1967

A Bimolecular Fragmentation Reaction Of Alkanesulphonyl Halides

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A BIMOLECULAR FRAGMENTATION REACTION
OF ALKANESULPHONYL HALIDES.

by

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

Faculty of Graduate Studies
The University of Western Ontario
London, Canada.
August 1967
ABSTRACT

While studying reactions of sulphenes (RR'C = SO₂) a new reaction of alkanesulphonyl halides was encountered, a halide ion catalysed desulphonylation reaction

\[ \text{RCH}_2\text{SO}_2\text{X} + \text{X}^- \rightarrow \text{RCH}_2\text{X} + \text{SO}_2 \]

The reaction was shown to be bimolecular by kinetics, a Hammett plot and the carbon-13 isotope effect. Both R(-)-phenylmethanesulphonyl-l-d bromide and S(+)-phenylmethanesulphonyl-l-d bromide were prepared, desulphonylation of which with bromide ions resulted in benzyl α-d bromide having the opposite configuration to that of the starting material. This showed that the reaction was S\text{N}2 rather than S\text{N}1.

The reaction was shown, mainly by the lack of reaction of some compounds containing the sulphonyl group, to proceed through transition state 2, in which both the C-S and the S-X bond are partially broken.

These results indicate that the reaction studied is an example of a bimolecular concerted fragmentation.
ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Professor J.F. King for his guidance, advice and constant enthusiasm throughout the course of this project. Thanks are also due to all members of the staff and graduate students with whom it has been the author's privilege to work, especially Professor J.B. Stothers and Mr. A.J. McNamara for help with the carbon-13 kinetic isotope effect studies described in this thesis.

The generous financial support of the Petroleum Research Foundation, the National Research Council of Canada and the Department of University Affairs of the Province of Ontario is gratefully acknowledged.

Finally the author wishes to thank his wife, Dorothy, whose continuing encouragement and patience enabled this thesis to be completed.
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PART I

GENERAL INTRODUCTION

It was first suggested by Wedekind (1) that oxythioacyl \( \text{Cl} \) halides (R-C=SO) might exist as chemical entities. More recently, King and Durst (2) not only proved that these species could be made, but isolated both the \textit{cis} and \textit{trans} isomers of oxythiobenzoyl chloride from the reaction of phenylmethanesulphonyl chloride with triethylamine in non-polar media. This was the first example of geometrical isomerism about a carbon-sulphur double bond. One of the more interesting aspects of this work was the mechanism of formation of these compounds. A tentative mechanistic scheme proposed by Durst (3) consisted of the following steps.

\[
\begin{align*}
\text{PhCH}_2\text{SO}_2\text{Cl} & \quad + \quad \text{Et}_3\text{N} & \quad \text{PhCH=SO}_2 & + \quad \text{Et}_3\text{NH}^+\text{Cl}^- & \quad [1] \\
\text{PhCH=SO}_2 & \quad + \quad \text{Cl}^- & \quad \xrightarrow[\text{Cl}^-]{} & \quad \text{PhCH-SO}_2^- & \quad [2] \\
\text{PhCH-SO}_2^- & \quad + \quad \text{PhCH=SO}_2 & \quad \xrightarrow[\text{Cl}^-]{} & \quad \text{PhCH}_2\text{OSO}_2\text{CH}_2\text{Ph} & \quad [3] \\
\text{PhCH}_2\text{O-SO}_2\text{CH}_2\text{Ph} & \quad + \quad \text{Et}_3\text{N} & \quad \xrightarrow[\text{Cl}^-]{} & \quad \text{PhC}=\text{SO} & \quad + \quad \text{PhCH}_2\text{SO}_3^-\text{H}^+\text{NEt}_3 & \quad [4]
\end{align*}
\]
The intermediacy of a sulphene (equation [1]) in the reaction of sulphonyl halides with amines has been demonstrated conclusively by a number of workers (4,5). Studies on reactions believed to involve sulphenes have indicated that attack by a nucleophilic species normally occurs at the sulphur atom. This is analogous to the corresponding reactions of ketones. In this particular case however such an attack leads back to starting material, if a proton is picked up, while attack on carbon, which may be many orders of magnitude slower, leads to an intermediate chlorosulphinate anion which may react further, equation [2]. Evidence for such a step was obtained by Durst and King (6) in the photolysis of unsaturated sultams. In that example, as in the one under discussion, attack at sulphