}{k_{ST}} = \phi_{SX} \quad \text{with} \quad \phi_{XC} = 1 \]

a) The inefficiency of the photocyclization could be explained in this case by an inefficient formation of the intermediate, which then gives quantitatively the final product, i.e. \( \phi_C = \phi_{SX} \phi_{XC} = \phi_{SX} \). Since \( \phi_{SX} = \phi_{ST} k_{SX} / k_{ST} \) and \( \Phi_C = 10^{-3} \) therefore \( \phi_{SX} = \phi_{ST} k_{SX} / k_{ST} = 10^{-3} \). In this case the inefficiency of cyclization is therefore ascribed entirely to properties related to the reactive state (\(^1\)Th). It follows that the low yield of intermediate is due to rapid photophysical deactivation of \(^1\)Th relative to photophysical deactivation. Photophysical deactivation of other singlet excited state aromatic thiones is fast: about \( 10^{11} \text{s}^{-1} \). If the value for PNT is near \( 10^{11} \text{s}^{-1} \) then \( k_{SX} = 10^8 \text{s}^{-1} \).

b) The intermediate \( X \) was not detectable in laser flash photolysis. This could be explained in part by its very low quantum yield \( \phi_{SX} = 10^{-3} \) in case 1. Instead, the \(^3\)Th, formed more efficiently, can be detected.
c) As for the intermediate lifetime \( \tau_X = (k_{XC} + k_{XG})^{-1} \) it should be \( \tau_X = 1/k_{XC} \) since \( X \) is considered to react faster than it reverts. It is difficult to give even an order of magnitude for \( k_{XC} \) so it is uncertain how long-lived \( X \) could be. In case 1 \( \Phi_C = \Phi_{SX} \).

d) There are some substituent effects on the disappearance quantum yields when PNT is substituted in the para position of the benzene ring. The \( \Phi_{dis} \) increases for electron withdrawing substituents. In the formalism of case 1 it should be \( \Phi_{dis} = \Phi_{SX} = k_{SX} / (k_{ST} + k_{SG}) \). This means the variations in \( \Phi_{dis} \) are due to variations in the quantum yield of formation of \( X, \Phi_{SX} \). This in turn depends on the competition between chemical reaction from \(^1\text{Th} \) and its non-chemical decay. Since a competition is involved, more than one factor could be affected by the substituents, leading perhaps to cancellation of effects, making difficult the interpretation of results. The observed changes in \( \Phi_{dis} \) are not dramatic enough to single out one factor as being almost entirely responsible for the changes in \( \Phi_{dis} \) with substituents. Therefore, just one possibility will be considered here; it is a likely case, but there may be others. Only if the substituents affected the chemical pathway \( (k_{SX}) \) more than the non-chemical pathways \( (k_{ST} + k_{SG}) \), then one could associate the observed changes in \( \Phi_{dis} \) with changes in \( k_{SX} \) and conclude that larger \( k_{SX} \) values are obtained when electron withdrawing groups are present.

e) A small solvent effect on product quantum yield was obtained by Lapouyade et al. In the context of case 1 the changes ought to be related to the chemical versus non-chemical deactivation of \(^1\text{Th} \) as mentioned for the previous points, i.e. \( \Phi_C = k_{SX} / (k_{ST} + k_{SG}) \). The observed changes are within a factor of \( \approx 2.5 \). In case 1 then this could
be explained by saying that the rate constants from $^{1}$Th do not change dramatically with the solvent. This could well be the case considering that $k_{ST}$ is already very large and likely $k_{ST} > k_{SG}$. As for $k_{SX}$ the question arises as to how much charge separation is involved in $^{1}$Th and how much it could be affected by the solvent. It has been suggested that $^{1}$Th is expected to exhibit a high degree of "biradical character" in its chemical reactions. A small solvent effect on $k_{ST}$ and $\Phi_C$ would then not be surprising if case 1 were in operation.

f) Rigid media hinder the reaction as shown in Table 4. This may indicate that some rotation is required for the reaction to occur, which is impeded in rigid media. In case 1 since $\Phi_C = \Phi_{SX} = k_{SX} / (k_{ST} + k_{SG})$ only $k_{SX}$ appears to be a candidate susceptible to be greatly changed by the rigidity of the media. For example, if, for the reaction to take place, a conformation is required which is not the same as that reached upon excitation of the ground state thione, and if the rigid medium maintains this unfavorable conformation for some time, then all the excitation energy would be lost by the still rapid non-chemical decay $k_{ST} + k_{SG}$.

g) The overall absence of insertion into other aromatic hydrocarbons indicates either that the stereoelectronic requirements for the insertion reaction are met only intramolecularly or that if some initial attack occurs it does not succeed in giving final products, but simply reverts to starting material. This brings about a related question. Is there any process occurring between singlet thione and ground state thione or more specifically is there self-quenching of $^{1}$Th by ground state Th, e.g. in PNT7. The plots for the disappearance quantum yields are linear at least up to the maximum conversion followed (≈ 20%). The
solutions used, however, were in the range of $10^{-3}$ to $10^{-4}$ M, and since $^{1}\text{Th}$ was likely very short-lived, very little quenching ought to have been manifested, if there was quenching of $^{1}\text{PNT}$ at all. The same slope for the disappearance quantum yield was obtained from a $7 \times 10^{-3}$ M and a $7 \times 10^{-4}$ M solution of PNT in acetonitrile, following irradiation with 362 nm light.

h) Deuterium incorporation was observed by Lapouyade et al. when the solvent contained D$_2$O. This observation has been considered to provide evidence for the participation of a discrete intermediate in the reaction pathway. One important prediction from case 1 is that $\Phi_c$ should be independent of the D$_2$O concentration. This follows because $\Phi_c = \phi_{\text{ST}}$ and $\phi_{\text{XC}} = 1$ in case 1. So even though the rate $X+C$ may change, $\phi_{\text{XC}} = 1$ already, so $\Phi_c$ should not vary with [D$_2$O]. This could provide a test of whether X does reverts or not, because in case 2b $\Phi_c$ ought to vary with [D$_2$O] as will be mentioned later.

3.2.2 Case 2b. Predominant reversion of the insertion intermediate

$$\phi_{\text{dis}} = \Phi_c = \phi_{\text{ST}} \frac{k_{\text{SX}} k_{\text{XC}}}{k_{\text{ST}} k_{\text{XG}}} = \phi_{\text{SX}} \frac{k_{\text{XC}}}{k_{\text{XG}}} = \frac{k_{\text{XG}}}{k_{\text{XC}}}$$

with $\phi_{\text{SX}} = 1$

a) The inefficiency of the photoreaction should be due to an efficient reversion of the intermediate X in case 2b. If $\phi_{\text{SX}} = 1$ then $\Phi_c = \phi_{\text{XC}} = k_{\text{XC}} / k_{\text{XG}}$ i.e. the hydrogen-transfer from the intermediate is inefficient, not the initial insertion from the $^{1}\text{Th}$.

Not much is known about rates of 1,3 H-transfer (they may be slow thermally if uncatalyzed, but fast if catalyzed by protons). It should be noted that Lapouyade et al.\textsuperscript{51-52} reported, also, the related photocyclization of 1-phenyl,1-(1-naphthyl)ethylene from the singlet state.
(see Chapter 1, pp 15-16). There the product quantum yields were about 0.005 (cyclophenylacenaphthene) and 0.014 (phenylacenaphthylene) in cyclohexane.

b) The intermediate X was not seen and since in case 2b X ought to be formed very efficiently, the explanation would have to be ascribed in this case to a short lifetime for X, i.e. the rate of formation of X should be smaller than its rate of disappearance.

c) In case 2b the lifetime of the intermediate X is \( \tau_X = \frac{1}{k_{XF} + k_{XC}} = \frac{1}{k_{XC}} \) and thus \( \tau_X = 10^{-3} / k_{XC} \). So if a short lifetime for X were the only problem then a \( k_{XC} \) of 10^6 s^{-1} or greater should bring the \( \tau_X \) to 1 ns or shorter, making it difficult to observe X. The \( k_{XC} \) is not known for this 1,3 H-shift. Although Lapouyade\textsuperscript{52} considered the usefulness of flash photolysis to detect the intermediate in the photocyclization of the olefin corresponding to PMT (i.e. 1-phenyl,1-(1-naphthylethylene), he only reported the intermediate of a photocyclization involving an intramolecular 1,5 H-shift to form a six-membered ring to have \( k_{XC} \) = 10^2 s^{-1}. This value may not be relevant to the photocyclization of PMT which may involve a 1,3 H-shift to form the five-membered ring.

d) To analyze the substituent effects according to case 2b consider again the equation \( \Phi_{dis} = \Phi_c = \phi_{SX} k_{XC} / k_{XC} \approx k_{XC} / k_{XF} \). Only changes in the ratio \( k_{XC} / k_{XF} \) (of \( \approx 10^{-3} \)) should change \( \Phi_c \). Since \( k_{XC} \) and \( k_{XF} \) belong to competitive processes some cancellation of effects may take place. In case 2b though \( k_{XC} < k_{XF} \) it is smaller of the two \( (k_{XC}) \) should be comparatively more affected than the other, if similar changes in free energy due to substitution occur in both processes. This is not probable. However, if this were the case then electron-donating substi-
tments, which ought to increase the hydrogen-transfer rate, should increase $\Phi_C$ by increasing $k_{XC}$ more than $k_{XG}$. Experimentally the reverse is observed, so $k_{XC}$ is not affected more than $k_{XG}$ by the substituents if case 2b is to remain in operation.

e) The small solvent effect on the product quantum yield should be ascribed in case 2b to small variations in the ratio $k_{XC}/k_{XG}$. Small variations are likely if only intramolecular processes are involved. If, however, there is also an intermolecular contribution (e.g. catalysis of the $X+C$ process) the ratio could start changing more markedly, since it seems that the process $X+C$ should be more susceptible than $X$-thione to the presence of e.g. $H^+$ donating solvents.

f) The observation that rigid media hinder the reaction could be explained by a transformation of case 2b into case 1, i.e. $\Phi_{SK}$ being drastically changed from unity to near zero by the absence of a rotation that might be a requirement for the formation of $X$. The other possibility is that the intermediate is formed in rigid media but the H-transfer does not occur. The absorption spectrum in a matrix at 77 K indicates that the thione continues to be the absorbing species after irradiation at 77 K. This would require $k_{XC}$ to be much more temperature dependent than $k_{XG}$.

g) The absence of intermolecular insertion should also be explained as in case 1.

h) The deuterium incorporation observed when $D_2O$ was part of the solvent mixture could be occurring during the $X+C$ transformation as suggested by Lapouyade et al. If this were so then one ought to expect in this case $\Phi_C$ to be dependent on the $D_2O$ concentration. In case 2b $\Phi_{SK}$
1 already and so it should not vary, but $\phi_{Xc}$ should vary since $\phi_c = \phi_{Xc} = k_{Xc} / k_{XG}$ unless both $X^+ C$ and $X^+ Th$ are affected in exactly the same way by $D_2O$, which seems unlikely. Lapouyade reports complete deuteration at the benzilic position using MeCN-$D_2O \ (20:1 \ v/v)$ but without measuring quantum yields. This test could distinguish case 2b from 1.

3.2.3 A comparison of case 1 and case 2b

In the foregoing discussion an attempt was made to relate the predictions from case 1 and case 2b to the experimental observations. Even in the absence of measurements of rate constants for PNT, it seems though, that case 2b presents problems to explain all the observations, whereas the explanations using case 1 are more reasonable.

Thus, with the only assumption that $(k_{ST} + k_{SG}) = 10^{11} \sim 10^{10} \ s^{-1}$ for $S_1$ of PNT, as reported for other aromatic thiones, one can see that the value of $k_{SX}$ predicted for case 1 and case 2b is very different. In case 1 a value of $k_{SX} = 10^{8} \sim 10^{7} \ s^{-1}$ is expected.

In case 2b, instead, if the intermediate is to be formed very efficiently ($\phi_{SX} = 1$), then the formation of the intermediate needs to compete favorably with the non-chemical decay of $^1$Th. Again the assumption of $(k_{ST} + k_{SG}) = 10^{11} \sim 10^{10} \ s^{-1}$ requires a very high value for $k_{SX}$, say $10^{13} \sim 10^{12}$ in case 2b. Since the insertion step is intramolecular, this high value could be achieved in principle with a high preexponential factor and a low activation energy $E_a$.

But this situation, i.e. $\phi_{SX} = 1$, a very high $k_{SX}$ at room temperature and a low $E_a$, would lead to very favorable conditions for the detection of the intermediate at low temperature. This, however, was not detected even under conditions where the reaction proceeded at low
temperature (e.g. in media still fluid) or ceased altogether (i.e. in rigid media). A disappearance of X faster than its formation in order to explain this, presents the added problem of claiming a $k_{XG} \gg k_{SX}$ while claiming already a very high $k_{SX}$ for case 2b at room temperature.

In case 2b the $\Phi_c$ are dependent on the ratio $k_{XC} / k_{XG}$. One would expect this ratio to be quite sensitive to proton donors, especially taking into account the fact that the benzylic proton is considered to be derived intermolecularly. In benzene, benzene-methanol (4:1) and benzene-acetic acid (4:1) Lapouyade observed $\Phi_c$ equal to 0.0012, 0.0018 and 0.0015 respectively, i.e. only slightly changed despite the presence of proton donors. In case 1, instead, $\Phi_c$ ought to be independent of $k_{XC}$. Proton donors could only increase the rate $X \cdot C$, but the solvent effect on $\Phi_c$ would involve only the intramolecular process $k_{SX}$ and $k_{ST} + k_{SG}$.

Case 2b would require as well a very low quantum yield of triplet formation. However, the experimental $\Phi_{ST}$ for PNT is high, 0.71, as mentioned in section 2.5.3.

3.2.4 Consideration of charge transfer states being involved

So far we have not considered the involvement of intramolecular charge transfer states which are generated by transfer of charge between two parts of the molecule. One should remember that the chromophores in PNT are conjugated, so there are already interactions in the ground state. If from the $S_1$ state a more pronounced transfer of charge between the chromophores occurs, one could consider a CT as a discrete species on the reaction coordinate.

The intention here will be to consider what would happen if a CT state were involved in the mechanism. The involvement of charge transfer
states in intramolecular photoreactions of ketones containing an amino substituent has been discussed in the literature.\textsuperscript{66-67} For a $\beta$-ketosulphide the involvement of electron transfer has been suggested as well.\textsuperscript{68} In these systems, though, there is one or more methylene groups separating the two parts of the molecule that are involved in the electron transfer process.

An appealing feature of the CT pathway is that protonation could begin during the $^{1}\text{CT} \rightarrow X$ transformation, as may be suggested by the charge separation in the $^{1}\text{CT}$. Let us consider the involvement of an intramolecular charge transfer state (ICT) in the PNT photocyclization.

\textbf{Scheme 2}

\begin{equation*}
^{1}\text{Th} \xrightarrow{} ^{1}\text{CT} \rightarrow X \rightarrow C
\end{equation*}

\begin{equation*}
3^{\text{Th}}
\end{equation*}

\begin{equation*}
^{\text{Th}}
\end{equation*}

Using $Z$ to represent $^{1}\text{CT}$, $Z_{3}$ to represent $^{3}\text{CT}$ (not shown in the scheme), and again using the first and second subscript to indicate the initial and final state respectively, the following expression is obtained, under steady state conditions for the intermediates:

\begin{equation*}
\Phi_{C} = \frac{k_{SZ}}{k_{SZ} + k_{ST} + k_{SG} + k_{ZX} + k_{ZG} + k_{ZZ}} \left( \frac{k_{ZX}}{k_{ZX} + k_{ZG} + k_{ZZ}} \right) = \Phi_{SZ} \cdot \Phi_{ZX} \cdot \Phi_{XC}
\end{equation*}

So the quantum yield of photocyclization depends here on three quantum yields, such that their product results in a $\Phi_{C} = 10^{-3}$ to make it comparable with the experimental order of magnitude. Since the individual values of these three quantum yields are not available, only three limiting situations will be analyzed:
1) If $\phi_{SZ} = 10^{-3}$ and so $\phi_{ZX} \phi_{XC} = 1$ the situation corresponds to case 1 discussed earlier, but with $k_{SZ}$ playing the role that $k_{SX}$ had in case 1. So the ratio $k_{SZ} / (k_{SZ} + k_{SG})$ is the key factor in this case to explain the experimental facts. Z could not be seen due to its low yield of formation ($\phi_{ZX} = 10^{-3}$) or to a short lifetime or to spectral overlap. Some of these reasons could explain why X was not seen either. $\Phi_{C}^*$ is expected to be nearly independent of $[D_2O]$ in this case.

2) If $\phi_{SZ} \phi_{ZX} = 1$ but $\phi_{XC} = 10^{-3}$, the situation corresponds to that of case 2b discussed earlier. Most comments made there apply here also. But now two transient species both formed with efficiency near unity are not observable. As before one could claim a too short lifetime for X at room temperature, but at low temperature one would expect to see it. Experimentally this does not seem to happen. As for Z, in turn, one could claim that either a too short lifetime or spectral overlap with other species could account for its non-observability. Concerning the entropic requirements involved, they should be minimal for $k_{SZ}$ (the constant that needs to be very fast to compete with $k_{ST} + k_{SG}$) but not for $k_{ZX}$ (since some rotations are expected to be restricted in X). $\Phi_{C}$ should be expected to increase with increasing $[D_2O]$, due to enhancement of the process X+C.

3) If $\phi_{SZ} = 1$, $\phi_{ZX} = 10^{-3}$ and $\phi_{XC} = 1$, a new case appears, case 3. It shares some features from both case 1 (e.g. X is formed with low efficiency $= 10^{-3}$ and X gives C quantitatively) and case 2 (it needs a process that competes favorably with the photophysical deactivation of $^{1}{\text{Th}}$). In case 3 Z could not have been seen due to a too short lifetime or spectral overlap. The intermediate X is formed with a quantum yield
of only $= 10^{-3}$ and therefore it may have been difficult to observe. Besides that, there could be problems of spectral overlap. $\phi_C$ ought to increase with increasing $[D_2O]$ by facilitating the transformation $Z\rightarrow X$.

3.2.5 Considerations concerning conformations and rotations

Other factors that could play a role in the photocyclization of PNT are those connected with the conformational requirements for the reaction.

From examination of a space-filling molecular model of PNT it appears that there is strong steric hindrance to a planar configuration of the molecule as a whole.

a) In particular, a strong steric hindrance builds up between the atoms of $S$ and $\beta$-H as the C=S bond becomes coplanar with the naphthalene moiety and the $S$ atom points away form the peri-hydrogen. In this conformation there is also steric hindrance to the rotation of the phenyl ring due to the presence of the peri-H.

b) The other planar conformation with the C=S bond coplanar with the naphthalene ring and with the $S$ atom approaching the peri-H, brings about steric interaction between the $S$ and peri-H atoms, and between the $\beta$ and ortho-H atoms of the naphthalene and benzene ring respectively. The planar conformations are unlikely to occur, at least in solution.

c) Configurations in which the C=S bond has been rotated from the naphthalene plane seem quite free from steric interactions. In fact this angle could be considerably smaller than a right angle without producing much steric hindrance (but favoring conjugation). When the $S$ and peri-H become close to each other, yet at an angle to avoid overlapping, the thiobenzoylcarbon gets very close to the peri-H. If this were the geome-
try of the transition state for the cyclization, then it could be reached without steric problems from the stable conformation.

If some rotation is required from the reactive state to reach the transition state, it must of course occur within the lifetime of the short-lived reactive state.

The rate of rotation may be different for different angles due to an angular dependence of the rotational barrier. The rate constant for a complete rotation \( k_{rot} \) may be quite different from the rate constant for twisting \( k_{twist} \) by a small angle; it is the latter that may be relevant to the kinetics of reaction. This distinction has been considered in other cases. These rates are not available for PNT.

If the rate of twisting were faster than the formation of the intermediate, the original conformation of the ground state would not really matter. Conversely, if \( k_{twist} < k_{eq} \), some ground state conformations may not have enough time, after excitation occurs, to reach the transition state geometry. If \( k_{twist} \) involves a significant activation energy, then low temperatures and high viscosities could impair the photocyclization by slowing down the twisting rate (besides other effects that these environmental factors may have).

An experimental observation done only qualitatively due to equipment limitations at the time, was the following. The irradiation times needed to bleach PNT \((1.24 \text{ mg} / 5 \text{ cm}^3 \text{ solution})\) were 22 hr in benzene at 60-80\(^\circ\), 26 hr in methylcyclohexane at room temperature and 37 hr in methylcyclohexane at -80\(^\circ\) under comparable conditions. There is, then, not much temperature dependence in the PNT photocyclization (Table 4).

PNT did not photocyclize in a rigid matrix. This could be due to an
unfavorable conformation of PNT in a matrix and hindered group rotation; the photophysical processes still could take place but not the photocyclization.

Another observation was that phenyl 3-fluoranthenyl thione remained unreactive towards photocyclization even at high temperature (≈ 100°C). The intermediate X may not be formed for this thione, or if formed, it reverts almost quantitatively. The problems with this second alternative, reversion of X, were already discussed in case 2b.

The absence of X formation might be due to electronic factors. In connection with the possible absence of formation of X, it is noteworthy that during studies of photocyclization of aromatic hydrocarbons leading to six-membered rings, many cases were reported of compounds that failed to undergo photocyclization, even though geometrically they were expected to do so.

The explanations given were derived from the properties of the excited state. For many systems it was reported that whether photocyclization occurred depended on whether the sum of the free valence indices in the first excited state, at the two bonding positions during the cyclization, exceeded a critical value. Lapouyade has successfully applied this to 1-phenyl,1-(2-biphenyl)ethylene and related compounds that photocyclize to form six-membered rings, and to substituted and unsubstituted 1-phenyl,1-(1-naphthyl)ethylenes, that undergo photocyclization to form five-membered rings.

The interplay between electronic configuration, flexibility and planarity in determining the reactivities of the singlet and triplet states towards photocyclization were analyzed in a comparative study of
1-(2'-p-terphenyl)-1-phenylethylene.\textsuperscript{71}

Rotational equilibrations in the triplet state are known.\textsuperscript{72} Recently laser flash photolysis studies of 1,2-diarylethenes\textsuperscript{73} and of 1,1-diarylethenes\textsuperscript{74} indicate that fast equilibration occurs between the planar and perpendicular configurations of the triplets. In the latter work the olefin analogue of PNT, i.e., 1-phenyl,1-naphthylethylene was studied. It presented T-T absorption bands broad and centered at around 400 nm (assigned to the perpendicular triplet) and around 500 nm (assigned to the planar triplet). The lifetime was 40 nm at both wavelengths.

3.3 Conclusions

The disappearance quantum yield of PNT is increased by electron withdrawing substituents.

The photocyclization of PNT is impeded in rigid media.

The transients observed by laser flash photolysis in the range 300-800 nm and in the 10-200 ns time scale seem to be due predominantly to thione triplets rather than to insertion intermediates.

The PNT transient is quenched by O\textsubscript{2} with rate constant of $2.8 \times 10^9$ \text{M}^{-1} \text{s}^{-1}. This transient was also quenched by tetracene. From the relative yield of triplet tetracene produced, a high isc quantum yield for the thione following 337 nm excitation was derived.

The parameters reported here for triplet PNT are compatible with those of some aromatic thiones lacking peri-hydrogens and unable to photocyclize, like thiobenzophenone.\textsuperscript{75}

The main reason for the disappearance quantum yield being low is...
not the reversion of an intermediate, but its inefficient formation owing to competing photophysical processes.
CHAPTER 4 - EXPERIMENTAL OF PART I

4.1 General procedures

Melting points were determined on a Gallenkamp apparatus, and are uncorrected. Chemical shifts are in ppm downfield from Me₄Si. The following instruments were used: Cary 118 and 219 UV spectrometers, Varian T-60 and XL-100 NMR spectrometers, Beckman IR 5A and Beckman Acculab 4 IR spectrometers, Varian MAT 311 mass spectrometer.

4.2 Preparation of para substituted aromatic ketones

p-Methoxyphenyl 1-naphthyl ketone was prepared by the Friedel-Crafts reaction of p-methoxybenzoylchloride and naphthalene using AlCl₃ as catalyst (Baddeley, G. J. Chem. Soc. 1949, 899) and ethylene chloride as solvent; mp 100-101° literature 101-101.5°.

p-Methylphenyl 1-naphthyl ketone was prepared by using the above procedure (Baddeley) starting with p-methylbenzoylchloride and naphthalene; mp 84-85°, literature 85°.

p-Chlorophenyl 1-naphthyl ketone was also prepared by the Friedel-Crafts reaction of p-chlorobenzoylchloride (Org. Syn. Coll. III, 29) with naphthalene using ethylene chloride as solvent. The mp reported in the literature (J. Chem. Soc. 1933, 444) 127-128° was subsequently shown to correspond to the β-isomer by preparing the α-compound via a Grignard reaction. The α compound, however, was not obtained in crystalline form. In the present work the α-compound was crystallized from methanol at low temperature using a methylene chloride / dry ice bath; mp 54-55°.

p-Fluorophenyl 1-naphthyl ketone was prepared by the Grignard reaction from 1-bromo-4-fluorobenzene and 1-naphthonitrile. (α-cyanonaphthalene was prepared from α-bromonaphthalene; J. Org. Chem. 1961, 26, 2522),
An ethereal solution of 1-naphthonitrile was added to a Grignard reagent prepared from 1-bromo-4-fluorobenzene. After boiling to reflux for 4 hr, the reaction mixture was decomposed with ice and hydrochloric acid. The solid ketimine hydrochloride formed was collected by filtration and hydrolized by boiling with water. After extraction with ether, the organic layer was neutralized, washed and dried with CaCl₂. Vacuum distillation provided a fraction, 120° at 0.25 torr (0.033 kPa), which easily crystallized from methanol as colourless prisms; mp 74-75°.

All purifications of these ketonic compounds were conveniently followed by thin layer chromatography using hexane/methylene chloride (1:1) as solvent. The α and β-isomers migrate close together, the α-isomer being faster. Also the β-isomer is highly fluorescent on the plate whilst the α- is not. No β-isomer was present in the reaction mixture of the fluorinated ketone.

4.3 Synthesis of para substituted aromatic thiones

p-Fluorophenyl 1-naphthyl thione. The corresponding ketone (0.5 g) was dissolved with 40 mL of methanol, the solution was poured into a three necked flask, and kept at -4°. HCl and H₂S were bubbled for 5 hr. The reaction flask was closed quickly with glass stoppers, sealed with Parafilm, and kept in the fridge at -20° for 36 hr; a deposit of blue crystals was present on the wall and at the bottom of the flask. The solvent was removed and the solid recrystallized from methanol, under nitrogen, until the mp was sharp (101-102°), and the IR showed no carbonyl stretching.

MS: 266(M⁺,54); 265(M⁺-1;100); Z3(M⁺-S); 171(M⁺-Ph); accurate mass M⁺-1: 265.04873, requires 265.04871.
IR (CCl₄): 3085, 1600, 1508, 1250, 1160 cm⁻¹.

UV-Vis (cyclohexane): 371.5(3.46), 384(3.42), 610(2.08) [nm(logε)].

**p-Methoxyphenyl 1-naphthyl thione.** The ketone (0.5 g) was dissolved with 40 mL of methanol and poured into a 100 mL round bottom flask; this was then closed with a cork provided with three glass tubes for the entrance and exit of the gases. HCl was bubbled for a total of 4 hr and H₂S for a total of 21 hr. The solution became navy blue and some blue solid was present on the wall. The cork was removed and immediately replaced by a glass stopper; Parafilm was used to seal the joint. The flask was kept in the fridge at -20° until crystallization was complete. The sample was filtered quickly under nitrogen. The filtrate was discarded and the solid purified by repeated recrystallizations from methanol. The resulting blue prisms had mp 61-62°. IR: free of carbonyl stretching.

**MS:** 278(M⁺), 277(M⁺-1;100), 267(M⁺-CH₂), 234(M⁺-CS), 171 (M⁺-PhOCH₃);
accurate mass M⁺: 278.07696, requires 278.07653.

IR (CCl₄): 3060, 2940, 1594, 1160, 1250, 1500 cm⁻¹.

**NMR (DCCl₃):** 3.84 ppm (singlet).

**p-Methylphenyl 1-naphthyl thione.** The ketone (0.1 g) was dissolved with 20 mL of methanol. HCl was bubbled for 11 hr and H₂S for 12 more hours. A blue crystalline solid resulted, which was collected by filtration under nitrogen. The blue solid was washed twice with small portions of methanol and recrystallized from the same solvent; blue needles, mp 87°.

**MS:** 262(M⁺,65), 261(M⁺-1;100), 247(M⁺-CH₂,19), 171(M⁺-PhCH₃,25);
accurate mass M⁺: 262.08018, requires 262.08162.
IR (CCl₄): 3080, 1605, 1156, 1260 cm⁻¹.

NMR (DCCl₃): 2.33 ppm (singlet).

UV-Vis (cyclohexane): 222(4.33), 333(3.78), 380(3.08)sh. and 608(2.21, benzene) [nm(logε)].

*p-Chlorophenyl 1-naphthyl thione. The ketone (0.52 g) was dissolved in 20 mL of methanol. HCl was bubbled for 4 hr and H₂S for a total of 6 hr at -4°. The solution turned dark green. The reaction mixture was then poured quickly into a separatory funnel that contained hundred mL of water. The aqueous layer was discarded; the pentane was evaporated and the sample passed through a column that contained methylene chloride and 40 g of Florisil. The first fraction gave after evaporation of the solvent, a green oil (52%) which showed no CO stretching in the IR spectrum.

MS: 282(M⁺,52), 281(M⁺-1,100), 283(M⁺+1,45), 245(M⁺-Cl), 171(M⁺-PhCl), 127(C₁₀H₇⁺); accurate mass M⁺-1: 281.01855, requires 281.01856.

IR (CCl₄): 3080, 1585, 1250, 1100 cm⁻¹.

UV-Vis. (benzene): 330(4.08), 613(2.20) [nm(logε)].

4.4 Photocyclization products

The photocyclizations were performed using a 450-W medium-pressure mercury lamp in conjunction with a Corning 3-66 filter to absorb wavelengths shorter than 560 nm. Solutions were degassed by freeze-pump-thaw cycles (2 x 10⁻⁵ torr: 2.6 mPa) and irradiated until disappearance of the thione colour.

2-(4-Fluoro-phenyl)-2H-naphtho[1,8bc]thiophene. The thione (5.25 mg) in 5 mL of benzene was irradiated as indicated above. The product was chromatographed on TLC (silica gel; hexanes) to give white crystals.
(2.17 mg, 41%); mp 110.5-111°; white needles, methanol.

MS: 266 (M⁺, 78), 265 (M⁻,1,100), 171 (M⁺-PhF, 60); accurate mass M⁺: 266.0562, requires 266.0565.

NMR (DCCl₃): singlet at 6.3 ppm.

2-(4-Methoxy-phenyl)-2H-naphtho[1,8bc]thiophene. The thione (10.08 mg) was diluted to 5 mL with benzene and irradiated as indicated above. Isolation on TLC (silica gel; hexanes) gave 5.28 mg (52%) of cyclized product; mp 122° (white needles; methanol).

MS: 279 (M⁺, 99), 277 (M⁻,1,100), 247 (M⁺-OCH₃, 58), 234 (M⁺-CS, 41), 171 (M⁺-PhOCH₃); accurate mass M⁺: 278.07614, requires 278.07653.

NMR (DCCl₃): 3.78 ppm (s, 3H), 6.28 ppm (s, 1H).

2-(4-Methyl-phenyl)-2H-naphtho[1,8bc]thiophene. The thione (10.05 mg) was diluted with benzene to 5 mL and irradiated as above. Isolation on TLC (silica gel; hexanes) gave 3.78 mg (38%) of the cyclized product. The yield was 38.5% when irradiated into the S₂ band.

MS: 262 (M⁺, 100), 261 (M⁺-1, 98), 171 (M⁺-CH₃, 78), 247 (M⁺-CH₃, 47); accurate mass M⁺: 262.08125, requires 262.08162.

2-(4-Chloro-phenyl)-2H-naphtho[1,8bc]thiophene. A solution of the thione (4 mL; 6.709 x 10⁻³ M) was irradiated as indicated above. Isolation on TLC (silica gel; hexanes) gave 3.75 mg (49.5%) of cyclized product; mp 83-84° (methanol).

MS: 284 (M⁺,2, 29), 283 (M⁺-1, 41), 282 (M⁺, 75), 281 (M⁺-1, 74), 171 (M⁺-PhCl, 100).

4.5 Disappearance quantum yields

Solutions of thione in benzene were degassed by the freeze-pump-thaw method to a residual pressure of 2 x 10⁻⁵ torr (2.6 mPa) and the
samples sealed on the vacuum line. Cells of 1 cm optical path were used. The samples were irradiated in a Jasco-CR-FA Spectro Irradiator, provided with an electronic integrator that displayed the number of counts, proportional to the integrated number of photons. Two holes of the irradiator were used: one centered at 362 nm and the other at 596 nm (or at 620 nm). The first was calibrated with potassium ferrioxalate, actinometer, and a thermopile was used to measure the ratio between the energies incident on the long and short wavelength holes. From this ratio the calibration factor at short wavelength was obtained by

$$\kappa_l = \kappa_s \frac{E_l \lambda_l}{E_s \lambda_s}$$

where $E$ are thermopile readings, $\lambda$ are wavelengths and the subscripts $l$ and $s$ refer to the long and short wavelength case, respectively.

The temperature was fixed at 20°. The disappearance of the thione was followed spectrophotometrically at long wavelength ($S_1$ thione band). The irradiations were carried out typically to conversions < 10%.

Short wavelength irradiation case ($S_2$ band)

The absorption of light was complete. The quantum yields were calculated from

$$\Phi_{dis} = \frac{V \Delta A}{\varepsilon b K_s \mu}$$

where $\Delta A/\mu$ is the slope of the straight line of the plot $\Delta A$ vs. $\mu$ (decrease in absorbance at the monitoring wavelength vs. number of counts), $\varepsilon$ is the molar extinction coefficient at the monitoring wavelength, $b$ is the optical path (1 cm), $K_s$ is the calibration factor (moles of photons/count) at short wavelength, and $V$ is the volume of the sample ($4 \times 10^{-3}$ L).
Long wavelength irradiation case ($S_1$ band)

Since the samples were not absorbing all of the incident light (transmittances were < 5%), the quantum yields were calculated from

$$\log (10^{A_{1}} - 1) = - (\Phi_{\text{dis}} \varepsilon b K_1 u / V) + \log (10^{A'_{1}} - 1)$$

by plotting the left hand side of this equation versus $u$ and evaluating $\Phi_{\text{dis}}$ from the corresponding slope,

$$\frac{-(\text{slope}) V}{\varepsilon b K_1} = \Phi_{\text{dis}}$$

$A'$ is the absorbance (initially $A_{1}'$) at the irradiation wavelength, $\varepsilon$ is the molar extinction coefficient at the irradiation wavelength, $K_1$ is the calibration factor at long wavelength in moles of photons per count, $V$ and $b$ are as before $4 \times 10^{-3}$ L and 1 cm, respectively.

4.6 Attempt to observe fluorescence from aromatic thiones

A dilute solution of phenyl 3-fluoranthenyl thione in hexane was prepared. The solvent was purified by passing it through an alumina column. The standard of fluorescence was quinine bisulphate in $1\text{N H}_2\text{SO}_4$ ($\Phi_f = 0.55$). The excitation wavelength was 320 nm. A Perkin-Elmer MFP4 spectrofluorimeter was used. A signal, if at all meaningful, was observed centered around 470-460 nm. The quantum yield for that band, calculated from

$$ \frac{\text{Area} / \text{sensitivity(sample)}}{\text{Area} / \text{sensitivity(standard)}} x \Phi_f(\text{standard}) = \Phi_f(\text{sample}) $$

was $= 4 \times 10^{-5}$, i.e. it could be ignored (refractive index variations were not considered). Also PNT did not fluoresce appreciably even at 77 K.
4.7 Laser flash photolysis experiments

The laser flash photolysis equipment was one already described in detail. 77-78

Sample preparations: The cells were made of Suprasil. For use with the nitrogen laser the dimensions were typically 3 x 7 mm (3 mm being the optical path). The solutions were prepared in such a way that the absorbances at the laser wavelength were typically around 0.4. Thione concentrations were calculated from the absorbance in the S2 band. Solutions were purged by bubbling N2 through a septum and sealed with Parafilm.

The absorption spectrum of the sample was recorded before the laser experiment. It was also recorded after the experiment to check that permanent photochemical reactions were not significant.

When the excimer laser was used samples were prepared in a similar way, but the cells were 7 mm wide and had 7 mm optical path. Excitation with this laser (XeCl excimer laser) occurred at a right angle from the monitoring beam.

4.8 Quenching of the transient of PNT by molecular oxygen

A stock solution of PNT in benzene was prepared. To each of three equal Suprasil cells (3 mm optical path) 1.00 mL of this stock solution was added. One of the cells was purged by passing N2. Another cell was saturated with air. The third cell was purged with O2 from a lecture bottle. The rubber septa were sealed with Parafilm. The decay rate of each sample was then measured under similar conditions without turning the laser off. The conditions were: excitation wavelength, 337 nm; monitoring wavelength, 420 nm; temperature of the cell, 300 K; number of
shots, 20 per decay curve. Since there was the possibility of having a noticeable amount of reaction when oxygen was present, the decay rates of the above three samples were remeasured (set b) following the determination of the decay rate of the fresh samples (set a).

The molar concentrations of oxygen were calculated from the molar percentage composition of \(O_2\) in the gases (taken as 0%, 20%, and 100%, for solutions saturated with \(N_2\), air, and \(O_2\), respectively), the vapor pressure of benzene (104 torr; 13.8 kPa) and the gas molarity at 760 torr (101 kPa) pressure (0.00919 M).

The results are reproduced in Table 8 and Figure 1.

4.9 Intersystem crossing experiments using laser flash photolysis

a) Procedure. The thione was dissolved in benzene (Aldrich, Gold Label). A cell of 3 mm optical path was used. An accurate volume of the solution was introduced into a cell. The same procedure was done with the standards used (benzophenone or butyrophenone). The absorbances of the solutions at the laser wavelength (337 nm) were about 0.7, to make the matching of the absorptions relatively easier. The acceptor (tetracene) had minimal absorption at 337 nm. In the experiments using tetracene (Princeton Organics) a saturated solution of tetracene in benzene was prepared in the dark and separated from the solid by decantation. By using \(\epsilon_{474} = 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\) the concentration of the tetracene solution used was determined spectrophotometrically to be \(2.66 \times 10^{-4} \text{ M}\).

To the solution under study increasing amounts of the tetracene solution were added. The resulting solutions were purged with \(N_2\) and the decay measured after each addition of tetracene.

Without turning the laser off or changing other conditions, the
other samples were treated in a similar way.

The decays were followed at 470 nm, where the triplet tetracene absorbs with minimum interference from the thione transient. The parameter of interest was the maximum absorbance due to the tetracene triplet (the decay of the tetracene triplet is long-lived, > 5 μs).

b) Consideration of the effect due to the dilution of the donor. There is a dilution effect on the absorbance of the donor (a thione or a standard ketone) caused by the increase in volume due to the addition of tetracene solution

\[ OD' = OD \frac{V}{V'} \]

where the original donor solution had a volume \( V \) and optical density \( OD \). These values change to \( V' \) and \( OD' \) after a certain volume \( (V' - V) \) of tetracene solution has been added. The prime then, is used to indicate the dilute case.

The fraction of light at 337 nm that the thione originally absorbed \( (1 - 10^{-OD}) \), becomes \( (1 - 10^{-OD} \frac{V}{V'}) \) due to the dilution effect caused by the addition of a certain volume of tetracene solution \( (V' - V) \).

The fraction of 337 nm light absorbed by the ground state of the donor will determine the magnitude of the signal due to the transient. If we divide the observed signal from the transient by the fraction of light that has been absorbed by the donor, we obtain the signal that we would have obtained if complete absorption at 337 nm had occurred. In particular, from the observed top value of the absorption by the transient \( (TOD') \) we can find the top value that we would have obtained if all the 337 nm light had been absorbed \( (TOD) \), as follows

\[ TOD = TOD' \left(1 - 10^{-OD} \frac{V}{V'} \right)^{-1} \]
after a given addition of tetracene solution that increased the volume to V'.

4.10 Preparation of trans-1,1,4-triphenylbutadiene

At the end of the process outlined below, the crude mixture was distilled between 175-180° at 0.8 torr (0.10 kPa). Then it was chromatographed on TLC plates of silica gel using hexane as eluent. Finally it was recrystallized twice from methanol; mp 100.5-101° (white needles).

\[ \text{N}_2\text{CHCOOEt + PhCH=CH}_2 \quad \rightarrow \quad \text{Ph} \Delta \text{COOEt} \]

(J. Org. Chem. 1964, 29, 2814)

\[ \text{Ph} \Delta \text{COOEt + 2 BrMgPh} \quad \rightarrow \quad \text{Ph} \Delta \text{C(Ph)}_2\text{OH} \]

(J. Am. Chem. Soc. 1960, 82, 1405)

\[ \text{Ph} \Delta \text{C(Ph)}_2\text{OH} \quad \stackrel{I_2}{\longrightarrow} \quad \text{trans-PhCH=CH=CH(Ph)}_2 \quad \text{benzene} \]

(J. Am. Chem. Soc. 1960, 82, 1405)
CHAPTER 5 - INTRODUCTION TO THE PROBLEM OF WATER-HYDROCARBON CONTACT IN MICELLES

5.1 Introduction to the subject

Micelles (from Latin micella: small bit) simply stated are molecular or ionic aggregates formed in aqueous solutions of detergents above a certain concentration region.\(^{79-80}\)

Micelles are made of amphiphiles, molecules which have a hydrophobic part and a hydrophilic part with a marked separation of their solvation properties.\(^{81}\) Amphiphiles can be ionic (anionic or cationic depending on the charge of the larger ion) or nonionic (dipolar or zwitterionic, the latter can be amphoteric).

Some amphiphiles have structures containing a single long alkyl chain (with or without a substituent) and a polar head group and undergo extensive aggregation in water. This type of micelle-forming amphiphiles will be considered in this thesis.

Examples of amphiphilic substances are surfactants. The term surfactant (contraction for surface-active agent) is applied to a compound that changes the properties of the surface of the liquid to which it is added. Detergent surfactants (and soap, which is also a surfactant formed by the reaction of fats with alkali) lower the water's surface tension, facilitating for example the wetting of materials, and when micelles form, the solubilization of hydrophobic substances.

Although opposed by repulsion between the head groups, aggregation of dissolved surfactants to form micelles is promoted by hydrophobic interactions of the tails with water.\(^{81}\)

Micelles form predominantly above a certain critical micelle con-
centration (cmc). This occurs over a range of concentrations for relatively short chain surfactants which have high cmc's, but the range can be very narrow for long chain surfactants which have low cmc's. Many properties change markedly around the cmc region and they can be used in principle to determine the cmc.\textsuperscript{82}

In general micelles in water are viewed as roughly spherical clusters formed by about 50 - 100 surfactant monomers,\textsuperscript{83} with their alkyl chains towards the inside and the polar head groups towards the outside.

Some dynamic information is also available. The lifetime for the relaxation of a micelle is considered to be in the millisecond range and that of a monomer to leave the micelle in the microsecond time scale. The interior of the micelles is generally accepted to be quite fluid-like.\textsuperscript{84}

Although micelles in aqueous solution have been studied intensively for years and by a variety of techniques,\textsuperscript{82} some vexing problems remain, among them the extent of water-hydrocarbon interaction. This problem is crucial to the understanding of the typical average structure of micelles, to the interpretation of many experimental results and the evaluation of theoretical studies, but it has been much debated and is highly controversial.

In the rest of this chapter several studies by others on the extent of water-hydrocarbon interaction in aqueous micelles, the difficulties that arise in the use of spectroscopic probes, and some models of micellar structure will be mentioned. Subsequently some results obtained during the course of this thesis by using nitrite and carbonyl probes will be presented in Chapter 6 and discussed in Chapter 7, with the
hope of making some contribution to the subject. The main conclusion from this part of the thesis is that for a small probe—intrinsic (directly bonded) to a dodecanoate surfactant chain the environment of the probe in micelles is always polar, regardless of the position of substitution.

Let us turn our attention now to reports on the extent of water to hydrocarbon contact in aqueous micelles.

5.2 Reports on water-hydrocarbon contact in micelles

Rather than an exhaustive coverage of the many papers that directly or indirectly bear relation to this subject, only an overview of the main types of studies will be presented here, to understand some of the difficulties involved.

5.2.1 Reports claiming limited water-hydrocarbon contact

Limited water-hydrocarbon contact is used here to mean that the hydration of the micellized amphiphile is basically that of the head groups,\(^\text{84}\) perhaps also of the \(\alpha\)-methylenes, and at the most of the \(\beta\)-methylenes.

A summary of arguments against deep water penetration into micelles was given by Lindman et al.\(^\text{85}\) They are mentioned here with some comments at times.

a) A claim has been made that it is possible to pack molecular models of surfactant molecules into micelles without leaving sizeable voids filled with water.\(^\text{82,85}\)

b) The global hydration numbers (i.e. the number of water molecules that move with a particle as a kinetic entity) as derived from viscosity or diffusion data were small for micelles (e.g. 5 to 10 water molecules
per amphiphile ion). This was rationalized in terms of hydration of the polar head groups and their counterions implying limited water-amphiphile interaction.\textsuperscript{86-89}

The self-diffusion coefficient of water decreased with concentration of surfactant, the decrease being less dramatic above than below the cmc. This observation was taken to indicate that a strong dominating part of the water-amphiphile contact is eliminated on micellization.\textsuperscript{85}

c) The isentropic apparent compressibilities of several surfactants in micelles were estimated to be large and positive, and taken as an indication of a hydrocarbon-like environment inside the micelles.\textsuperscript{90}

d) For alkanes solubilized in micelles the partial molar volumes and compressibilities were found to be closer to those in liquid alkanes than to those in water.\textsuperscript{91}

e) The low solubility of water in alkanes was taken as support for the absence of water penetration into micelles.\textsuperscript{85}

f) The low rate of water diffusion between reversed micelles\textsuperscript{92} and between bilayers\textsuperscript{93} was taken as indication against water penetration in aqueous micelles.\textsuperscript{85}

g) The stability ranges of different phases were considered inconsistent with penetration of water into micelles.\textsuperscript{85}

h) The H/D isotope effect on $^{19}$F-NMR relaxation for partially or fully fluorinated surfactants seemed to disappear on micelle formation. This was attributed to a decreased water-hydrocarbon contact in micelles.\textsuperscript{94}

i) The failure to observe H/D isotope effect on the $^1$H-NMR relaxation of the alkyl-protons together with its observation for the ethoxy protons, for nonionic surfactants micelles, was taken as an indication of
water interaction up to the ethoxy proton level only.\textsuperscript{95}

j) Neutron diffraction studies using the D\textsubscript{2}O/H\textsubscript{2}O exchange method showed water penetration up to the glycerol-fatty acid ester group for phospholipid bilayers.\textsuperscript{96-98} Neutron diffraction studies of micelles have also appeared. The results were analyzed using a model of micelle with hydration mainly of the head groups,\textsuperscript{99} or by others with allowance for wetting of the first few methylenes.\textsuperscript{100}

No comments will be made here on the scope of the applicability of the older techniques, like calorimetry, viscosimetry, etc., nor on the explicit or implicit assumptions involved in the derivation of the equations used and the conclusions reached from the rough data, since they can be found in early papers.\textsuperscript{102}

The modern approaches deserve further comments. Ulmius and Lindman studied the \textsuperscript{19}F-NMR spin-lattice relaxation in H\textsubscript{2}O and D\textsubscript{2}O solutions of the amphiphiles: CF\textsubscript{3}(CF\textsubscript{2})\textsubscript{2}COOH, CF\textsubscript{3}(CF\textsubscript{2})\textsubscript{6}COONa, CF\textsubscript{3}(CH\textsubscript{2})\textsubscript{8}COONa and CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{3}CF\textsubscript{2}(CH\textsubscript{2})\textsubscript{4}COOK. Since an important relaxation mechanism of \textsuperscript{19}F involves magnetic dipolar interaction with nearby hydrogens,\textsuperscript{94} the relaxation being slower in D\textsubscript{2}O, they considered that the H/D isotope effect on the relaxation reflected on the direct contact of an amphiphile to water, and the key idea was that the differences tended to disappear when the amphiphile was mainly in micelles, due to the decreased water contact.\textsuperscript{94}

Their experimental results seemed to support this for perfluoro- butyrate. For perfluorooctanoate in turn, the isotope effect on the fluorine relaxation seemed very small at C\textsubscript{2}, not significant from C\textsubscript{3} to C\textsubscript{7} and noticeable only below the cmc at C\textsubscript{8}. For CF\textsubscript{3}(CH\textsubscript{2})\textsubscript{6}COONa the small
isotope effect seemed to disappear when the concentration was increased above the cmc.

For the partially fluorinated decanoate \( \text{CH}_3(\text{CH}_2)_3\text{CF}_2(\text{CH}_2)_4\text{COOK} \) there was no isotope effect below the cmc, and above it the rates in \( \text{D}_2\text{O} \) seemed slightly higher than in \( \text{H}_2\text{O} \). These authors suggested that there could be a slower reorientation for the micelles in \( \text{D}_2\text{O} \), and for the monomers of this amphiphile an "intramolecular hydrophobic effect" that impaired water contact even in the monomers.\(^{94}\)

In general these authors are of the opinion that no appreciable water contact occurs except near the micellar surface.\(^{94}\)

Hayter and Penfold studied micelles of sodium dodecyl sulphate (SDS) by static and dynamic neutron small-angle scattering techniques.\(^{100}\) The scattered intensity \( I(Q) \) can be written for spherical micelles of uniform dimensions as proportional to a product of a structure factor for the correlations between micelles \( S(Q) \) and the single-particle scattering function \( P(Q) \). For the former they derived a method of calculating it for the case of macroions interacting through a screened Coulomb potential. For the latter, the single-particle scattering function in which one is usually interested, they calculated it to fit experimental results by using a three-shell model of a micelle: a paraffinic sphere, surrounded by a narrow hydrocarbon shell in which water could penetrate, and on the outside, a polar region where ions, their hydration water and the first few methylenes could be present.

Their calculation of the scattering intensity with all parameters free would thus require fitting of six parameters: two radii, two scattering length densities, the charge and the aggregation number. With the
assumed model they reduced it to two parameters by using some physical considerations; for example, they assumed that water could not penetrate the central paraffinic region. They left the aggregation number and total charge as adjustable parameters. They used a radius of the paraffinic region and a radius of the core which were not dramatically different. The resulting fitting to the experimental curve was good, and they inferred that there was not a deep water penetration.  

More recently others applied neutron scattering techniques to the study of lithium dodecyl sulphate (LDS) micelles, claimed to fulfill the requirement of monodispersity better than SDS. They studied LDS in mixtures of H₂O/D₂O, perdeuterated and protonated LDS mixtures in D₂O, and LDS mixed with LDS containing CD₃ instead of CH₃. From their extensive experimental results and analysis they concluded that the spatial distribution of the methyl groups was Gaussian-like with a half-width of 8.8 Å around the center, implying that the alkyl chains were not radially directed in an all-trans configuration, nor likely as in a completely disordered liquid.

They concluded also that water penetrated the core at most to the α-CH₂ level, and favored a picture of micelle with a close-packed core of hydrocarbon chains with intermediate order, in general accordance with the Dill and Flory theoretical model of micelles. Menger objected to the application of the Dill and Flory model to micelles.

5.2.2 Reports claiming extensive water-hydrocarbon contact

Extensive water to hydrocarbon contact is taken here to mean that water is not restricted to the head groups region, mainly on the outside of the micelle, but considerably inside so that several carbons of the
hydrocarbon chain are wet on an average basis.

It should be emphasized that the focus of interest here is the contact of water with the hydrocarbon chains rather than the total hydration of the micelle. The latter is extensive in terms of volume even if water does not penetrate deeply inside the micelle. For example, simple volume calculations for SDS assuming a spherical model indicate that when only the head groups region is hydrated as much as 50% of the total micellar volume is hydrated. This becomes 75% if the α- and β-methylenes are also wet. 84

5.2.2.1 Studies using no probes

Using molecular models of a surfactant, Menger constructed a model of micelle that shows extensive water penetration. 105 Others claim the contrary. 85

A small-angle X-ray scattering of sodium octanoate solutions was done by Svens and Rosenholm. 106 To obtain structural information from their measured scattering curve they used a model of a micelle, which could give a close fitting between the theoretical and experimental scattering curves.

They used a spherical model of a micelle with two regions: a paraffinic one at the centre and a polar region in the outside. Several parameters were involved in the calculation, among them the electronic densities of both regions and their radii. Curve fitting with certain choices of electronic densities lead to calculated values of the radii which were small (4.5 to 6.5 Å) for the paraffinic region and very large (26.5 to 27.5 Å) for the polar region. They considered this polar region to consist of the Stern as well as part of the Gouy-Chapman layer.
micelle model presented "wedges" where water and counterions penetrated. Their analysis was objected to by Lindman and Wennerström, who considered the predicted total micellar volume to be too high. 89

A laser-Raman spectroscopic investigation of short-chain carboxylates (up to C₉) in aqueous solution has been reported. 81 This technique was considered promising because it was claimed that separation of polar and conformational effects was possible. 81

Thus some C-C vibrations were considered as sensitive probes for trans-gauche configurational changes. The ratio of the 1080 or 1040 cm⁻¹ vibrations to the vibration characteristic of all-trans configurations at 1125 cm⁻¹ was observed to decrease sharply with the concentration of sodium octanoate up to the cmc, remaining practically constant above the cmc.

By contrast the region of the C-H stretchings was considered to be sensitive to packing, in particular to the polarity of the environment. Therefore they plotted the intensity ratio of the symmetric C-H stretching in CH₃ (2890 - 2880 cm⁻¹) or the antisymmetric C-H stretching in CH₂ (2918 - 2911 cm⁻¹) to the polarity sensitive symmetric C-H stretching in CH₂ (2948 - 2927 cm⁻¹), noticed that the ratio increased smoothly with octanoate concentration, and took this to imply a decreased polarity at high concentration.

Since the changes in the peaks sensitive to the polarity of the environment were much more gradual than the shift in the gauche-trans equilibrium, they concluded that the hydrocarbon chains were associating without a removal of the whole aqueous "cage" around them, and that the hydration of the micelles decreased at concentrations higher than the
Lindman et al. remarked that Rosenholm et al.'s interpretation was based on analogy rather than on theoretical considerations. A more recent Raman spectroscopic study of surfactant solutions claims that for the band at 2950 cm⁻¹ the concentration effect near the cmc is due to intermolecular vibrational coupling of the C-H bonds.

5.2.2.2 Studies using intrinsic probes

Muller studied the ¹⁹F-chemical shifts of partially fluorinated surfactants. The shifts were halfway between those in water and hydrocarbon. This could be taken to imply penetration of water into the micelle, but objections to this interpretation were raised by Mukerjee et al. who presented arguments for sampling of the CF₃ groups of the micelle surface based on the non-ideality of fluorocarbon and hydrocarbon solutions. Muller studied later the mechanism of the ¹⁹F-chemical shifts and found it too complicated to permit obvious conclusions.

Yoshioka studied by ESR the rotation of spin probes of some molecules, among them the following,

\[
\text{CH}_3(\text{CH}_2)_{12} - C - (\text{CH}_2)_3 \text{COOH}
\]

\[
\text{CH}_3\text{CH}_2 - C - (\text{CH}_2)_{14} \text{COOH}
\]

dissolved in SDS in basic medium. He measured the rotational correla-
tion time at different temperatures and derived a relationship to evaluate the activation free energy for the rotation.

He obtained activation enthalpies for the probe rotation in micelles considerably higher than in dodecane. The hyperfine splitting constants were high, consistent with polar environments, and this led him to conclude that there was penetration of water into the core. He disregarded the alternative explanation that the probe was near the surface, based on a comparison of enthalpies of activation for these probes and other less hydrophobic probes considered earlier to reside near the surface.\textsuperscript{112}

Whitten used as probes terminal trans stilbene substituted alkanoic acids of the type

\[
\begin{align*}
\text{\textcircled{O}} & - \text{\textcircled{O}} & (\text{CH}_2)_n \text{COOH} \\
S_n, \quad n = 4 - 6, 7, 10, 12, 16
\end{align*}
\]

dissolved in SDS. Fluorescence quenching by methyl viologen (MV\textsuperscript{2+}) and by the long chain methyl viologen N-methyl-N'-hexadecyl-4-4'-bipyridinium\textsuperscript{2+} (MV\textsubscript{16}\textsuperscript{2+}) was studied in SDS micelles. The fluorescence quenching was considered to occur predominantly by ground state complexation between the stilbene and the MV\textsuperscript{2+} chromophores. Complexation occurred readily regardless of where the stilbene chromophore was located in the surfactant molecule. They concluded that micelles have very open structures with extensive hydrocarbon-water interfaces. Furthermore they suggested that the distinction between polar and nonpolar sites was small, and that there was not a well-ordered phase boundary between "Stern layer" and hydrocarbon core.\textsuperscript{113} They also provide a two dimen-
sional picture of this open micelle model.\textsuperscript{114}

Turro et al. investigated two indole substituted surfactants as fluorescent probes for the location of chromophoric groups in micelles, 11-(3-hexyl-1-indolyl)undecyltrimethylammonium bromide, represented as 6-In-11\textsuperscript{+}, and sodium 11-(3-hexyl-1-indolyl)undecylsulphate, represented as 6-In-11\textsuperscript{−}. These substituted surfactants, as well as 1-methyilindole were studied at different concentrations of hexadecyltrimethylammonium bromide (HTAB) and SDS.\textsuperscript{115}

Changes in the absorption, fluorescence, fluorescence lifetime and quenching by Co\textsuperscript{2+} and NO\textsubscript{2}\textsuperscript{−} were studied. Although the results will not be presented here, they concluded that 1-methyilindole is bound on the surface of HUTBr micelles, while the chromophore of 6-In-11\textsuperscript{+} is at the interior of the micelle. The environment of 6-In-11\textsuperscript{−} was somewhat less hydrophobic. They concluded that the head group of the surfactant mattered. The NMe\textsubscript{3}\textsuperscript{+} groups were considered to be hydrophobic, tightly packed and thus able to preclude water penetration. The reverse was the case for the hydrophilic OSO\textsubscript{3}\textsuperscript{−} groups which permitted easy water penetration.

Menger studied the surfactant

\[ \text{CH}_3(\text{CH}_2)_7\text{CO}(\text{CH}_2)_7\text{N}^+\text{(CH}_3)_3\text{Br}^- \]

by \textsuperscript{13}C-chemical shift of the oxo-carbon. Though a reference to this paper appears in section 5.3, it suffices to mention here that in it a claim is made of water penetration into micelles up to at least the 7-th carbon.\textsuperscript{116}

5.2.2.3 Studies using extrinsic probes

Although solubilization of organic compounds in micellar media is
one of the most important properties of surfactants which render them useful in many applications,\textsuperscript{81,105} the use of solubilized probes to investigate the structure of micelles often has the drawback of providing ambiguous information if the average probe location is not securely known. Extrinsic probes have been very useful on the other hand in the evaluation of rates of entry and exit of probes into micelles and in quenching studies.\textsuperscript{117-120}

The problem of solubilization sites of the often used aromatic hydrocarbon probes (like pyrene) has been unsettled for several years,\textsuperscript{121-125,126} although later views appear to indicate solubilization near the surface,\textsuperscript{82,85,127-129} at low solubilizate concentration. The large probe size generated the concern of some, for example with the pyrene probe.\textsuperscript{130-132}

For extrinsic probes containing an ionic or a somewhat polar group, the average solubilization site is often considered to be near the surface.\textsuperscript{82,133-134,135}

It seems likely that most solubilized molecules in micelles experience a polar environment.\textsuperscript{94} Purely aliphatic hydrocarbons are a class in themselves; although they are the most likely candidates to be dissolved in the interior of micelles as assumed frequently,\textsuperscript{90-91} they are not very sensitive to polarity changes and ways to test their environments are rather indirect.

In closing it should be mentioned that caution is needed in extending conclusions based on analogies from related systems to micellar systems. For example it has been reported recently that carbenes generated from diphenyl diazomethane reacted with water much more easily in a
micellar system than in a microemulsion, indicating the ready accessibility of water molecules within the micelles, but not within the microemulsions. 136

5.3 Difficulties with the use of spectroscopic probes

Two problems associated with the use of spectroscopic probes to study the amphiphile-water contact have been pointed out by Lindman and Wennerström. 89

One is that "the relationship between the spectroscopic parameter and the nature of the molecular environment of the probe should either have a sound theoretical basis or it should be experimentally tested in detail". 89 Justifications for the use of the parameters of the probes used in this thesis are mentioned in Chapter 7. This is done in some detail for the oxo-carbon chemical shifts used here. Menger et al. had used them for some ketones, 116 but in a merely empirical way, with no theoretical basis, as noted by Lindman and Wennerström. 89

The other problem mentioned is that "to deduce anything about the molecular environment in the micelle one must independently determine how the probe is distributed in the micelle". 89 This problem is not easy to solve, and will not be studied in this thesis. It is, however, very important. That water penetrates into the micelle or that the probe is near the surface of the micelle, or both, could explain the high polarities that the probes might experience.

For example extrinsic probes may well be solubilized near the surface if they are polar, 84 or perhaps too if aromatic, 121 and therefore inform little about the micellar core. The same problem could happen with intrinsic probes, if the chains were able to adopt conforma-
tions that bring the probe towards the outside of the micelle.

Knowledge of whether the chains are coiled or not is thus crucial. Some papers in which the presence or absence of chain coiling is discussed will be mentioned in what follows, beginning with a list of some studies by Menger et al.:

1) For the amphiphile CH₃(CH₂)₇CO(CH₂)₇N⁺(CH₃)₃Br⁻ Menger argued that no coiling occurred, based on the following:¹¹⁶

a) The cmc of this keto-surfactant was only about three times larger than similar surfactants but lacking the oxo-carbonyl; he took this as an indication that a folded configuration was not likely.

b) Work of others was used by Menger to support his view that the above surfactant was not folded back. He quotes the work by Brown and Schofield,¹³⁷ who investigated the surfactants

Me(CH₂)₁₅N⁺Me₃Br⁻
Me(CH₂)₁₀CHOH(CH₂)₆N⁺Me₃I⁻
Me(CH₂)₅CHOH(CH₂)₄N⁺Me₃Cl⁻ or Br⁻

by ¹³C-spin-lattice relaxation times in the presence and absence of a Gd³⁺ relaxation reagent. In its presence all the T₁ values were diminished, but particularly of the carbons close to the head-group. They concluded that the hydroxy-group was buried in the micellar core rather than present close to the surface by chain coiling.

c) Menger's previous studies claiming that favorable looping of chain separating two polar functionalities at an air-water interface required chain lengths greater than eight.¹³⁸

2) Dissolved di-n-hexyl ketone (0.13 M) in HTAB bromide (0.27 M) presented a carbonyl ¹³C-chemical shifts almost 5 ppm smaller than the
corresponding shift of 8-oxohexadecyltrimethylammonium bromide (0.46 M) in 0.20 M HTAB. By comparing these shifts with the shifts in solvents he concluded that the average environment of di-n-hexyl ketone in micelles was equivalent to dioxane, that the carbonyl probe did not "pull" water into a normally aprotic micellar interior, and that water penetrated the micelles at least to the first seven carbons.\textsuperscript{116}

3) The diaxial-diequatorial equilibrium of (+)-trans-2-chloro-5-methyl-cyclohexanone changed with the solvent nature, as monitored by optical rotatory dispersion (ORD). The former conformation predominated in heptane and in reversed micelles of water and sodium dioctylsulfosuccinate (AOT) in heptane. The latter conformation predominated in water and in normal micelles of SDS or HTAB. Since the ORD results in heptane and in heptane/water/AOT were similar and there was water available in the reversed micelle system, Menger concluded that the probe in normal micelles did not "drag" water into the micelle, and the observed effects were explained by penetration of water into SDS or HTAB micelles.\textsuperscript{173}

4) Cases in which looping of the probe was impossible due to its natural rigidity were also considered by Menger. He used $\Delta^4$-steroidal enones as probes, some of which had polar substituents (e.g. 17$\beta$-carboxylate) away from the enone probe group.\textsuperscript{140}

They determined spectrophotometrically the second order rate constant for the steroidal enone reduction by sodium borohydride in aqueous HTAB in basic medium. The concentrations were 5.4 x $10^{-6}$, 0.016, 0.020 and 0.10 M, respectively. The relative rate constants (referred to the rate constant for the BH$_4^-$ reduction of 3-methyl-2-cyclohexen-1-one in water, 0.048 M$^{-1}$s$^{-1}$ at 25$^\circ$) ranged between 2.2 and 4.4 for the case of
polar substituents in the 17-position and somewhat larger (7.8, 9.2) when the substituent was non-polar. The fact that the rates were larger than those expected in water was ascribed to the local concentration effect of the anionic borohydride on the cationic micelles.

In 0.010 M dodecanoate (unspecified counterion) rate increases of 4- and 2-fold were observed for the reduction of the steroids containing CO₂⁻ and an alkyl chain, respectively, in the 17-position.

The results for the HTAB system were interpreted by Menger to indicate that binding of the carbonyls was not in water-free oil droplets, that the carbonyls did not loop out of an oil droplet onto the micelle surface because anchoring groups like CO₂⁻ were considered to be on the surface, nor that the carbonyl dragged water into a normally nonaqueous oil droplet, and that the only explanation was that the steroids were in hydrophobic patches near the micelle surface where water and BH₄⁻ were accessible.⁴¹

5) Acetylenic hydrogens have solvent sensitive shifts. Menger used this property to study the environment of the probe in 0.20 M surfactants of the type HC₆CD₂(CH₂)₁₀X where X = N⁺Me₃Br⁻ or OSO₃⁻ and in 0.010 M of HC₆CD₂(CH₂)₁₀N⁺(CH₃)₂(CH₂)₁₁CH₃Cl⁻. They all gave downfield shifts of around 2.1 ppm, which were closer to the shifts in polar solvents (2.19 ppm in 2:1 MeOH/water) than in cyclohexane (1.66 ppm). He concluded that chain termini were "wet" on an average basis.

The half-lives for the exchange of acetylenic protons by deuterium in D₂O at pH = 9.5 were respectively 30 min and 6 hr for the 0.20 M surfactant with the head group N⁺Me₃ and OSO₃⁻, but only 15 min for monomeric 1-pentyne under similar conditions. Menger considered these
variations in half-lives understandable in terms of micellization and electrostatic effects. For the anionic surfactant attack by OD\textsuperscript{-} is greatly slowed down. For the cationic surfactant in turn, the reaction should be accelerated, argued Menger, if the methyne termini were positioned among the cationic head groups; since a small inhibition was observed, he concluded that the methynes were more inwardly directed yet within reach of water molecules.\textsuperscript{141}

6) Recently Menger and Doll used olefinic probes also.\textsuperscript{104} The rates of oxidation were monitored spectrophotometrically by the decrease in absorbance of permanganate ion, the oxidizing agent. The second order rate constants were determined at about $2 \times 10^-5$ M initial MnO\textsubscript{4}\textsuperscript{-} and olefin concentrations of $8 \times 10^-3$ M and smaller. The SDS system contained 0.040 M SDS, 0.010 M NaOH and 0.20 M NaCl.

Some of the second order rate constants in M\textsuperscript{-1} s\textsuperscript{-1} were as follows:

a) For secondary olefins: trans-3-hexenoic acid 490 (no added surfactant) and 540 (in SDS); cis-3-hexenoic 440 (no added surfactant) the following had smaller rate constants in the SDS system: cis-palmitoleate (6.3), oleate (1.6), cis-vaccenate (1.4).

b) For primary olefins: 4-pentenoic acid 220 (no added surfactant) 5.6 (in 50% aq. MeCN) and 250 for undecylenate in SDS.

Menger considered that internal olefins were less exposed to water. (This conclusion seems to be based on the results only from long chain (C\textsubscript{15} to C\textsubscript{19}) olefinic surfactants, since he does not discuss the apparent increase in rate constant for the oxidation of trans-3-hexenoic system in SDS.) The terminal olefins were, according to Menger, mainly outside of the micellar core, thoroughly wet in the water-rich Stern
region. This is due to a rough surface, chain bending and micellar disorder (nonradially distributed chains), resulting in a random distribution of terminal methyls. 104

The two-dimensional diagram of a micelle provided by Menger, 104 turned out to be not very different from one published earlier by Fendler et al. 174 and by Whitten et al. 114

In this context of chain coiling, some studies by other authors should be mentioned. Breslow et al. studied the photolysis of para-benzoyl benzoate in HTAB micelles. A distribution of attack sites was obtained, and it was concluded that many of the chains must be disordered. 143-144

Van Backstaele et al. claimed that chain coiling must occur, based on a Gd\(^{3+}\) relaxation study of the Carbon-13 T\(_1\) relaxation of SDS. Only the T\(_1\) of carbons 1, 2, 3, and 12 were influenced. 142

The Type II photoreaction of long chain ketones was studied by Turro et al. 135,145 (octanophenone in cationic micelles) and by Whitten et al. 146 (16-oxo-16-p-tolylhexadecanoic acid). The latter observed that the Type II reaction was inefficient in monolayers, but a high quantum yield (0.8) of Type II was obtained in SDS micelles, four times higher than in benzene solution. In accordance with Turro's interpretation that the ketones were not solubilized exclusively in the hydrocarbon core, Whitten proposed that the fourteen carbon polymethylene chain was bent such that both ends lay near the micellar surface. 146

5.4 Models of micellar structure

Having described the experimental studies related to the problem of water-hydrocarbon contact in micelles, let us turn now to some of the
reported models of micellar structure.

1) The classical micelle is an aggregate of 50 to 200 monomers, roughly spherical in shape, with radius comparable to the extended length of the surfactant chain. In a few words, it looks like an oil drop with a polar coat. It consists of a hydrocarbon core, a compact and narrow Stern layer where the head groups and some counterions are present, and a wide Gouy-Chapman double layer where most of the counterions are found. Free counterions in bulk water represent about 10 to 40% of the total charge.\textsuperscript{84}

2) The porous cluster micelle was described by Menger using molecular models.\textsuperscript{105} It has a small interior, its core is held to a minimum. It presents considerable water penetration into the interior. This water-to-hydrocarbon contact changes little upon compacting the micelle. Chain folding results in deeper inward penetration of the headgroups and larger exposure of the chains to water. The micellar surface is much more rugged and poorly defined than in the classical model of the micelle. Solubilization takes place in aqueous environments within the micelle,\textsuperscript{84} with release of some water from the micelle.\textsuperscript{104-105}

In 1984 Menger summarized his model as Having a central hydrophobic core, surrounded by a much larger region composed of hydrocarbon chains, water, head groups and counterions.\textsuperscript{104} Disorganization is rampant and the surface is rough. Penetration of water is deep in the sense that the core is relatively small. Its main characteristics are: a large wet Stern region, a rough surface, and chains which are looped and disordered (with nonradially distributed chains).\textsuperscript{104}

3) A statistical theory using a lattice model was described by Dill and
Flory in 1980-81. The segments of each surfactant chain are assigned to locations on a 3-D curved lattice such that each lattice accommodates one chain segment. This artificial lattice is constructed with constant radial interlayer spacing and equal volumes of lattice sites. The resulting configurational freedom of the chains is greater towards the outside of the micelle; this is thus disordered, the center is more ordered. Due to folding, even internal methylenes may occur in the external layer of the lattice.

The lattice representation main features were summarized by Menger as comprising a smooth spherical surface in which the head groups are packed as close to each other as are the chains, a core center with a "degree of order approaching that in a crystal", a small exposure of the terminal methyl to water for long chains but a large one for short chains.

This model predicts that chain termini should be less wet than more centrally located carbons, and Menger considers that it incorrectly underplays the looping and disorder within the micelle. Some considerations of looping are described in a recent theoretical article. The surfactant block model was proposed in 1980 by Fromherz, who utilized surfactant models rigid throughout the chain except for the methylenes closest to the polar group. As summarized by Menger in 1984, it has low entropy, with almost crystalline appearance; it is constructed by placing blocks of 2 or 3 monomers into a cuboid structure following a series of arbitrary "block assembly" rules. Chain reversals are not permitted. Menger objected that it cannot explain his findings that termini are randomly distributed throughout the micelle.
Before closing this section some theoretical papers will be mentioned. One is concerned with the head group protrusion from the hydrophobic core.\textsuperscript{150} Monte Carlo studies of a simple model for micelle structure suggest that the head density profile appears to be broader than expected,\textsuperscript{151} and that fluctuations of micellar structure are important.\textsuperscript{152} A mathematical method that rationalizes some micellar aggregation numbers has appeared recently.\textsuperscript{153}
CHAPTER 6 - RESULTS RELATED TO THE PROBLEM OF WATER-HYDROCARBON CONTACT IN MICELLES

In this chapter results obtained in this thesis that bear relation to the problem of the extent of water to hydrocarbon interaction in micelles are reported. The results were obtained at room temperature by the use of two kinds of probes, the nitrite and the carbonyl probes.

6.1 Electronic absorption properties of nitrites

The first kind of probe used here was the nitrite function, i.e. -O-N=O. This was prompted by some early reports that there was a solvent influence on the nπ* absorption band of simple nitrites, as will be mentioned in section 7.1. The influence was especially evident in the vibrational resolution within the nπ* band rather than in the wavelength shifts of the absorption maxima.

6.1.1 Electronic absorption properties of nitrites in solvents

This was studied for comparative purposes.

The nπ* bands of alkyl nitrites presented structure particularly in nonpolar solvents. For secondary nitrites the main peaks in decreasing intensity order occurred at 370, 356 and 345 nm, as shown in Figure 26 for 4-heptyl nitrite in cyclohexane and in the lower spectrum of Figure 27 for 6-nitritododecanoate. For primary nitrites the order changed to 356, 345 and 370 nm (lower spectrum in Figure 28).

The UV-spectra of 2-butyl nitrite, 4-heptyl nitrite and 1-heptyl nitrite in cyclohexane, dioxane and benzene showed negligible change in the position of the maxima of the nπ* band. The spectrum of 4-heptyl nitrite in 4-heptanol was similar to that in the above solvents.

Some peculiarities occurred in the absorption spectra of 2-butyl
Fig. 26 Absorption spectrum of 4-heptyl nitrite in cyclohexane.

$\varepsilon = 70 \text{ M}^{-1} \text{ cm}^{-1}$ at 370.7 nm.
Fig. 27 Absorption spectra of 6-nitritododecanoic systems in solvents and micellar solutions: 1) 6-nitritododecanoic acid in hexane; 2) ibid. in acetonitrile; 3) 0.04 M potassium 6-nitritododecanoate in water; 4) 0.04 M potassium dodecanoate containing 0.002 M potassium 6-nitritododecanoate in water; 5) 0.3 M potassium dodecanoate containing 0.002 M potassium 6-nitritododecanoate in water. Absorbance scales were selected to obtain all spectra of easily comparable sizes; spectra were displaced vertically to avoid superposition.
Fig. 28 Absorption spectra of 12-nitritododecanoate in dodecanoate solution and of 1-heptyl nitrite in dodecanoate solution and in solvents: 1) 1-heptyl nitrite in cyclohexane; 2) ibid. in acetonitrile; 3) ibid. in 0.04 M potassium dodecanoate; 4) 0.002 M potassium 12-nitritododecanoate in 0.04 M potassium dodecanoate. Absorbance scales were selected to obtain all spectra of easily comparable sizes; spectra were displaced vertically to avoid superposition.
nitrite when the solvent was methanol or water. This will be mentioned in section 6.1.5.

6.1.2 Absorption spectra of simple nitrites in micellar solutions of potassium dodecanoate

When 4-heptyl nitrite was dissolved in a 40 mM potassium dodecanoate solution, the absorption spectrum showed essentially the same \( \lambda_{\text{max}} \) as when dissolved in cyclohexane, although the sharpness of the vibrational structure appeared slightly decreased (Figure 29).

Equivalent results were obtained also for 1-heptyl nitrite in a 40 mM potassium dodecanoate solution, except for the fact that this is a primary nitrite and therefore the peak at 344 nm appeared as more intense than that at 370 nm.

6.1.3 Electronic absorption properties of the nitrito substituted potassium dodecanoates

The most notable feature was that the nitritododecanoates in micellar solutions presented little structure in their absorption spectra.

The spectrum of potassium 6-nitritododecanoate (0.002 M) in aqueous micellar potassium dodecanoate (0.04 M) presented a very small blue shift (around 1 nm). Considerably less vibrational structure was observed. (Figure 27). The spectra of 8-nitritododecanoate and 10-nitritododecanoate were essentially identical to the spectrum of 6-nitritododecanoate under the same conditions. The absorption spectrum of 5-nitritododecanoate was also analogous to that of 6-nitritododecanoate.

The absorption spectrum of the primary 12-nitritododecanoate also showed a very small blue shift (\( \approx \) 1 nm) and greatly worsened fine structure (Figure 28).
Fig. 29 Absorption spectrum of 4-heptyl nitrite in 0.04 M potassium dodecanoate. Apparent ε at 370.4 nm was 21 M⁻¹ cm⁻¹.
6.1.4 Concentration effect on the absorption properties of nitrito substituted potassium dodecanoates

The maximum in wavelength for the two main peaks in the absorption spectra are reproduced in Tables 10 and 11 for 6-nitritododecanoate under different conditions, and for different concentrations of

<table>
<thead>
<tr>
<th>[Nitrite]/mM</th>
<th>[KL]/mM</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\lambda_{\text{max}}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>40</td>
<td>355.5</td>
<td>367.6</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>355.5</td>
<td>367.5</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>355.5</td>
<td>367.5</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>355.9</td>
<td>368.3</td>
</tr>
</tbody>
</table>

KL: Potassium dodecanoate (laurate).

<table>
<thead>
<tr>
<th>[Nitrite]/mM</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\lambda_{\text{max}}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>355.7</td>
<td>367.5</td>
</tr>
<tr>
<td>16</td>
<td>355.6</td>
<td>367.5</td>
</tr>
<tr>
<td>8</td>
<td>355.6</td>
<td>367.5</td>
</tr>
<tr>
<td>3.2</td>
<td>355.6</td>
<td>367.5</td>
</tr>
<tr>
<td>1.6</td>
<td>355.6</td>
<td>367.5</td>
</tr>
<tr>
<td>0.4</td>
<td>355.6</td>
<td>367.6</td>
</tr>
</tbody>
</table>
12-nitrotetradecanoate, respectively.

The peak positions appeared almost completely unchanged, perhaps with a small shift at high concentration. The solutions in Table 11 obeyed the Lambert-Beer law.

6.1.5 Other observations concerning alkyl nitrites

When 2-butyl nitrite was mixed with methanol, the absorption spectrum became sharper in vibrational structure and a blue shift of about 4 nm from the maximum in cyclohexane as solvent was observed. This however was due to an exchange reaction, as was shown by the NMR spectrum of a sample (4:1 by volume) recorded immediately after mixing. Methyl nitrite and 2-butanol were the products; a decreased signal from the remaining 2-butyl nitrite was also noted. The reaction occurred as well when the methanol contained some pyridine.

An exchange reaction was also observed by NMR for 4-heptyl nitrite in methanol and in tert-butanol.

When 2-butyl nitrite was dissolved in 1,4-dioxane containing varying amounts of water, a red shift from the maximum in wavelength value obtained in pure dioxane was observed. This shift was of about 2 nm when the solvent mixture contained about 2% water. Only small shifts were obtained when the water content was further increased to 16% and 37% of the solvent. The spectrum in pure water was described previously.

A rapid exchange reaction was observed by NMR when D₂O was added to a solution of 2-butyl nitrite in dioxane. Also appearance of 2-butanol was detected by NMR when H₂O was added to a solution of 2-butyl nitrite in d₆-acetone.

When 2-butyl nitrite was mixed with water the absorption maxima
were at the same wavelengths as in hydrocarbon, although the extinction coefficients were markedly decreased. This has been suggested to be due to the formation of aggregates. Alkyl nitrites are not easily solubilized in water and slowly undergo decomposition.

An aqueous solution of HNO₂ presented an absorption spectrum that resembled that of a secondary alkyl nitrite in hydrocarbon, with extinction coefficient at 371 nm of at least 51 M⁻¹ cm⁻¹. When base was added in varying amounts, the absorption spectrum became that of NO₂⁻ consisting of a broad band with no structure, and with extinction coefficient of 15 M⁻¹ cm⁻¹ at 354 nm. This was reversed several times by alternate additions of small amounts of strong acid and base.

The H-NMR of a mixture of 0.2 mmol of 4-heptyl nitrite and 0.5 mL of 0.2 M potassium dodecanoate solution in D₂O showed a multiplet at about 5.5 ppm, as expected for the alkyl nitrite and at about 3.7 ppm, as expected for 4-heptanol, with comparable amplitudes.

The integrity of the nitritododecanoate in micelles was confirmed by NMR. A 40 mM potassium 6-nitritododecanoate micellar sample in D₂O presented a multiplet at about 5.5 ppm downfield from Me₄Si, as was expected for the hydrogen bound to the carbon that bears the nitrite.

The nitrito substituted potassium dodecanoates decomposed slowly in aqueous micellar systems (about 0.6% per hr). These observations were only qualitative. No attempt was made to measure the influence of the position of the nitrite in the surfactant chain upon the rate of decomposition, but they did not seem to be very different. The spectra considered were always taken immediately after preparation.
6.2 Electronic absorption properties of oxo-compounds

The lowest electronic absorption band of ketones are useful to monitor solvent polarities. They are often $n\pi^*$ in character, consistent with the blue shifts of their absorption in polar solvents.

6.2.1 Electronic absorption properties of oxo-substituted dodecanoic systems and some simple carbonyl compounds

The blue shifts of oxo-compounds as polarity probes were studied here in the specific case of oxododecanoates in micellar solutions, to gain information about the polarity in these systems. For comparison, UV-absorption measurements were also made of other carbonyl compounds. The absorption properties of 6-oxo- and 10-oxododecanoic systems are recorded in Tables 12 and 13, respectively.

<table>
<thead>
<tr>
<th>X</th>
<th>Concentration/M</th>
<th>Solvent</th>
<th>$\lambda_{max}$/nm</th>
<th>$\bar{v}_{max}/10^3,\text{cm}^{-1}$</th>
<th>$\epsilon_{max}/\text{M}^{-1},\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.01</td>
<td>c-C$<em>6$H$</em>{12}$</td>
<td>284</td>
<td>35.21</td>
<td>25.8</td>
</tr>
<tr>
<td>H</td>
<td>0.013</td>
<td>MeCN</td>
<td>282</td>
<td>35.46</td>
<td>27.2</td>
</tr>
<tr>
<td>H</td>
<td>0.01</td>
<td>EtOH</td>
<td>280.4</td>
<td>35.66</td>
<td>29</td>
</tr>
<tr>
<td>H</td>
<td>0.01</td>
<td>MeOH</td>
<td>280</td>
<td>35.71</td>
<td>25.5</td>
</tr>
<tr>
<td>K</td>
<td>0.5</td>
<td>H$_2$O</td>
<td>277.5</td>
<td>36.04</td>
<td>22.2</td>
</tr>
<tr>
<td>K</td>
<td>0.1</td>
<td>H$_2$O</td>
<td>275.4</td>
<td>36.31</td>
<td>41</td>
</tr>
</tbody>
</table>
Table 13. Absorption properties of 10-oxododecanoic systems

<table>
<thead>
<tr>
<th>X</th>
<th>Concentration/M</th>
<th>Solvent</th>
<th>(\lambda_{\text{max}}/\text{nm} )</th>
<th>(\bar{\nu}_{\text{max}}/10^3 \text{cm}^{-1} )</th>
<th>(\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.01</td>
<td>(-C_6H_{12})</td>
<td>282</td>
<td>35.46</td>
<td>24</td>
</tr>
<tr>
<td>H</td>
<td>0.01</td>
<td>MeCN</td>
<td>279.8</td>
<td>35.74</td>
<td>25</td>
</tr>
<tr>
<td>H</td>
<td>0.01</td>
<td>EtOH</td>
<td>278</td>
<td>35.97</td>
<td>26</td>
</tr>
<tr>
<td>H</td>
<td>0.01</td>
<td>MeOH</td>
<td>277.3</td>
<td>36.06</td>
<td>28.3</td>
</tr>
<tr>
<td>K</td>
<td>0.1</td>
<td>(H_2O)</td>
<td>272</td>
<td>36.76</td>
<td>36.5</td>
</tr>
</tbody>
</table>

The correlation between the wavenumber of the absorption maximum of the \(n\pi^*\) band and the solvent polarity empirical parameter \(E_T(30)\) are included in Figure 30 for the 6-oxododecanoic and for the 10-oxododecanoic systems. (The \(E_T(30)\) scale is mentioned in sections 7.3 and 7.5).

6.2.2 Concentration dependence of the electronic absorption of oxododecanoates in water

The results in Table 14 for potassium 7-oxododecanoate show that the UV-spectra presented changes both in wavelength and in extinction.

Table 14. UV-Absorption properties of potassium 7-oxododecanoate

<table>
<thead>
<tr>
<th>Concentration/M</th>
<th>Solvent (\eta)</th>
<th>(\lambda_{\text{max}}/\text{nm} )</th>
<th>(\bar{\nu}_{\text{max}}/10^3 \text{cm}^{-1} )</th>
<th>(\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>(H_2O)</td>
<td>279</td>
<td>35.84</td>
<td>25.2</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1M KL</td>
<td>276.6</td>
<td>36.15</td>
<td>32.8</td>
</tr>
<tr>
<td>0.1</td>
<td>(H_2O)</td>
<td>275.6</td>
<td>36.28</td>
<td>40.7</td>
</tr>
</tbody>
</table>

KL: potassium dodecanoate (laurate).
Fig. 30 Plot of wavenumber of the absorption maximum for oxododecanoates versus the solvent polarity parameter $E_T$. Solvents are: a) cyclohexane; b) acetonitrile; c) ethanol; d) methanol.
coefficient of the maximum of the n\* transition with the concentration of surfactant.

The primary interest was to characterize the polarity of the average environment of the carbonyl. This however was not unique since the concentration of surfactant appeared to play a very important role, as can be seen from a comparison of the first and last entries in Table 14 for 7-oxododecanoate and of the last two entries of Table 12 for 6-oxododecanoate. The largest blue shifts were observed for dilute solutions, indicating an average a more polar environment for these solutions. Interestingly, the maximum in the extinction coefficient also varied with concentration, being larger in dilute surfactant solutions.

It is apparent that the total concentration of surfactant is what matters, as shown by the last two entries in Table 14; both were 0.1 M in substituted surfactant, yet the average polarity near the carbonyl was decreased by addition of unsubstituted potassium dodecanoate.

6.2.3 Electronic absorption properties of some carbonyl containing molecules solubilized in micellar systems

UV-spectral measurements were done of some oxo-compounds dissolved in aqueous potassium dodecanoate and in some alcoholic solvents. The purpose was to use these measurements to compare with what was found for the oxo-substituted surfactants. Thus 4-heptanone was used first, since it is a typical acyclic ketone of reasonable chain length (Table 15).
Table 15. UV-Absorption properties of 4-heptanone in different media

<table>
<thead>
<tr>
<th>Concentration/M</th>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\bar{\nu}_{\text{max}}$/10$^3$cm$^{-1}$</th>
<th>$\varepsilon_{\text{max}}$/M$^{-1}$cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>EtOH</td>
<td>281.0</td>
<td>35.58</td>
<td>26.9</td>
</tr>
<tr>
<td>1.0</td>
<td>MeOH</td>
<td>280.8</td>
<td>35.61</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>1M KL</td>
<td>280.7</td>
<td>35.62</td>
<td>25.6</td>
</tr>
<tr>
<td>0.1</td>
<td>1M KL</td>
<td>279.5</td>
<td>35.78</td>
<td>29</td>
</tr>
<tr>
<td>0.05</td>
<td>1M KL</td>
<td>279.5</td>
<td>35.78</td>
<td>29</td>
</tr>
<tr>
<td>0.01</td>
<td>1M KL</td>
<td>279.3</td>
<td>35.80</td>
<td>28.7</td>
</tr>
<tr>
<td>0.002</td>
<td>1M KL</td>
<td>279.3</td>
<td>35.80</td>
<td>27.8</td>
</tr>
<tr>
<td>0.1</td>
<td>0.5M KL</td>
<td>279.3</td>
<td>35.80</td>
<td>24.9</td>
</tr>
<tr>
<td>0.1(sat.)</td>
<td>0.1M KL</td>
<td>278.0</td>
<td>35.97</td>
<td>21.3</td>
</tr>
<tr>
<td>0.002</td>
<td>0.1M KL</td>
<td>277.5</td>
<td>36.03</td>
<td>35.2</td>
</tr>
</tbody>
</table>

Other solubilized carbonyl-containing molecules used were the bulky and rigid D-camphor and the linear heptanal with its carbonyl at the end of the chain.

Table 16. UV-Absorption properties of oxo-compounds in alcohols and in micelles

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\bar{\nu}_{\text{max}}$/10$^3$cm$^{-1}$</th>
<th>$\varepsilon_{\text{max}}$/M$^{-1}$cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-Camphor</td>
<td>MeOH</td>
<td>291</td>
<td>34.36</td>
<td>33</td>
</tr>
<tr>
<td>D-Camphor</td>
<td>1M KL</td>
<td>287</td>
<td>34.84</td>
<td>44</td>
</tr>
<tr>
<td>Heptanal</td>
<td>2-PrOH</td>
<td>292.5</td>
<td>34.18</td>
<td>13</td>
</tr>
<tr>
<td>Heptanal</td>
<td>1M KL</td>
<td>286</td>
<td>34.96</td>
<td>11</td>
</tr>
</tbody>
</table>
Direct comparison between different carbonyls in this table is not straightforward since they have very different structures. Fair comparisons can be made between a given carbonyl in a quite polar alcohol and in micellar solution. Clearly all carbonyls investigated seemed to be in a very polar environment in micellar solutions of potassium dodecanoate.

6.3 Carbon-13 chemical shifts of the oxo-carbon in solvents and in micellar systems

Another property that can be used for micellar studies is the solvent dependence on the $^{13}$C-chemical shift of the oxo-carbon ($\delta_{CO}$). The $^{13}$C-shifts of the oxo-carbon of 6-oxododecanoic acid obtained in a series of solvent systems of different polarities are reproduced in Table 17. The solvent systems are listed in decreasing order of the empirical parameter of solvent polarity $E_m$ (section 7.5).

The use of $\delta_{CO}$ to study micellar structure had been reported earlier using 8-oxohexadecyltrimethylammonium bromide at only one concentration (section 5.3). The results obtained here for oxododecanoates are reproduced in Table 18.

The $\delta_{CO}$ values from Table 18 indicate that the polarity in the neighbourhood of the oxocarbonyl is very high in all cases, being highest at low concentration of surfactant. This is also evident in Figure 31 for potassium 7-oxododecanoate. At 25°C this surfactant has a cmc of 0.0667 M, as determined by the specific conductivity method (section 9.1.3.2).
### Table 17. Chemical shift of the oxo-carbon of 6-oxododecanoic acid in solvents and aqueous mixtures

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_T$</th>
<th>$\delta_{CO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol/water (4:1)</td>
<td>56.6</td>
<td>214.6</td>
</tr>
<tr>
<td>Methanol</td>
<td>55.5</td>
<td>213.4</td>
</tr>
<tr>
<td>Ethanol/water (4:1)</td>
<td>53.7</td>
<td>213.7</td>
</tr>
<tr>
<td>Ethanol</td>
<td>51.9</td>
<td>212.0</td>
</tr>
<tr>
<td>2-Propanol/water (4:1)</td>
<td>51.6</td>
<td>212.7</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>49.6</td>
<td>211.2</td>
</tr>
<tr>
<td>3-Methyl-1-butanol</td>
<td>47.0</td>
<td>211.05</td>
</tr>
<tr>
<td>Dimethysulphoxide</td>
<td>45.0</td>
<td>211.4</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>43.8</td>
<td>210.5</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>41.1</td>
<td>211.2</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>37.4</td>
<td>209.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>34.5</td>
<td>208.8</td>
</tr>
</tbody>
</table>

In ppm downfield from Me$_4$Si.

### Table 18. Chemical shifts of the oxo-carbon of some oxo-substituted potassium dodecanoates at different concentrations in water

<table>
<thead>
<tr>
<th>comp./conc.</th>
<th>1.0 M</th>
<th>0.5 M</th>
<th>0.1 M</th>
<th>0.05 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-oxo</td>
<td>216.6</td>
<td>217.9</td>
<td>220.8</td>
<td></td>
</tr>
<tr>
<td>7-oxo</td>
<td>216.8</td>
<td>219.1</td>
<td>221.1</td>
<td>221.2</td>
</tr>
<tr>
<td>10-oxo</td>
<td>218.2</td>
<td></td>
<td>221.5</td>
<td></td>
</tr>
</tbody>
</table>

In ppm downfield from Me$_4$Si.
\[ \delta_{\text{CO}} / \text{ppm} \]

\[ \begin{array}{ccc}
0.1 & 0.1 & 215.8 \\
1.0 & 1.0 & 213.7 \\
\end{array} \]

KL: Potassium dodecanoate.

Cycloheptanone, forced to be far from linear, was studied at two
different concentrations in micellar potassium dodecanoate.

<table>
<thead>
<tr>
<th>[c-heptanone]/M</th>
<th>[KL]/M</th>
<th>δ CO/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1</td>
<td>221.5</td>
</tr>
<tr>
<td>1.0</td>
<td>1</td>
<td>219.6</td>
</tr>
</tbody>
</table>

KL: Potassium dodecanoate (laurate).

6.4 Proton spin-lattice relaxation rates of potassium 7-oxododecanoate and of potassium 10-oxododecanoate in deuterium oxide

Since some pioneering $^1$H-NMR relaxation studies of surfactants in micellar solution have been made, one might wish to find whether the oxo-substituted surfactants will resemble or differ from other unsubstituted surfactants in their proton relaxation behaviour.

To check this the spin-lattice relaxation times of the chain protons of potassium 7-oxododecanoate (and 10-oxododecanoate) in D$_2$O have been measured at different concentrations.

Whenever signal overlap occurred, the signals were taken together. Some signals appeared as distinct from the rest, namely the hydrogens α to CO, α to CO$_2^-$ and the methyl hydrogens. Furthermore, the components of a given multiplet (like the triplet from CH$_3$) were analyzed separately and then an average value was calculated for them.

The spectra as a function of time are reproduced in Figures 32 to 35, at 1 M surfactant concentration. The numerical results are given in Tables 19 and 20.
Fig. 32 Spin-lattice relaxation of 1 M potassium 7-oxododecanoate in D$_2$O in the upfield region (roughly 0 < δ < 3 ppm; no reference; lettering as in Table 19).
Fig. 33 Spin-lattice relaxation of 1 M potassium 7-oxodecanoate in D$_2$O in the downfield region (roughly 3 < $\delta$ < 5 ppm; no reference; lettering as in Table 19).
Fig. 34: Spin-lattice relaxation of 1 M potassium 10-oxododecanoate in D$_2$O in the upfield region (roughly $0 < \delta < 3.5$ ppm; no reference; lettering as in Table 20).
Fig. 35. Spin-lattice relaxation of 1 M potassium 10-oxododecanoate in D$_2$O in the downfield region
(roughly 3.5 < $\delta$ < 5.5 ppm; no reference; lettering as in Table 20).
Table 19. Spin-lattice relaxation of potassium 7-oxododecanoate in deuterium oxide

| Molarity: | 1.00 | 0.50 | 0.25 | 0.125 | 0.03 | 1.00 | 0.50 | 0.25 | 0.125 | 0.03 |
| Temp. (°) | 24.7  | 25.1  | 24.9  | 24.9  | 24.7 | 24.7 | 25.1  | 24.9  | 24.9  | 24.7 |
| \( T_1 \) in seconds | 1.49  | 1.03  | 1.32  | 1.00  | 0.58 | 1.88  | 1.51  | 1.54  | 1.05  | 0.74 |
| 1/\( T_1 \) in sec\(^{-1} \) | 0.06  | 0.15  | 0.15  | 0.15  | 0.15 |
| \( \alpha \) to CO | 0.67  | 0.97  | 0.76  | 1.00  | 1.71  | 0.67  | 0.97  | 0.76  | 1.00  | 1.71  |
| \( \alpha \) to COO\(^-\) | 0.71  | 1.26  | 0.94  | 0.87  | 0.71  | 1.26  | 0.94  | 0.87  |
| \( \beta \) | 1.37  | 0.54  | 0.85  | 1.09  | 1.73  | 0.73  | 1.86  | 1.17  | 0.92  | 0.58 |
| \( \gamma \) | 0.83  | 0.91  | 1.39  | 1.45  | 1.74  | 0.83  | 0.91  | 1.39  | 1.45  | 1.74  |
| \( \text{other CH}_2\) | 0.70  | 0.55  | 1.15  | 1.16  | 1.49  | 0.70  | 0.55  | 1.15  | 1.16  | 1.49  |
| \( \text{OH}_3\) | 1.29  | 1.47  | 2.41  | 2.63  | 2.44  | 0.78  | 0.68  | 0.42  | 0.38  | 0.41 |
| \( \text{average} \) | 0.81  | 0.72  | 0.42  | 0.40  | 0.40  | 0.81  | 0.72  | 0.42  | 0.40  | 0.40 |
Table 20. Spin-lattice relaxation of potassium 10-oxododecanoate in deuterium oxide at 25°

<table>
<thead>
<tr>
<th>Molarity</th>
<th>1.0</th>
<th>0.5</th>
<th>0.03</th>
<th>1.0</th>
<th>0.5</th>
<th>0.03</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;1&lt;/sub&gt; in seconds</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/T&lt;sub&gt;1&lt;/sub&gt; in sec&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α to CO</td>
<td>0.68</td>
<td>a</td>
<td>1.47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.23</td>
<td>b</td>
<td>0.81</td>
<td>0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.14</td>
<td>c</td>
<td>0.88</td>
<td>0.88</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.79</td>
<td>d</td>
<td>1.26</td>
<td>0.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>average:</td>
<td>0.96</td>
<td>1.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α' to COO&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.60</td>
<td>e</td>
<td>1.67</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.61</td>
<td>f</td>
<td>1.64</td>
<td>1.30</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>g</td>
<td>1.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>average:</td>
<td>0.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β</td>
<td>0.39</td>
<td>h</td>
<td>2.56</td>
<td>1.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>other CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.37</td>
<td>i</td>
<td>2.70</td>
<td>2.22</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.97</td>
<td>j</td>
<td>0.51</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.91</td>
<td>k</td>
<td>0.52</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.06</td>
<td>l</td>
<td>0.49</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>average:</td>
<td>1.98</td>
<td>3.82</td>
<td>6.14</td>
<td>0.50</td>
<td>0.26</td>
<td></td>
</tr>
</tbody>
</table>
6.5 Partition of tert-butoxy radicals in micellar solutions

Here it was intended to use the solvent dependence on the reactions of tert-butoxy radicals, to find whether these radical probes are solubilized exclusively in micelles or exist to a significant extent in the aqueous phase. Ketyl radicals are usually accepted as good models of carbonyl triplets at least in their hydrogen abstraction properties (section 7.8).

Excited di-tert-butyl peroxide reacts to give tert-butoxy radicals, which then β-cleave to give acetone or abstract hydrogen from hydrogen donors to form tert-butanol. The resulting tert-butanol / acetone ratio, which corresponds to the abstraction / β-cleavage ratio, has been reported to be solvent dependent.

Consequently di-tert-butyl peroxide was irradiated in a few aqueous micellar solutions, namely aqueous potassium dodecanoate (KL), sodium dodecyl sulphate (SDS), hexadecyltrimethylammonium chloride (HTAC) and hexadecyltrimethylammonium bromide (HTAB). Two other neat liquids, dodecane and octanoic acid were chosen for comparison. The results are presented in Table 21.

The effect of surfactant concentration on the abstraction / β-cleavage ratio was of particular interest, and this was studied for SDS at different concentrations (Table 22 and Figure 36).
Table 21. Irradiation of di-tert-butyl peroxide in hydrogen donating micellar systems and other aliphatic liquids

\[
\text{Me}_3\text{CO-O-OMe}_3^+ \rightarrow \text{Me}_2\text{CO} + \text{Me}_3\text{COH}
\]

<table>
<thead>
<tr>
<th>System</th>
<th>[Me₂CO]</th>
<th>[t-BuOH]</th>
<th>a+b</th>
<th>a/(a+b)</th>
<th>b/(a+b)</th>
<th>R = b/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecane</td>
<td>0.000</td>
<td>189</td>
<td>189</td>
<td>0.000</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Dodecane</td>
<td>0.507</td>
<td>166</td>
<td>167</td>
<td>0.00365</td>
<td>0.99</td>
<td>273</td>
</tr>
<tr>
<td>Dodecane</td>
<td>1.39</td>
<td>3033</td>
<td>3631</td>
<td>0.00038</td>
<td>0.999</td>
<td>2610</td>
</tr>
<tr>
<td>Octanoic acid</td>
<td>11.3</td>
<td>16.5</td>
<td>176</td>
<td>0.0644</td>
<td>0.936</td>
<td>14.5</td>
</tr>
<tr>
<td>KDodecanoate</td>
<td>41.6</td>
<td>58.8</td>
<td>142</td>
<td>0.293</td>
<td>0.41</td>
<td>1.41</td>
</tr>
<tr>
<td>HTAB</td>
<td>40.4</td>
<td>65.0</td>
<td>105</td>
<td>0.383</td>
<td>0.61</td>
<td>1.61</td>
</tr>
<tr>
<td>HTAC</td>
<td>51.1</td>
<td>61.5</td>
<td>113</td>
<td>0.453</td>
<td>0.54</td>
<td>1.21</td>
</tr>
<tr>
<td>SDS 0.16 M</td>
<td>31.4</td>
<td>30.3</td>
<td>69.6</td>
<td>0.509</td>
<td>0.49</td>
<td>0.964</td>
</tr>
<tr>
<td>SDS 0.2 M</td>
<td>60.3</td>
<td>45.6</td>
<td>106</td>
<td>0.570</td>
<td>0.43</td>
<td>0.756</td>
</tr>
</tbody>
</table>

Acetone and tert-butanol concentrations are in mM.
Table 22. Irradiation of di-tert-butyl peroxide at different concentrations of sodium dodecyl sulphate

\[
\text{Me}_3\text{CO-OCMe}_3 \xrightarrow{\text{h} \nu} \text{Me}_2\text{CO} + \text{Me}_3\text{COH}
\]

<table>
<thead>
<tr>
<th>[SDS]/M</th>
<th>[Me₂CO]</th>
<th>[t-BuOH]</th>
<th>a+b</th>
<th>a/(a+b)</th>
<th>b/(a+b)</th>
<th>R = b/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.030</td>
<td>0.123</td>
<td>0.067</td>
<td>0.190</td>
<td>0.647</td>
<td>0.353</td>
<td>0.546</td>
</tr>
<tr>
<td>0.040</td>
<td>0.259</td>
<td>0.142</td>
<td>0.402</td>
<td>0.646</td>
<td>0.354</td>
<td>0.549</td>
</tr>
<tr>
<td>0.050</td>
<td>0.215</td>
<td>0.110</td>
<td>0.325</td>
<td>0.662</td>
<td>0.338</td>
<td>0.511</td>
</tr>
<tr>
<td>0.070</td>
<td>0.140</td>
<td>0.213</td>
<td>0.353</td>
<td>0.397</td>
<td>0.603</td>
<td>1.521</td>
</tr>
<tr>
<td>0.100</td>
<td>0.051</td>
<td>0.142</td>
<td>0.193</td>
<td>0.266</td>
<td>0.734</td>
<td>2.755</td>
</tr>
<tr>
<td>0.150</td>
<td>0.116</td>
<td>0.301</td>
<td>0.417</td>
<td>0.278</td>
<td>0.722</td>
<td>2.594</td>
</tr>
<tr>
<td>0.200</td>
<td>0.160</td>
<td>0.483</td>
<td>0.643</td>
<td>0.248</td>
<td>0.752</td>
<td>3.025</td>
</tr>
<tr>
<td>0.300</td>
<td>0.462</td>
<td>0.217</td>
<td>0.263</td>
<td>0.176</td>
<td>0.824</td>
<td>4.693</td>
</tr>
</tbody>
</table>

Acetone and tert-butanol concentrations are in mM.

Initial peroxide concentration was 5.43 mM.
Fig. 36 Plot of tert-butanol / acetone ratio versus sodium dodecyl sulphate concentration
6.6 *Lifetimes of some ketone transients in micellar solutions and quenching of long chain aliphatic ketone triplets by biphenyl*

The triplet transients of some ketones in micellar solutions were studied by laser flash photolysis. Although the triplet oxododecanoates were too short lived, the triplet of simpler ketones dissolved in micelles were conveniently monitored. The alternative for too short lived triplets was to monitor the triplet energy transfer to an acceptor of longer triplet lifetime, biphenyl.

The transient lifetimes appeared to be shorter in 0.20 M SDS solutions for aliphatic ketones capable of Type II reaction (Table 23).

In HTAC the transient lifetime of 1-phenyl-1-decanone varied somewhat with wavelength, presumably reflecting different contributions from the biradical and the triplet ketone to the observed decay.

The values of $k_{q \tau}$ for the quenching of triplet ketones by biphenyl were obtained by exciting the ketone with laser light at 308 nm and monitoring at 370 nm the triplet biphenyl resulting from energy transfer, at different concentrations of biphenyl (Table 24).

Thus the $k_{q \tau}$ value for 10-oxododecanoic acid is larger than for 7-oxododecanoic acid, both in methanol, presumably due to the larger number of $\gamma$-hydrogens for the latter, with a concomitant decrease in triplet lifetime.

Clearly 5-nonanone showed a solvent dependence on the $k_{q \tau}$ values (this could be due to a change in triplet lifetime or in solvent viscosity).

The $k_{q \tau}$ value for quenching of 5-nonanone triplets by biphenyl in 0.20 M SDS solution was much higher than in normal organic solvents.
This most likely reflects the fact that a triplet ketone can be quenched also by biphenyls already present in the same micelle.

Table 23. Transient lifetimes of some carbonyl compounds in micellar systems.

<table>
<thead>
<tr>
<th>Ketone</th>
<th>Solvent</th>
<th>Concentration</th>
<th>$\lambda_{mon}$/nm</th>
<th>$\tau$/ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Pentanone</td>
<td>0.20 M SDS</td>
<td>0.00026 M</td>
<td>320</td>
<td>182</td>
</tr>
<tr>
<td>4-Heptanone</td>
<td>0.20 M SDS</td>
<td>0.00018 M</td>
<td>325</td>
<td>143</td>
</tr>
<tr>
<td>5-Nonanone</td>
<td>0.20 M SDS</td>
<td>0.046 M</td>
<td>no signal</td>
<td></td>
</tr>
<tr>
<td>Ph-1-decanone</td>
<td>0.20 M SDS</td>
<td>0.0090 M</td>
<td>375</td>
<td>77.8</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.055 M HTAC</td>
<td>0.010 M</td>
<td>4 M</td>
<td>84.3</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>375</td>
<td>82</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>325</td>
<td>109</td>
</tr>
</tbody>
</table>

Excitation at 308 nm.

Table 24. Values of $k_q \tau$ for the quenching of some aliphatic ketone transients by biphenyl.

<table>
<thead>
<tr>
<th>Ketone</th>
<th>Solvent</th>
<th>Concentration</th>
<th>$k_q \tau$/M$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-Nonanone</td>
<td>Decane</td>
<td>0.15 M</td>
<td>15.5</td>
</tr>
<tr>
<td>5-Nonanone</td>
<td>Methanol</td>
<td>0.23 M</td>
<td>39.7</td>
</tr>
<tr>
<td>5-Nonanone</td>
<td>0.20 M SDS</td>
<td>0.045 M</td>
<td>162</td>
</tr>
<tr>
<td>7-oxododecanoic acid</td>
<td>Methanol</td>
<td></td>
<td>36.9</td>
</tr>
<tr>
<td>10-oxododecanoic acid</td>
<td>Methanol</td>
<td></td>
<td>59.1</td>
</tr>
</tbody>
</table>

Excitation at 308 nm; monitoring at 370 nm.
CHAPTER 7 - DISCUSSION ON THE PROBLEM OF WATER-HYDROCARBON CONTACT IN MICELLES

In this chapter justification is provided for the parameters used in Chapter 6. The electronic absorption of nitrites and of ketones and the oxo-carbon chemical shifts, are indicative of the polarity of the environment around the probe. The conclusions from the results obtained by these techniques are also listed. The main conclusion is that for substituted dodecanoates the probes experience high polarities, regardless of the position of substitution.

In the case of the oxo-carbon chemical shifts, an explanation is given on how they can be used as polarity probes. Menger et al. had used the shifts in an empirical way, simply by plotting $\delta_{CO}$ versus $E_T$\textsuperscript{158} but their procedure was questioned by Lindman and Wennström.\textsuperscript{111}

The average location of the probe in the micelles will not be discussed, since no direct experimental approach to the problem was used. It should be remembered, though, that the extrinsic probes usually showed polarities a bit smaller than the intrinsic probes.

The extrinsic probes containing several carbon atoms are likely to be associated predominantly with the micelles. Some techniques for measuring the partitioning of extrinsic probes have now appeared,\textsuperscript{196-199} but they were not applicable or available.

7.1 Justification for the use of electronic absorption of nitrites as polarity probes

The near UV-absorption of nitrites can be used to probe polarity changes. This is more evident in the loss of vibrational structure in polar solvents.\textsuperscript{157-162} The $\lambda_{max}$ are hardly changed by polarity changes.
since an n(N) → π* transition is involved. The n electron located mainly on the N atom is being promoted to the π system of theONO group with presumably little change in the dipole moment when the transition takes place.161-162

In passing it should be mentioned that some alkyl nitrites can exist in a cis-oid and a trans-oid conformation. The equilibrium between these conformations is detectable by vibrational159 and NMR154 spectroscopy, and its probable influence on the electronic absorption has been considered.159

7.2 Conclusions from the electronic absorption of nitrites experiments
1) The electronic absorption of nitrites indicated high polarities around the probe. Interestingly high polarities were noticed regardless of the place of substitution in the chain. Positions 5, 6, 8, and 10 and the primary 12 as substituent bearing positions indicated high polarities around the probe.

2) The total surfactant concentration determined the polarity around the nitrite when some unsubstituted dodecanoate was added. The same results were obtained when the nitrito substituted dodecanoates were unmixed than when they were mixed with unsubstituted dodecanoate, comparing at the same total concentration of surfactant. Two frequently used points of view can be used to rationalize this. a) The substituted dodecanoate produces little change in the average 'structure' of the dodecanoate micelles. b) The fraction of nitrites actually micellized or the average residence time of the nitrito dodecanoate in micelles depends on the the total surfactant concentration.

3) The concentration effect on the electronic absorption of nitrito
dodecanoates was almost negligible. The known mild dependence of the nitrites absorption on the polarity of the environment precludes a neat observation of a concentration effect in micellar solutions. (This should be considered too for point 2 just mentioned).

4) Simple nitrites dissolved in aqueous dodecanoate indicated a significant polarity for the nitrite, yet smaller than when the nitrite was part of the dodecanoate. Thus either these simpler nitrites (e.g. heptyl nitrites) spend longer time in the micelle, or the location of the simpler nitrites is deeper inside the micelles, or the solubilization of nitrites occurs at the expense of some water removal from the micelle (according to Menger's view of solubilization into micelles).

Applying Menger's reasoning to the nitrites, the lower polarities observed for the simple nitrites than for the nitrito dodecanoate could be taken to imply that the probe doesn't 'drag water in' to the micelle interior.

7.3 Justification for the use of electronic absorption of carbonyls as polarity probes

The blue shifts in the UV-spectra of carbonyls were larger than for nitrites, reflecting a larger sensitivity of the carbonyls to polarity changes.

The \( n\pi^* \) bands of these carbonyls are broad even in nonpolar solvents, so their polarity changes are best followed by changes in their absorption maxima rather than in their fine structure.

The blue shifts of the \( n\pi^* \) band of carbonyls in polar solvents have been usually explained by the ability of these solvents to stabilize preferentially the ground state \( n \)-electrons located mainly on the oxygen
atom; more energy then is required to promote them to the \( \pi^* \) orbitals.\textsuperscript{63,163-164} Particularly effective are solvents which can be hydrogen bonded to the \( n \)-electrons of the oxygen atom.\textsuperscript{164}

Plots of the wavenumber of the absorption maxima \( \tilde{\nu}_{\text{max}} \) versus \( E_x(30) \), the empirical solvent polarity parameter based on a pyridinium \( \text{N-phenoxide betaine} \) dye as proposed by Dimroth and coworkers\textsuperscript{164,166-168} were found to be nearly linear for 6-oxo- and 10-oxo-dodecanoates (Figure 30). The carboxylic group of the dodecanoic acid then does not seem to disturb much the absorption by the oxo-carbonyl group.

For the carbonyls the molar extinction coefficient at the maximum of the \( n\pi^* \) also changed with polarity. This is in accordance with earlier observations made for simple carbonyls in dioxane-water mixtures,\textsuperscript{169} These increments in \( \epsilon_{\text{max}} \) help to monitor increases in polarity around the carbonyl probe.

7.4 Conclusions from the electronic absorption of carbonyls experiments

1) The blue shifts of the oxododecanoates in micelles indicate that the probes are in high polarity environments.

The high polarities were noticed regardless of whether the position of substitution was the 6, 7, or 10-th carbon.

The blue shifts were even larger than in pure water. A precedent for this was reported for benzophenone in SDS micelles.\textsuperscript{170}

2) Mixing oxododecanoate with dodecanoate produced a change in the absorption maximum that seemed more compatible with the shift being determined by the total concentration of surfactant rather than only the oxo-dodecanoate concentration.

Again the two views may be considered: the substituted dodecanoate
produces little change in the average 'structure' of dodecanoate micelles, or the fraction of oxo-surfactant in the micelles depends on the total surfactant concentration.

3) The concentration effect of the oxododecanoates in water on their nπ* bands was clearly observable. The largest blue shift was observed in dilute aqueous solution, decreasing (although still high) as the concentration of oxododecanoate was increased.

Apparently, this is simply due to the increased fraction of micelized oxododecanoate as its total concentration is increased. This seems reasonable since the fraction of oxododecanoate in micelles is estimated to be 0.33 and 0.93, respectively at 0.1 M and 1 M total concentration, using the approximate expression \((c - \text{cmc}) / c\) and a cmc of 0.0667 M for potassium 7-oxododecanoate.

4) Dissolved alkyl ketones also appeared to be on average in a considerably high polarity environment in micellar dodecanoate solutions. Yet this was less polar than when the oxo-probe belonged to the surfactant chain.

Again this fact may lead one to think that these solubilized ketones spend longer times in micelles, or their average location is deeper inside the micelles, or the solubilization occurs at the expense of some water removal from the micelles (Menger's view),\(^{105,171}\) or following Menger's arguments the lower polarities observed for the dissolved ketones than for the oxododecanoates may indicate that the probe does not 'drag water in' to the micellar interior.
7. Justification for the use of carbon-13 chemical shifts of the oxo-carbon as polarity probes

Since the carbon-13 chemical shifts ($\delta_{CO}$) will be taken to indicate the polarity around the carbonyl probe, a basic description of how the $\delta_{CO}$ shifts are expected to be related to the polarity will be presented here.

For second-row elements the paramagnetic term $\sigma_p^A$ is the dominant factor in the expression derived for the $^{13}$C nuclear shielding $\sigma$ (proportional to the chemical shift $\delta$):

$$\sigma_p^A = -\frac{2 \epsilon^2 \hbar^2}{3 m^2 c^2 \Delta E} \langle r^{-3}\rangle_{2p} \sum_B Q_{AB}$$

where $A$ indicates the nucleus under investigation

$\epsilon$ is the electron charge

$\hbar$ is the Planck constant over $2\pi$

$m$ is the mass of the electron

$c$ is the speed of light

$\langle r^{-3}\rangle_{2p}$ is the average value of $r^{-3}$ for a 2p orbital

$\sum_B Q_{AB}$ is the summation $B$ running over all atoms of the charge-density and bond-order matrix elements for the unperturbed wavefunctions

The term $\Delta E$ is the average excitation energy, defined by

$$\frac{\langle 0|\hat{H}|10\rangle}{\Delta E} = \sum_{n\neq0} \frac{\langle 0|\hat{H}|n\rangle \langle n|\hat{H}|10\rangle}{E_n - E_0}$$
ΔE is thus a weighted average over the excited states.\textsuperscript{172}

For carbonyl containing compounds an important contribution to the
ΔE is supplied by the low-lying nπ\textsuperscript{*} transition.\textsuperscript{173} Therefore plots of
δ_{CO} versus λ_{max} of the nπ\textsuperscript{*} transition of carbonyls have been used to
check the influence of ΔE on σ_{p}.\textsuperscript{172}

One way to change the λ_{max} of the carbonyl nπ\textsuperscript{*} bands is by changes
in the polarity of the medium. It seems convenient now to correlate the
chemical shifts with a solvent polarity scale. A common way to introduce
the solvent polarity is by use of a solvent polarity parameter based on
spectroscopic measurements. Let us write the known relationship for the
molar transition energy E_{T} as follows

\[ E_{T} \text{[Kcal/mol]} = h \, c \, \nu \, \nu_{L} = 4,859 \times 10^{-3} \, \nu \text{[cm}^{-1}] \]

This serves as definition of a polarity scale.\textsuperscript{164,168} The constants h, c
and ν_{L} are respectively the Planck constant, the speed of light in a
vacuum and the unit conversion factor to the typical units, Kcal mol\textsuperscript{-1}.

The polarity scale requires specification of the reference compound
used. In this work the well known E_{T}(30) values were used, based on the
pyridinium N-phenoxo betaine dye labelled 30 in a Dimroth's re-
ference.\textsuperscript{166-167}

That E_{T} is linear with ν_{max} of the nπ\textsuperscript{*} band of some carbonyls has
been reported,\textsuperscript{174} and the linearity also holds for the ketoacids used in
this work (Figure 30).

Since δ_{CO} should be linear with λ_{max} of the nπ\textsuperscript{*} band of carbonyls,
the correlation with the polarity scale E_{T} should be simply

\[ δ_{CO} \sim \lambda_{max} = 1 / \nu \sim 1 / E_{T}(30) \]
The plot of $\delta_{CO}$ versus $E_{T}^{-1}$ is shown in Figure 37. This shows that the $\delta_{CO}$ shifts are most sensitive to an environment of proton donors, as expected from results for other systems.175-176

The importance of hydrogen bonding in explaining changes in $\delta_{CO}$ is discussed in a detailed study of acetone in water at different concentrations,177 in which it was found that the $\delta$ ($^{17}$O) was strictly linear with the $\lambda_{max}$ of the nπ*$ band. The negative slope in the relationship between $\delta$ ($^{13}$C) and $\delta$ ($^{17}$O) was taken as confirmation of a polarity effect. The variations of $\delta$ ($^{13}$C) and $\delta$ ($^{17}$O) were explained by changes in carbonyl polarity due to hydrogen bond formation. The hydrogen bonding accounted also for the blue shifts observed.173

As mentioned above, for carbonyl compounds an important factor contributing to the shifts is the mean excitation energy term $\Delta E$, variations of which are reflected by the energies of the nπ*$ transitions. If all other factors remain constant, a variation of 1.3 ppm per nm shift in the nπ*$ $\lambda_{max}$ is to be expected. A plot of $\delta_{CO}$ versus $\lambda_{max}$ for 6-oxo-dodecanoic acid in alcohols and of different concentrations of its potassium salt in water, shows an overall change of about 1.4 ppm per nm for the oxo-carbonyl (Figure 38). The assignment of the observed variations in chemical shifts as due to direct medium effects rather than to conformational effects seems reasonable. Conformational effects were suggested for methylene carbons in a chain.178 The fact that 10-oxododecanoate exhibits a similar shift for the oxo-carbonyl to the 6- and 7-oxododecanoate (though this has more hydrogens γ to the oxo-carbon) suggests that conformational alterations have a minor influence
Fig. 37 Plot of oxo-carbon chemical shift of potassium 6-oxododecanoate versus $1 / E_T$ of solvents. Numbering is in decreasing order of $E_T$ (see Table 17).
Fig. 38 Plot of oxo-carbon chemical shift versus wavelength of the absorption maximum for 6-oxo-dodecanoic systems in alcohols and aqueous potassium dodecanoate solutions. Potassium 6-oxo-dodecanoate 0.1 M (a) and 0.5 M (b); 1 M 6-oxo-dodecanoic acid in methanol (c) and ethanol (d).
on the oxo-carbonyl shift.\textsuperscript{179}

In summary, the very low-field chemical shift of the oxo-carbon of the oxododecanoates can be explained by strong hydrogen bonding interactions present even when micellization takes place.

7.6 Conclusions from the oxo-carbon chemical shift experiments

The observations with $\delta_{\text{CO}}$ parallel qualitatively the findings from the UV-absorption of the same systems. This can be observed from the results in Chapter 6, and serves as a test of self-consistency.

Although $^{13}\text{C}$-chemical shifts measurements of very dilute samples present problems of sensitivity or long acquisition times, most samples of oxododecanoates were susceptible to analysis by both UV-absorption and $^{13}\text{C}$-chemical shifts in the same concentration ranges.

The main observations from $\delta_{\text{CO}}$ were in accordance with those found from UV-absorption. Thus high polarities for the micellized oxododecanoates regardless of whether the position of substitution was the 6, 7, or 10-th carbon were apparent.

Mixing oxododecanoate with dodecanoate produced a chemical shift of the oxo-carbon that seemed compatible with the total concentration of surfactant rather than of the oxododecanoate alone.

The concentration effect on the $\delta_{\text{CO}}$ of potassium 7-oxododecanoate in water was pronounced. The largest shifts were obtained below the cmc, but they were high even at high concentration.

Dissolved ketones in micelles presented large downfield shifts, yet smaller than when the carbonyl was part of the micellar chain. The concentrations of ketone were large, due to the long acquisition times needed to obtain the $\delta_{\text{CO}}$.
7.7 Discussion on the proton spin-lattice relaxation rates of potassium 7-oxo- and 10-oxo-dodecanoates

The spin-lattice relaxation rates ($1/T_1$) of chain protons of surfactants have been reported to increase with surfactant concentration, particularly above the cmc region. Examples are studies of short chain alkanoates from C$_2$ to C$_6$,\textsuperscript{180} and of sodium sulphates from C$_2$ to C$_{12}$.\textsuperscript{181}

The interpretation of $T_1$ relaxation rates from unsubstituted surfactants is difficult because both intermolecular and intramolecular contributions to the relaxation are operative,\textsuperscript{182} and signal overlap of the methylene peaks is large. In the present work with oxododecanoates a somewhat better resolution of the proton-chemical shifts occurs due to the presence of substituents.

Generally speaking the observed $^{1}$H-relaxation rates of oxododecanoates were considerably larger above than below the cmc (0.0667 M for 7-oxododecanoate). In this respect the relaxation behavior of oxododecanoates resembles that of unsubstituted surfactants. For unsubstituted surfactants a similar observation was proposed to reflect the increased concentration of hydrogens in the micelles, although a slower molecular motion in the micelles as compared to the free alkanoate could not be excluded completely on the basis of $^{1}$H relaxation studies alone.\textsuperscript{180}

From carbon-13 spin-lattice relaxation studies, in general, it has been concluded that the alkyl chain motions within the micelles are very rapid,\textsuperscript{183} with slower motions of the micelle as a whole contributing also to the relaxation.\textsuperscript{183–184} Thus, before more detailed conclusions are drawn from Tables 18 and 19, information on the $^{13}$C-relaxations of
7.8 Partition of a solubilized probe: tert-butoxy radicals in micellar systems

An important consideration in micellar studies is whether the extrinsic probes are exclusively associated with micelles or to a great proportion are in the aqueous phase. In this work tert-butoxy radicals, which are good models for carbonyl triplets with respect to hydrogen abstraction,\textsuperscript{185} were used in an attempt to clarify the above point.

Tert-butoxy radicals, generated here by photolysis of di-tert-butyl peroxide, are known to react by β-cleavage or by hydrogen abstraction from a hydrogen donor.\textsuperscript{185–195} The tert-butanol to acetone ratio is solvent sensitive.\textsuperscript{186–188} The solvent effect was interpreted by Wagner and Walling in terms of solvated tert-butoxy radicals which decrease their solvation in the transition states for hydrogen abstraction, but which have strongly solvated transition states for β-scission.\textsuperscript{186–188}

In the present work a solvent effect was noticed too when some long chain containing solvents were used. The results in Table 21 show that the tert-butanol / acetone ratio is much smaller in octanoic acid than in dodecane. In micellar solutions it is even smaller, about ten times smaller than in octanoic acid. For anionic and cationic micellar systems, the small tert-butanol / acetone ratios may be considered to indicate a strong solvation on average for the tert-butoxy radicals.

There are different ways to explain the strong solvation: the probe might be dissolved in polar environments of the micelle, or in the aqueous phase, or a combination of both might be occurring. Some insight into the problem may be gained by considering the following simplified
mechanism in which the tert-butoxy radicals are denoted by BO, and m and aq refer to the micellar and aqueous pseudophase, respectively; M represents a micelle without a BO radical, and $K_{eq}$ the association equilibrium

$$
\begin{align*}
(BO)_m & \overset{k_H}{\longrightarrow} BOH \\
(BO)_m & \overset{k_β}{\longrightarrow} Me_2CO \\
(BO)_m & \overset{k_α}{\longrightarrow} Me_2CO \\
(BO)_{aq} & \overset{k_{eq}^{-1}}{\longrightarrow} (BO)_{aq} + M
\end{align*}
$$

Abstraction from unmicellized surfactants has been neglected due to their low concentration. Another assumption, justified in part by the results obtained, is that the BO radicals reach the equilibrium distribution with the micelles. From the above mechanism it follows that the relative yield of tert-butanol to acetone is given by the following,

$$
R = \frac{k_H [BO]_m}{k_β [BO]_m + k_α [BO]_{aq}}
$$

Two limiting cases may be distinguished. In the first case, in which almost all BO radicals are in micelles, further formation of micelles should have little effect on the reactions of BO, so $R$ would be expected to become constant.
\[
R = \frac{k_H [BO]_m}{k_B [BO]_m} = \frac{k_H}{k_B}
\]

The constants \(k_\alpha\) and \(k_\beta\) are only mildly sensitive to the medium.\(^1\)86–188

In the second case, in which the BO radicals are largely in the aqueous phase, most of the scission will occur from this phase. Under these conditions an increase in \([M]\) brings more BO into association with micelles and consequently the relative yield of abstraction increases.

\[
R = \frac{k_H [BO]_m}{k_\alpha [BO]_{aq}} = \frac{k_H}{k_\alpha} K_{eq}[M]
\]

From the results in Table 22, in turn, it is apparent that when solutions containing different concentrations of SDS were irradiated under the same conditions, considerably larger tert-butanol / acetone ratios were obtained at high concentration of SDS. In all cases the ratio tert-butanol / acetone was smaller than in neat octanoic acid and much smaller than in dodecane, indicating that even at the higher concentrations of SDS the hydration of the tert-butoxy radicals was high.

A decrease in the occupancy number of BO radicals per micelle should not favor \(\cdot\) abstraction. The increases in relative yield of abstraction to scission, observed at higher \([SDS]\), should then simply be due to the larger fractions of BO radicals brought into association with micelles.

The experimental points, done only once, are represented in Figure 36. They show that the second limiting case mentioned above rather than the first, represents the actual situation in the concentration ranges used. A large proportion of BO radicals resided then in the
aqueous phase, which accounts for the strong solvations shown by the data on this system.

The method described in this section has two obvious limitations. If the actual partition coefficient is sought, then rate constants measurements are needed. Secondly, the conclusions for a small probe like tert-butoxy radical may not be very relevant for larger molecular weight molecules.

7.9 Concluding remarks

In this thesis the variations of oxo-carbon chemical shifts of oxododecanoates are shown to be due to direct medium effects and therefore to reflect the polarity around the probe. Those shifts, as well as the electronic absorption properties of the oxododecanoates and of nitritododecanoate, give consistent indications of the polarities around the probes.

Evidence is provided which indicates that for a systematic change in the position of substitution of a small probe on a dodecanoate chain the polarities are uniformly high in the neighbourhood of the probe.

The locations of the probes in the micelles are not easy to prove, which may lead to some reservation on the superficial extension of these conclusions to unsubstituted surfactants. The unsubstituted surfactants are of special interest, but their methylenes are not very sensitive to polarity changes.

To put these findings into perspective let us summarize what is known and part of what remains perhaps to be done. The bulk of the literature on micellar structure is concerned directly or indirectly with the Hartley and the Menger views of micelles. A defense of the
Hartley model of micelle was comprehensively provided by Lindman et al. The proposed evidence came mainly from studies of unsubstituted surfactants by viscosity, diffusion and thermodynamic analysis. There are also some recent studies using neutron scattering techniques. A model has to be assumed in order to interpret the scattering data. The Hartley model, or a slight modification of it, was used by different authors. Alternative models, however, were not tried.

Studies of substituted surfactants, in turn, generally indicate high polarities around the probes, and have been used to support the Menger model of micelles. Since there are opposing views in the literature concerning water penetration into micelles, some tests of methodology seem appropriate. For example, it should be interesting to test functionalized surfactants, which seemingly experience high polarities around the probes, by means of those techniques used to substantiate claims of little water penetration in micelles of unsubstituted surfactants, like viscosity, self-diffusion, thermodynamic, and neutron scattering techniques. On the other hand, the possibility of using a Menger type of micelle to interpret neutron scattering data, if feasible, should be considered. These proposals would test the validity of the methodologies and interpretations used, and clarify perhaps the important yet not completely settled question of water-hydrocarbon contact in micelles.
CHAPTER 8 - PHOTODECOMPOSITION OF ALKANONES IN UREA INCLUSION COMPOUNDS

8.1 Introduction

There has been great interest in recent years in the study of photoprocesses in ordered and constrained systems. Examples are studies in micelles, vesicles, microemulsions, monolayers and liquid crystals, among those in fluid systems, and on adsorbed surfaces and within crystals and polymers, among those in solid phases. Some photochemical studies of guest molecules included in host crystals have appeared recently. Well-defined location and environment of the molecule under study are provided more typically by crystals, monolayers and in some cases by host crystals. Micelles are perhaps in the other extreme; although they provide a way of compartmentalizing reagents, the location of the latter is not always easy to define.

The effect of a microenvironment on the photoreactions of molecules is perhaps easier to investigate in reasonably well-characterized systems. As an example in what follows, urea inclusion compounds (UIC) are described that provide an environment wherein photoreactions may be carried out, with consequences different from those observed in homogeneous solution. The steric constraints imposed by the host upon the once formed inclusion compound are not as severe as the ready steric inhibition of formation might suggest.

The crystals, unit cell characteristics and dimensions of typical urea inclusion compounds are known. Urea in the inclusion compound crystallizes in hexagonal lattice (as opposed to tetragonal for free urea) in which there are long channels of \( \approx 5 \) \( \text{Å} \) internal diameter (see Figure 39). This is sufficient to accommodate linear paraf-
Fig. 39 Schematic representation of an urea inclusion compound.

The six molecules forming the unit cell occupy the edges of the prism spiraling over a length of 11.1 Å. The oxygen atoms are located in the edges, and the $\text{C}_N^N$ groups lie nearly flat in the plane between two adjacent prisms. These directions are indicated by arrows.

Right: cross-section with included hydrocarbons.
fin-like molecules in the planar zig-zag conformation. Longitudinal rotation of hydrocarbon segments is relatively free while other motions (e.g. gauche-trans isomerization) are more severely restricted.\textsuperscript{185-186} The restraints are such that one methyl substituent in a long chain is enough to make complex formation difficult.\textsuperscript{180}

It is this kind of structure, with relatively narrow channels that has made possible some applications of uic of organic compounds since they were first reported in 1940.\textsuperscript{180,182} Thus the formation of uic has been used in the fractionation of linear paraffins from oil crudes, for the enhancement of separation in gas chromatography, as preservatives against the autoxidation of fatty acids, and as an aid in structural and spectroscopic analysis.\textsuperscript{180,187-188}

Despite these uses, and the availability of structural and some dynamical information,\textsuperscript{189-190} studies directly concerned with photochemistry in uic were, at the onset of the investigation to be reported, lacking. Some radiation processes in uic had been reported, particularly in connection with EPR studies.\textsuperscript{191-197}

8.2 Results and discussion

Most of the results were reported were obtained with 5-nonanone/uic. The photochemistry of 5-nonanone in solution proceeds via the Norrish Type II photoprocess, resulting primarily in the formation of 2-hexanone, propylene, and two isomeric cyclobutanols (Scheme 3).
SCHEME 3
8.2.1 Characterization of 5-nonanone/urea

The inclusion compound was obtained by crystallization from concentrated urea solutions in methanol after addition of 5-nonanone. The resulting crystals were characterized by Raman spectroscopy, a very appropriate technique to differentiate unequivocally between urea in tetragonal or hexagonal lattices, which correspond to free urea and the clathrate, respectively. The most relevant band for this purpose is the symmetric C-N stretching at \( \approx 1090 \text{ cm}^{-1} \) for tetragonal and 1024 cm\(^{-1} \) for hexagonal urea. The slightly higher frequency in the clathrate has been considered to be due to a slight shortening of the C-N bond.\(^{196-199}\)

Although there is some partial overlap of the bands, it is estimated from the Raman spectrum (Figure 40) that around 90% of the urea is in the hexagonal form.

Scanning electron micrograph pictures of part of the sample shows features corresponding to tetragonal and hexagonal urea (Plate 1).

A top view picture of larger crystals taken with a common camera is shown in Plate 2. The hexagonal and tetragonal crystals were obtained by slow crystallization from methanol of a partially photolyzed 5-nonanone/urea inclusion compound.

Consistent with the Raman data the elemental analysis of the sample used in most studies gave 32.44% C, 36.67% N, 8.09% H. This corresponds to an urea-ketone molar ratio of about 8.6 (see Appendix 3 for equations) to be compared with 7.6 that can be estimated on the basis of molecular dimensions.\(^{180}\) An excess of urea should not alter the photochemistry of the included ketone.

The 5-nonanone in uic showed the broad emission typical of alpha-
Fig. 40 Raman spectrum of 5-nonanone/urea inclusion compound
Plate 1 Scanning electron micrographs of a 5-nanone/uric sample.
Plate 2 Top view photograph of the hexagonal and tetragonal crystals obtained by slow crystallization from methanol of a partially photolyzed 5-nonaone/uic sample.
tic ketones in solution or in polymers. There were also some extra peaks, sharper and overlapping the ketone emission; these were likely due to impurities, since they were present more strongly in the commercial urea used (Figures 41 to 43).

8.2.2 Results of Photolysis of 5-nonanone/uic

Irradiation of 5-nonanone/uic crystals at room temperature under nitrogen followed by addition of methanol to dissolve the product, and subsequent analysis by gas chromatography (GC), led to the detection of Type II products. These were 2-hexanone and propene, from fragmentation, and cyclobutanol, only one isomer, from cyclization. The results were surprising in some respects:

a) Only Type II products were formed even though a six membered transition state is required. Type I products which are also formed in solution photolysis were absent even though the cleavage does not require the formation of a ring structure intermediate or transition state.

b) The cyclization over fragmentation ratio was higher for irradiations in uic than in solution.

c) One cyclobutanol was formed in uic, the other isomer was almost entirely absent.

8.2.2.1 Characterization of photoproducts

Of the photoproducts, 2-hexanone was analyzed by GC and compared with an authentic sample. Propene formation was inferred from the presence in the GC trace of a very short retention time product, produced also during irradiation of 2-hexanone in solution. The cyclobutanols from irradiations in solution or in uic were analyzed by combined gas
Fig. 41 Front-face emission from a 5-nonanone/uic sample; excitation at 300 nm.
Fig. 43  Front-face emission from a 5-nonanone/uic sample. Comparison with an n-decane/uic sample.

Excitation at 300 nm.
chromatography/mass spectrometry (GC/MS). The irradiations in solution afforded both cyclobutanol isomers with a slight preference of one over the other. They were separated in ~ 90% purity by preparative GC.

GC/MS data for 5-nanonone irradiations

Column 12′,12″ OV-101; conditions for C₉ and C₆ compounds:

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cis cyclobutanol-C₆

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2-hexanone

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Column 12',12% OV-101; conditions for C₉ and C₆ compounds:

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cis cyclobutanol-C₉

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GC/MS data for 5-nonenone irradiations (cont.)

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trans cyclobutanol-C₉

Retention time = 34.7 min; scanned from 20 to 400 amu; lower cutoff 0.5%

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GC/MS data for 5-nonenone irradiations (cont.)

Column 12',12% OV-101; conditions for C₉ and C₆ compounds:

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5-nonenone (for comparison)

Retention time = 35.0 min; scanned from 20 to 400 amu; lower cutoff 0.5%

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8.2.2.2 **Relative yields from 5-nonenone irradiations**

The cyclization to fragmentation ratio as measured by the cyclobutanol/2-hexanone ratio for the irradiation of 5-nonenone/uic was 0.67, compared with 0.32 in methanol, taking into account both cyclobutanols. The two ratios were 0.65 and 0.19, respectively if only the cis isomer was taken into consideration. Product quantum yields of solid samples such as these are difficult to measure, although judging from the irradiation times required (by comparing with liquid samples) they must be only slightly lower.

Another change induced by the urea channels was the photoproduction of essentially only one cyclobutanol (cis - see next section, 8.2.2.3). Only ≈ 3% of the trans isomer could be detected, even in an experiment exceeding 95% conversion.

Interestingly, over-irradiation caused the 2-hexanone produced to undergo Type II process itself to give acetone and again essentially one cyclobutanol. This is believed to be the cis isomer from its gas-chromatographic behavior. (This assignment relies only on comparisons. For both ketones, and for 2-undecanone refered to later, the corresponding cyclobutanols that run faster on the GC-column were the ones formed almost exclusively in uic. They are assumed to have the same configuration. This is cis for the C₉-cyclobutanol, as shown in the next section). Only about 5% of the trans isomer was detected. This stereospecificity implies that the integrity of the lattice is preserved and that the 2-hexanone produced in the primary photodecomposition remains as an included molecule. This photodecomposition of 2-hexanone may introduce some error in the cyclization to fragmentation ratios reported
above, and therefore those ratios were determined at not too high conversion.

8.2.2.3 Determination of the configuration of cyclobutanols

The configurations of the cyclobutanol products from 5-nonanone were deduced from a comparison of the $^{13}$C-spectrum of each isomer. The peaks obtained which are relevant for the present purpose are listed below, others are reproduced in Figure 44.

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From the above values it can be inferred that one isomer has $^{13}$C-chemical shifts (in ppm from Me$_4$Si) consistent with the methyl being cis to the OH group; the other isomer has the corresponding signals consistent with the methyl group being trans to the OH, following arguments used for other systems.$^{210}$

Furthermore the $^1$H-chemical shift of the Me at C-2 of both cyclobutanol isomers was affected by addition of the shift reagent Pra-Resolve-II-$d_{30}$.$^{211}$ An example of the effect of a small amount of shift reagent on the NMR spectrum of the cis isomer is shown partially in Figure 45. A plot of the peak position of the doublet from the Me shift at C-2 of each isomer versus the molar fraction of shift reagent showed that the cis isomer was more affected (Figure 46), consistent with the above assignment.
Fig. 44 Carbon-13 shifts of C9-cyclobutanols and 5-nonanone. Assignments were made with the aid of $^1$H off-resonance decoupled spectra. Assignments with asterisk might be interchanged.
Fig. 45 Effect of shift reagent on the H-NMR spectrum of cis C$_5$-cyclo-
butanol in the methyl region.
Fig. 46 Plot of methyl hydrogen chemical shifts of C₈-cyclobutanols (as doublets) versus molar ratio of shift reagent (Pra-Rsolute-II-d₃₀) to cyclobutanol. Solvent: DCCl₃; Reference: Me₄Si.
permitting inclusion to occur.

Examination of space filling models shows that the formation of the cis-cyclobutanol has less stringent rotational requirements, thus favoring the formation of this isomer. In fact the cyclobutanol obtained, having both alkyl groups in pseudo-equatorial positions, is expected to be more compact.

Hydrogen bonding to the crystal lattice may help keep the biradical conformation quasi-frozen long enough for cyclization to occur (included molecules are known to have preferred orientations in the urea channels). 183-184

The product distribution seems to depend on the peculiarities of the system used. Related observation have been made in the irradiation of benzoin alkyl ethers adsorbed on silica gel, where the formation of only one cyclobutanol was noted. 212 In this system though the Type I products were by far predominant. Subsequently it was found that photolysis of some aralkyl ketones included in chroman clathrates (Dinan inclusion compounds) showed a product distribution not too different from those found in solution. 213 Phosphorescence of non-photoreactive \(\beta\)-phenyl-propiophenone, as well as that of acetophenone derived from photolyzed non-phosphorescent valerophenone was observed even at room temperature, when included in silicalite (a type of zeolite). 214

In summary, the photochemistry of 5-nonanone/uic is characterized by formation of Type II products, with higher cyclization to fragmentation ratio than in solution, and by the formation of essentially only one of the two possible cyclobutanol isomers.
8.2.4 Some results with 2-undecanone/uic

Some extension of the work was done using 2-undecanone, which by the Type II process can yield the photostable products acetone, 1-octene and cyclobutanols.

Preliminary experiments with 2-undecanone/uic showed that no Type I product was formed; only the Type II products were detected by GC or GC/MS.

Again one cyclobutanol was formed, believed to be the cis from its gas-chromatographic behavior (section 8.2.2.2), the trans was present in only \( \approx 7\% \).

The cyclization to fragmentation ratio for irradiations in uic was different from those in solution. Thus the ratio was 0.28 (or 0.25 if based in only the cis cyclobutanol) in uic and 3.37 (or 1.85 if based in only the cis cyclobutanol) in acetonitrile wet with 2% of water.

Emission from 2-undecanone/uic was also observed (Figure 47).
GC/MS data for 2-undecanone irradiations.

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1-octene

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trans cyclobutanol-C₁₁

Retention time = 20.9 min; scanned from 20 to 400 amu; lower cutoff 0.5%

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GC/MS data for 2-undecanone irradiations (cont.)

Conditions as for \( C_8 \) and \( C_{11} \) compounds above

2-undecanone (for comparison)

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Fig. 47 Front-face emission from a 2-undecanone/uric sample and comparison with emission from urea (Analar), curves a and b, respectively. Curve c is like b but using a larger scale. Excitation at 300 nm.
CHAPTER 9 - EXPERIMENTAL OF PART II

9.1 Experimental of micellar studies

9.1.1 Materials and methods for micellar studies

Solvents for UV and $^{13}$C-spectra of substituted dodecanoates were from Fisher, spectro grade, used as received. Tert-butanol was Fisher, certified.

The UV-Vis spectra of nitrites and oxododecanoates were taken with a Cary 118C spectrometer. Wavelengths were determined to ± 0.1 nm.

The $^{13}$C-NMR spectra were obtained using a concentrical cell arrangement with a solution of dioxane (10% v/v) in D$_2$O in the inner tube. The shieldings were measured relative to the dioxane signal and converted to the Me$_4$Si scale with the factor 67.4 ppm.

Fluorescence of acetone and other ketones in liquid systems were determined in a Perkin Elmer MPF4 fluorescence spectrophotometer.

9.1.2 Experimental of nitrites

9.1.2.1 Preparation of nitrito dodecanoates in micellar potassium dodecanoate

In a typical preparation the corresponding hydroxy-dodecanoic acid (21.6 mg, 0.1 mmol) was dissolved in minimum amount of ether to achieve dissolution and it was transformed to the nitrite by NOCI gas added dropwise by condensation with a dry-ice cold finger; the addition was stopped when the brown colour persisted in solution. (NOCI was prepared and distilled as described in Inorg. Synthesis 1953,4,48). The ethereal solution was then quickly washed three times with buffer of pH 5, twice with distilled water and dried (MgSO$_4$).

The ether was removed in a rotary evaporator and the nitrite was
immediately dissolved in 20 mL of 0.1 M potassium dodecanoate. The mixture was neutralized with potassium hydroxide \( (5.95 \text{ mL} \times 0.0168 \text{ M} = 0.1 \text{ mmol}) \). Then more 0.1 M potassium dodecanoate was added (the final amount in solution was 40 mL) and the content rinsed into a volumetric flask that was made up to 50 mL with distilled water. The resulting micellar solution was 2 mM (assuming quantitative yield) in nitrito-dodecanoate and 0.04 M in potassium dodecanoate.

Other concentrations were prepared in the same fashion but with other amounts of hydroxy-acid, potassium hydroxide and potassium dodecanoate.

9.1.2.2 Preparation of aqueous nitrito dodecanoate solutions

These were prepared as before except that the nitrito dodecanoic acid was neutralized directly by potassium hydroxide solution and the contents were transferred to a volumetric flask. Triply distilled water was used to rinse and to make up the volume to the mark.

9.1.2.3 Preparation of simple nitrites

The 2-butyl nitrite was prepared by the reaction of 2-butanol with \( \text{NaN}_2 \) and \( \text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O} \) in minimum amount of water \( (\text{J. Am. Chem. Soc.} \ 1955, \ 77, \ 5528) \ n_D = 1.3755 \ (22^\circ) \).

The 4-heptyl nitrite was prepared from 4-heptanol also by the \( \text{NaN}_2 \) and \( \text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O} \) procedure. The yellow liquid had \( n_D = 1.4043 \ (22^\circ) \).

The 1-heptyl nitrite was prepared in 94% yield from 1-heptanol by the action of \( \text{H}_2\text{SO}_4 / \text{H}_2\text{O} \) and \( \text{NaN}_2 \) \( (\text{as in J. Am. Chem. Soc.} \ 1933, \ 55, \ 3888) \).
9.1.3 Experimental of ketones

9.1.3.1 Preparation of oxo- and hydroxy-dodecanoates and related compounds

Preparation of 10-oxododecanoic acid methyl ester:

a) The procedure to convert 10,11-undecenoic acid to 10,11-undecenoate in good yield, by the use of MeI and anhydrous K₂CO₃ was adapted from J. Org. Chem. 1969, 34, 3717.

b) The methyl ester of 10,11-undecenoic acid (48.4 g) was allowed to react with 59.5 g of m-chloroperbenzoic acid (86% of per-acid content by titration with standardized Na₂S₂O₃ solution) in chloroform. At the end of the reaction, the chloroform was evaporated and replaced by low-boiling petroleum ether. The sample was worked up by treatment with KI solution, Na₂S₂O₃ and NaHCO₃, and then dried (MgSO₄). The NMR was consistent with the desired product. The sample was then distilled between 106-110° at 0.3 torr (0.04 kPa). Yield: 42.6 g (81.5%).

c) Methyl 10-hydroxydodecanoic acid was prepared by the reaction of LiCl(CH₃)₂ (2 equiv.) with methyl 10,11-epoxiundecanoate (1 equiv.), in anhydrous ether at 0° for 14 hr under nitrogen. (J. Org. Chem. 1973, 38, 4263). After work up, vacuum distillation gave the purified product in 35% yield (lit. 37%). The absence of the primary isomeric alcohol was confirmed by the absence of a carboxylic acid proton in the NMR spectrum of the Jones' oxidation product of the above sample.

Preparation of 8-oxododecanoic acid methyl ester:

a) Octanedioic acid momomethy1 ester was obtained by reaction of octanedioic acid with HCl and one equivalent of methanol. The monoester was distilled at reduced pressure using a spinning band column.
b) The monoester was converted to the corresponding acid chloride by reaction with \( \text{SOCl}_2 \) (see Org. Synthesis Coll. 3, 613 for the sebacic analog). The acid chloride was purified by distillation under reduced pressure (0.48 torr, 0.064 kPa; 98°) to give 83% of distilled product.

c) Methyl 8-oxododecanoate was prepared by addition of the above acid chloride to a n-butyl iodide / Zn(Cu) mixture. (Fette Seifen Antrichmittel 1963, 65, 995). Yield: 90%.

The reduction of keto-esters or keto-acids to the corresponding hydroxy-acids were accomplished in good yield by using \( \text{NaBH}_4 \) in 5% aq. NaOH.

The keto-or hydroxy-acid methyl esters were converted to the corresponding keto- or hydroxy-acids by the usual treatment with methanolic KOH followed by acidification with HCl and extraction with ether.

Their corresponding potassium salts were prepared by neutralization with methanolic KOH followed by repeated recrystallizations from methanol. The 5, 6 and 7-oxododecanoic acids obtained from Dr. K.Y. Law were purified by recrystallization from hexanes / ether.

9.1.3.2 Determination of the critical micelle concentration of potassium 7-oxododecanoate

The specific conductivity (\( \kappa \)) method was used. The conductivity cell had platinum black electrodes and a cell constant of 0.0201 cm\(^{-1}\) determined with a 0.0200 M KCl solution at 25.0°.

The more concentrated solution (0.1023 molal) was prepared by neutralization of 7-oxododecanoic acid with a slight excess of 0.2 M KOH and the required amount of triply distilled water. The others were obtained by addition of known masses of triply distilled water.
The plot of $K$ versus molality (m) was smoothly curved in the neighborhood of the cmc, with linear portions in the regions above and below it. The intercept of their tangents defined the cmc at 0.0659 m, or 0.0667 M after determination of the density at the cmc.

9.1.3.3 Proton spin-lattice relaxation times of potassium 7-oxododecanoate and potassium 10-oxododecanoate in deuterium oxide

The proton spin-lattice relaxation times were measured at 24-25° with a XL-100 Varian NMR-spectrometer. The inversion recovery method was used with pulse sequence $(\pi, \tau, \pi/2, \tau)_n$. 245

The stack of spectra at different times was analyzed by following the more relevant peaks. The peak heights were measured at different times. The logarithmic expression of the magnetization as a function of time was used,

$$\ln (M_0^Z - M_Z) = \ln (2M_0^Z) - \frac{t}{T_1}$$

For each signal considered the slope of the least-square fitting of the peak height versus time curve was used to calculate the spin-lattice relaxation time $T_1$ or the corresponding spin-lattice relaxation rate $R_1$

- Slope = $(1/T_1) = R_1$

9.1.4 Di-tert-butyl peroxide experiments

9.1.4.1 Materials

Octanoic acid was from Anachemia. Sodium dodecyl sulphate was from BDH, specially pure grade (>99%). Hexadecyltrimethylammonium chloride was precipitated with acetone from solution (K&K). Potassium dodecanoate was obtained by neutralization of dodecanoic acid (mp 43-45° from
Eastman) with potassium hydroxide (Fisher) in methanol (Fisher, spectrograde). The product was recrystallized several times from methanol. Hexadecyltrimethylammonium bromide was Merck p.a.. Acetone was Fisher (Certified ACS Spectranalyzed). Tert-butanol was Fisher, certified. Di-tert-butyl peroxide was passed through alumina before use.

9.1.4.2 Analysis

Product analyses were performed with a Varian Aerograph Series 1400 GC with flame ionization detector, connected to a Varian CDS 111 integrator and to a Fisher Recordal. Columns used are mentioned under the corresponding experiments.

9.1.4.3 Irradiation of di-tert-butyl peroxide in different media

The following liquid systems were used:

a. Dodecane
b. Octanoic acid
c. Sodium dodecyl sulphate 0.20 M
d. Hexadecyltrimethylammonium bromide 0.0136 M
e. Hexadecyltrimethylammonium chloride 0.055 M
f. Potassium dodecanoate 0.298 M
g. Sodium dodecyl sulphate 0.016 M

There was placed 2 mL of each solution into identical cylindrical tubes (Pyrex). To each there was added 25 mL of di-tert-butyl peroxide. Oxygen was removed from the samples by bubbling nitrogen slowly.

The tubes were placed in a merry-go-round and irradiated with a Hanovia 150-Watt Xe/Hg lamp for one hour.

Analysis of the acetone and tert-butanol produced was performed on a 12% OV-101-12' x 1/8" column at 50°. Authentic samples were used to
find the retention times of acetone and tert-butanol.

The 0.016 M SDS did not completely dissolve the peroxide. The irradiation was performed around the middle part of the tube. The samples in the hexadecyltrimethylammonium chloride systems were also likely close to saturation.

9.1.4.4 Irradiation of di-tert-butyl peroxide at different concentrations of sodium dodecyl sulphate

Solutions 0.30 M and 0.20 M in SDS were prepared by dissolving the appropriate amounts of SDS in water (Fisher HPLC grade). The others were prepared by dilution of stock 0.20 M SDS. The following concentrations of SDS were used: 0.30, 0.20, 0.15, 0.10, 0.07, 0.05, 0.04, 0.03 M.

To each tube containing 2 mL of one of the SDS solutions there was added 2 μL of di-tert-butyl peroxide. This resulted in a concentration of peroxide of 5.43 mM.

The solutions were freed of oxygen by bubbling nitrogen for one hour. They were placed in a merry-go-round and irradiated for 10 hr with a 150-Watt Xe/Hg lamp.

Analysis of acetone and tert-butanol was performed in the above mentioned GC using a 20% CARBOWAX 20 M 30' x .125" column at 129°C.

9.2 Experimental of urea inclusion compounds

9.2.1 Materials

Urea was Analar, analytical reagent 99.5%. 5-Nonanone was from Aldrich. Methanol, decane and 2,2,4-trimethylpentane were Aldrich, Gold label. 2-Undecanone (Aldrich, 95%) was fractionally distilled under vacuum. n-Pentane was Phillips 66 (>99%) or Photex for UV spectrophotometry 'Baker Analyzed' reagent. Acetonitrile was from Kodak, spectro
grade. Tert-butanol was from Fisher, certified. Benzophenone was from BDH, 99%.

9.2.2 Experimental for 5-nonanone urea inclusion compound

9.2.2.1 Preparation of 5-nonanone urea inclusion compound

Several procedures were tried, all of them involving crystallization from a hot methanolic solution of urea and 5-nonanone.

a) Urea (0.5 g) was mixed with 3 mL of methanol and dissolved by warming. To 0.1 g of 5-nonanone there was added the above hot solution. The resulting solution was boiled to decrease the volume of methanol. On cooling, white crystals separated. They were collected by filtration and recrystallized twice from a hot solution of urea in methanol (0.25 g / 3 mL, half-saturated at room temperature). The crystals were washed twice with ether. Yield: 0.37 g. Elemental analysis: 29.87% C, 7.92% H, 39.05% N.

b) Urea (0.5 g) was mixed with 3 mL of methanol (half-saturated at room temperature). After warming, a small portion of this solution was added to 0.1 g of 5-nonanone. A white solid formed immediately. This was then recrystallized from half-saturated urea in methanol (0.25 g / 3 mL). The crystals were then washed with ether. Elemental analysis: 33.09% C, 8.18% H, 36.32% N.

c) Urea (0.5 g), 5-nonanone (0.1 g) and 2 mL of absolute ethanol were mixed. On warming most of the solid dissolved. Crystallization occurred on standing. The small needles that resulted were collected by filtration and air dried. Elemental analysis: 26.92% C, 7.60% H, 42.87% N.

d) The same procedure as in c) was used but with triple amount of each component. Elemental analysis: 25.91% C, 7.32% H, 43.79% N.
e) The procedure and amounts were as in d) and 1.4 g of crystals were obtained. These were recrystallized by the use of a small amount of half-saturated urea in methanol. Yield: 1.23 g. Elemental analysis: 22.53% C, 7.03% H, 45.67% N.

9.2.2.2 Scanning electron micrographs

These were obtained with a SEMCO NOVASCAN 30 scanning electron microscope with a beam voltage of 15 kV. The samples were deposited on aluminum sample holders wetted with methanol, which was then allowed to evaporate.

9.2.2.3 Raman spectra

These were obtained at a resolution of ca. 2 cm⁻¹ with a Jarrell-Ash Model 15-100 double monochromator equipped with photon-counting detection. Excitation was provided by the 514.5 nm line from a Spectra-Physics 164 Argon ion laser delivering 150 mW at the sample.

9.2.2.4 Emission from 5-nonanone urea inclusion compound

Front face emission spectra were recorded using a computer controlled Perkin-Elmer LS-5 Fluorescence Spectrophotometer. The samples were contained in 3 x 7 mm Suprasil cells and kept under nitrogen.

9.2.2.5 Irradiations of 5-nonanone urea inclusion compound

The sample (elemental analysis: 33.09% C, 8.18% H, 36.32% N) was placed in a Quartz EPR tube (3 mm diameter), closed with a septum and nitrogen gas passed through very slowly for one and a half days. Then it was sealed off under nitrogen. The sample was then irradiated using a 150-W Xe/Hg lamp. No filter was used for this irradiation. The sample was tumbled over occasionnally to expose other crystals to direct light. The irradiation was carried out for 6 hr. For analysis the sample tube
was broken open and immediately closed with a septum. With a syringe methanol was added to dissolve the sample. The resulting solution was analyzed by GC as indicated in the next section, 9.2.2.6.

Another sample of 5-nonanone / urea (50.05 mg, analysis 22.53% C, 7.03% H, 45.67% N) was irradiated with a 150-W Xe/Hg lamp. The sample was placed in a Pyrex NMR tube type 505 PP, and closed with a septum. After passage of nitrogen gas and sealing with Parafilm, the sample was irradiated for about five hours. For analysis 0.4 mL of methanol was added through the septum to achieve dissolution of the sample.

9.2.2.6 Analysis and characterization of the irradiation products from 5-nonanone urea inclusion compound

Products were analyzed by GC using a Varian Aerograph Series 1400 with flame ionization detection, connected to a Varian CDS 111 integrator and to a recorder (Fisher). For analytical purposes a 12% OV-101-12' x .125" column was used. The temperature was increased at 6° per min. from 60 to 130°.

GC/MS spectra were recorded in a Hewlett-Packard 5992 GC/MS system also using a 12'-12% OV-101 column.

The two cyclobutanol isomers were obtained in better than 90% purity by preparative gas chromatography of the reaction products from the irradiation of 5-nonanone in tert-butanol (1 to 9 volume ratio). Preparative irradiations were carried out by the use of twelve Rayonet RPR-3000 lamps, and were followed by GC using a 12% OV-101-12' x .125" column at 110°. Preparative gas chromatography was performed by the use of a Varian Aerograph Model 920 with a 10' x 3"/8 column packed with 20% OV-101 on Chromosorb P (AW-DMCS) operated at about 100°.
Carbon-13 NMR spectra were obtained in a Bruker WP-80 spectrometer. Deuterated chloroform was used as the solvent and Me₄Si as internal standard.

For the shift reagent study the cyclobutanol was mixed with deuterated chloroform that contained Me₄Si as internal standard. The ¹H-NMR spectra were recorded in a Varian EM 360A NMR spectrometer. The shift reagent Pr(C₁₀D₁₀F₂O₂)₃ was from Ventron, Alfa Division (Pra-Resolve-II-d₃₀), a gift from Dr. W. J. Leigh.

9.2.2.7 Laser flash photolysis experiments

The laser flash photolysis equipment was one already described in detail,⁷⁷-⁷⁸ and the procedure was similar to that described in section 4.7, using a N₂ laser.

Appropriate amounts of a concentrated solution of quencher were added to the cell containing the sample. Nitrogen was bubbled before the measurements.

9.2.2.8 Electron paramagnetic resonance spectra

These were recorded with a Varian E-4 EPR spectrometer, with the sample (under nitrogen) in a 3 mm-diameter cylindrical Quartz tube for EPR. The spectra are reproduced in Appendix 4.

9.2.3 Experimental of 2-undecanone urea inclusion compound

9.2.3.1 Preparation of 2-undecanone urea inclusion compound

Two literature procedures for hydrocarbon / urea inclusion compounds (Anal. Chem. 1954, 24, 1331) were adapted for 2-undecanone.

The first procedure was followed using the amounts there indicated. After three washings with 2,2,4-trimethylpentane, 3 g of product were obtained; its elemental analysis gave: 30.36% C, 7.94% H, 38.63% N.
The alternative literature procedure, using 0.5 g of 2-undecanone, 1.5 g of urea and 6 mL of ethanol, yielded after washing three times with 2,2,4-trimethylpentane and air drying, 1.52 g of white crystals.

9.2.3.2 Irradiation of 2-undecanone urea inclusion compound

The sample (50.1 mg) of 2-undecanone urea compound (30.36% C, 7.94% H, 38.63% N) was placed inside a Pyrex NMR tube and irradiated for 5.5 hr. The conditions were as for the 5-nonanone/uic irradiation, as was the analyzing procedure, except that the column temperature was increased at 4° per min from 60 to 170°.

9.2.4 Irradiations of aliphatic ketones in solution

These irradiations were done either in a reactor with twelve Rayonet RPR-3000 lamps, or by irradiation with a Hanovia 150-Watt Xe/Hg lamp. Light filtering was provided by the thin glass wall of the NMR sample tubes used, or when a Quartz cell was used, by a thin glass cover in front of the lamp housing. Oxygen was removed by bubbling nitrogen.
APPENDIX 1 - TRANSIENTS OF SOME TETRAMETHYLCYCLOBUTANETHIONES FOLLOWING LASER PHOTOLYSIS

A laser flash photolysis study of the transients of tetramethyl-3-thio-1,3-cyclobutanedione (hereafter referred to as TMCB-thiodione or 1a) and of 2,2,4,4-tetramethyl-1,3-cyclobutanedithione (hereafter referred to as TMCB-dithione or 1b) is reported here, since there has been no report on these transients. The photochemistry of 1a,\textsuperscript{1-2} 1b,\textsuperscript{3-4} and some related thiolactones\textsuperscript{5-6} had been studied by Ramamurthy et al., who proposed mechanisms to explain product formation. In brief they involve the following steps:

\[ 1 \text{ (a or b)} \rightarrow \text{Excited States} \rightarrow \text{Biradicals} \rightarrow \text{Carbenes} \]

\[ + 1 \]

\[ \rightarrow \text{Product} \rightarrow \text{Products} \]

The transient absorption spectra and some decays obtained here are reported in Figures A1 to A13.

**SUMMARY OF THE TRANSIENT ABSORPTION AND DECAY OF TETRAMETHYLCYCLOBUTANETHIONES**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp</th>
<th>Spectrum</th>
<th>Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>approx. ( \lambda_{max} ) in nm</td>
<td>( \lambda_{moni} ) in nm (( \tau ) in ns)</td>
</tr>
<tr>
<td>Freon 113</td>
<td>RT</td>
<td>490(b,w); 360; e&lt;320</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freon 113</td>
<td>-30</td>
<td>490(b,w); e&lt;390(s)</td>
<td>500(73ns); 360(64ns)</td>
</tr>
<tr>
<td>Methanol</td>
<td>-32</td>
<td>480(w,b); e&lt;400(s)</td>
<td>470(63ns)</td>
</tr>
<tr>
<td>Methanol</td>
<td>-59</td>
<td>480(w,b); 380(w); e&lt;360</td>
<td>480(94ns); 380(96ns)</td>
</tr>
</tbody>
</table>

202
TETRAMETHYL-1,3-CYCLOBUTANE DITHIONE (1b)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp</th>
<th>Spectrum</th>
<th>Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freon 113</td>
<td>RT</td>
<td>660(b,v); 390(b,v)</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>RT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freon 113</td>
<td>-31</td>
<td>660(b,v); 390(b,v)</td>
<td>650(147ns); 380(129ns)</td>
</tr>
<tr>
<td>Methanol</td>
<td>-32</td>
<td>660(b,v); 390; e&lt;380(s)</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>-57</td>
<td>660(b,v); 380; e&lt;370</td>
<td>660(256ns); 370(259ns)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>410(sh); 550(sh)</td>
<td>425(238ns)</td>
</tr>
</tbody>
</table>

* b=broad, sh=shoulder, w=weak, s=strong, v=very strong, e=emiss/bleach

The samples, kept under nitrogen, had concentrations adjusted to produce absorbances of about 0.4 at the laser wavelength used (308 nm, XeCl excimer laser). Samples for use at 337 nm (nitrogen laser) gave no detectable transient.

The laser wavelengths used should cause both 1a and 1b to undergo transitions to their ππ* singlet states, localized mainly on their corresponding C=S chromophore.

Since for the dithione 1b the a-cleavage occurs from its lowest (nπ*)=triplet, the transient observed by laser flash photolysis could be either the triplet state, a triplet biradical, or one of the carbenes produced. But these carbenes react with methanol, and so use of neat methanol should produce a large decrease in their lifetime. Experimentally the lifetimes of the transient in methanol were only slightly smaller than in Freon 113. Carbenes therefore do not seem to contribute significantly to the transient absorption. For 1b then the transients
observed are likely due to the triplet state of 1b or to triplet biradicals produced by (or derived from) α-cleavage.

For the thiodione 1a the transient absorbance is likely due to the triplet or to a biradical; carbenes are excluded by the reason given above for 1b. The transient from 1a presented shorter lifetime and an absorbance maximum at shorter wavelength than that of 1b.

The α-cleavage of 1a, believed to occur from the $^3(n\pi^*)$ state, may in principle take place next to the thiocarbonyl or next to the carbonyl. An interesting question is whether intramolecular (singlet or triplet) energy transfer occurs following excitation of the carbonyl chromophore. Related to this is the observation that the phosphorescence of 1a at 77 K seemed to occur from the lowest triplet state of the C=S chromophore of TMCB-thiodione, regardless of whether the excitation was into the C=S or the C=O chromophore.

This question of energy transfer may be relevant also to the photochemistry of 1a. Continuous irradiation of 1a above 280 nm (where the C=S and even more the C=O chromophores absorb) produced an extra product, a thiolactone, not formed by irradiation above 460 nm, where only the thiocarbonyl chromophore absorbs. This extra product was therefore considered to arise from α-cleavage next to the carbonyl.

It has not been reported whether the thiolactone formation is a singlet or triplet state reaction. The production of this thiolactone formally resembles the formation of lactone via α-cleavage of TMCB-dione, known to occur from the singlet. The thiolactone is not the major photoproduct; the other products resemble those formed from the lowest triplet of TMCB-dithione.
More mechanistic studies seem necessary before a final conclusion is drawn concerning the occurrence of this intramolecular energy transfer. The possibility of intermolecular energy transfer should also be analyzed, since ground state thionegs are normally fast quenchers.

In summary, laser photolysis at 308 nm produced very different transients from 1a and 1b, in terms of both their absorptions and their lifetimes. They followed first order decays, with some residual absorbances in certain cases. The transients were not detectable when the 337 nm N₂ laser was used. This could be due to the lower laser power, or perhaps to the higher concentration of thione needed to reach the required absorbance.

***

References for Appendix 1
9. For both thiones the ground state absorbances at 308 nm were 0.41 in Freon 113 and 0.42 in methanol, at room temperature.
10. 3-Mercapto-2,2,4-trimethyl-3-pentenoic acid β-(thiolactone).
Fig. A1 Tetramethyl-3-thio-1,3-cyclobutanedione transient decay at 500 nm, in Freon 113 at -30°C
Laser: 308 nm; 15 shots/point; fluorescence correction mode
Dashed line: first order decay fit
Top OD = 0.01176

\[ \ln A \text{ vs. time} \]
\[ A = OD(t) - OD(\infty) \]
\[ OD(\infty) = 0.0009 \]
\#points (\n): 13
Correlation: 0.99886

\[ t = 73.5 \text{ ns} \]
\[ \ln A: -4.62 \pm 5.91 \]

100 300 500 time/ns

204 time/ns 299
Fig. A2  Tetramethyl-1,3-cyclobutanedithione transient
absorption spectrum in methanol at -57°C
Laser: 308 nm; background correction mode
ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 660 nm
Range: 200 ns
X: 1→100
Markers: 28:42
Fig. A3 Tetramethyl-1,3-cyclobutanedione transient decay at 670 nm, in methanol at -33°.

Settings: 10 mV; 100 ns; 10 shots/point; fluorescence correction mode

Laser: 308 nm; 10 shots/point; fluorescence correction mode

Top OD = 0.06375

First order decay fit

\[ \ln A \text{ vs. time} \]

\[ A = OD(t) - OD(\infty) \]

\[ OD(\infty) = 0.0000 \]

#points (\#): 27

correlation: 0.99936

\[ \tau = 133 \text{ ns} \]

\[ \ln A: -2.79 + -4.31 \]
Fig. M Tetramethyl-1,3-cyclobutanedithione transient

absorption spectrum in methanol at -32°C

Laser: 308 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 470 nm

Range: 100 ns
X: 1×100
markers: 33;40
Fig. A5  Tetramethyl-1,3-cyclobutanedithione transient decay at 650 nm, in Freon 113 at -32°C
Laser: 308 nm; 15 shots/point; fluorescence correction mode
Dashed line: first order decay fit

Top OD = 0.05782

First order decay fit

\[ \ln A \text{ vs. time} \]

\[ A = OD(t) - OD(\infty) \]
\[ OD(\infty) = 0.0000 \]
\[ \# \text{points (V): 32} \]
\[ \text{correlation: 0.99885} \]

\[ t = 148 \text{ ns} \]

\[ \ln A: -2.88 + 4.53 \]

\[ 212 \text{ time/ns} \]

456
Fig. A6  Tetramethyl-1,3-cyclobutanedithione transient absorption spectrum in Freon 113 at 27°

Laser: 308 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 670 nm

Range: 100 ns
X: 1+100
Markers: 29;46
Fig. A7  Tetramethyl-1,3-cyclobutanedithione transient
absorption spectrum in Freon 113 at 22°

Laser: 437.1 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 350 nm
Range: 50 ns
X: 1×100
markers: 68:98
**Fig. A8** Tetramethyl-1,3-cyclobutanedithione transient absorption spectrum in Freon 113 at 21°C

Laser: 308 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 660 nm
Range: 50ns
X: 1×100
markers: 29:40
Fig. A9 Tetramethyl-3-thio-1,3-cyclobutanedione
transient absorption spectrum in methanol at -58°C
Laser: 308 nm; background correction mode
ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 480 nm
Range: 100ns
X: 1+100
markers: 31,43
Fig. A11  Tetramethyl-3-thio-1,3-cyclobutanedione transient absorption spectrum in Freon 113 at -30°C

Laser: 308 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/Div.; λ in nm

Decay at 360 nm

Range: 100 ns
X: 1×100
markers: 31, 47
Fig. A12  Tetramethyl-3-thio-1,3-cyclobutanedione
   transient absorption spectrum in Freon 113 at 23°

Laser: 308 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 490 nm
Range: 50 ns
X: 1+100
markers: 25, 35
Fig. A13 Tetramethyl-3-thio-1,3-cyclobutanedione

transient absorption spectrum in Freon 113 at 23°C

Laser: 308 nm; background correction mode

ΔOD display ranges are: 0.1, 0.02 & 0.004 OD/div.; λ in nm

Decay at 415 nm

Range: 50 ns
X: 1 + 100
markers: 30:36
### APPENDIX 2 - CARBON-13 CHEMICAL SHIFTS OF SOME OXO-DODECANOIC SYSTEMS

#### 6-oxododecanoic acid (1.0 M) in different solvents and aqueous mixtures

<table>
<thead>
<tr>
<th>Solvent</th>
<th>δ (ppm)</th>
<th>COOH</th>
<th>Diox (ext)</th>
<th>DM (ext TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>208.9</td>
<td>180.0</td>
<td>67.5</td>
<td>42.6</td>
</tr>
<tr>
<td>THF</td>
<td>209.0</td>
<td>174.5</td>
<td>67.7</td>
<td>42.9</td>
</tr>
<tr>
<td>DMF</td>
<td>210.5</td>
<td>174.8</td>
<td>67.5</td>
<td>42.6</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>211.2</td>
<td>179.8</td>
<td>67.0</td>
<td>43.1</td>
</tr>
<tr>
<td>DMSO</td>
<td>211.4</td>
<td>175.5</td>
<td>67.4</td>
<td>42.7</td>
</tr>
<tr>
<td>i-PrOH</td>
<td>211.5</td>
<td>175.9</td>
<td>67.3</td>
<td>42.8</td>
</tr>
<tr>
<td>80% i-PrOH</td>
<td>212.7</td>
<td>176.7</td>
<td>67.3</td>
<td>42.9</td>
</tr>
<tr>
<td>1PrOH</td>
<td>211.2</td>
<td>175.8</td>
<td>67.4</td>
<td>42.9</td>
</tr>
<tr>
<td>EtOH</td>
<td>211.8</td>
<td>176.1</td>
<td>67.4</td>
<td>42.8</td>
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<tr>
<td>EtOH</td>
<td>212.0</td>
<td>176.4</td>
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<td>43.1</td>
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<tr>
<td>50% EtOH</td>
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<td>177.0</td>
<td>67.4</td>
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<tr>
<td>MeOH</td>
<td>213.4</td>
<td>177.2</td>
<td>68.2</td>
<td>43.4</td>
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<tr>
<td>80% MeOH</td>
<td>214.6</td>
<td>177.7</td>
<td>68.0</td>
<td>43.3</td>
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</table>

#### Potassium 6-oxododecanoate in water

<table>
<thead>
<tr>
<th>Concentration</th>
<th>δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M</td>
<td>216.6</td>
</tr>
<tr>
<td>0.1 M</td>
<td>220.8</td>
</tr>
</tbody>
</table>

#### Potassium 7-oxododecanoate in water

<table>
<thead>
<tr>
<th>Concentration</th>
<th>δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M</td>
<td>216.8</td>
</tr>
<tr>
<td>0.5 M</td>
<td>219.1</td>
</tr>
<tr>
<td>0.1 M</td>
<td>221.1</td>
</tr>
</tbody>
</table>

#### Potassium 10-oxododecanoic acid in different solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Concentration</th>
<th>δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-PrOH</td>
<td>1 M</td>
<td>183.7</td>
</tr>
<tr>
<td>EtOH</td>
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</tr>
<tr>
<td>MeOH</td>
<td>1 M</td>
<td>214.7</td>
</tr>
<tr>
<td>0.5 M</td>
<td>214.4</td>
<td></td>
</tr>
<tr>
<td>0.1 M</td>
<td>214.7</td>
<td></td>
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#### Potassium 10-oxododecanoate in water

<table>
<thead>
<tr>
<th>Concentration</th>
<th>δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M</td>
<td>221.5</td>
</tr>
</tbody>
</table>

219
APPENDIX 3 - FORMULAE RELATING COMPOSITION WITH MOLAR OR MASS RATIO OF UREA IN NONANONE/UREA INCLUSION COMPOUNDS

a) Formulae relating percentage composition ($\% w_1$) and molar ratio ($n$)

The formula for the nonanone/urea may be represented like this

$\text{(nonanone)} \cdot \text{(urea)}_n$ or $(\text{C}_9\text{H}_{18}\text{O}) \cdot (\text{C}_4\text{H}_{12}\text{N}_2\text{O})_n$, and so $(142.24) + (60.06)n$ corresponds to a formula weight.

Rather than the composition by mass, it will be used for brevity, composition by atomic fractions; this for atoms of type $i$ can be obtained as follows,

$$n_i = \frac{\% w_i/100}{\text{Atomic mass}_i}$$

It can be easily demonstrated from stoichiometry that the molar ratio $n$ of urea to nonanone is given by the following alternative expressions:

$$n = \frac{n_N 142.24}{2 - n_N 60.06} \quad n = \frac{9 - n_C 142.24}{n_C 60.06 - 1} \quad n = \frac{18 - n_H 142.24}{n_H 60.06 - 4}$$

b) Calculation of the mass ratio of urea to nonanone based on $%\text{C}$ and $%\text{N}$

A 100 g sample contains the following mass of urea and of nonanone

Mass of urea $= \frac{\% N}{28.0134} \cdot 60.06$

Mass of nonanone $= 142.24 \times \left(\frac{1}{9}\right) \times \left(\frac{1}{12.01115} \times \frac{1}{28.0134}\right)$

so their ratio is given as follows,

$$\text{Mass Ratio Urea/Nonanone} = \frac{142.24}{60.06 \times \left(\frac{12.01115}{9} \times \frac{\% \text{C}}{\% \text{N}} - 1\right)}$$
APPENDIX 4 - ELECTRON PARAMAGNETIC RESONANCE OF IRRADIATED UREA INCLUSION COMPOUND OF 5-NONANONE

A few EPR spectra of a sample of 5-nonanone/urea inclusion compound were recorded following irradiation through Quartz. The spectra are reproduced here, but no attempt was made to identify the radicals, since they may not be relevant to the Type II photoprocess that the ketone undergoes. Hydrogen radicals were perhaps involved (last figure).
Reference: Ruby
REFERENCES


9. Ibid. 1965, 84, 304.


54. Fournier de Violet, P.; Bonneau, R.; Lapouyade, R.; Koussini, R.
Pays-Bas 1976, 95, 165.


75. Kumar, C.V.; Qin, L.; Das, P.K. J. Chem. Soc., Faraday Trans. II 1984, 80, 783. For thiobenzophenone the values given are:

\[ k_{SQ} = 3.3 \times 10^9 \ (\pm 15\%) \ M^{-1} s^{-1}; \ k_{OXY} = 2.9 \times 10^9 \ (\pm 15\%) \ M^{-1} s^{-1} \]

\[ \tau_T = 1.7 \mu s (\pm 2\%); \ \phi_T = 0.6 \text{ at } 337 \text{ nm and } 1.0 \text{ at } 600 \text{ nm both } \pm 15\% \]


102. see eg. ref. 81 - 83 and for simpler ions Hinton, J.F.; Amis, E.S. Chem. Rev. 1971, 71, 627.


131. Ibid. 1976, 43, 587.


155. The slow thermal decomposition of 2-butylnitrite in water and the occurrence of Barton photoreactions of nitrito substituted potassium dodecanoate in aqueous potassium dodecanoate further substantiate this point.


163. Turro, N.J. "Molecular Photochemistry"; W.A. Benjamin: San Francisco
1965.


165. See e.g. pp 201-203 of ref. 122.


187. Ibid. 1964, 86, 3368.
188. Ibid. 1965, 87, 5179.
200. see ref. 4 to 11 of ref. 201 for examples.


204. Ibid. 1981, 5, 475.


220. Ibid. 1977, 11, 82.
226. Ibid. Advances in Raman Spectroscopy 1972, 1, 570.


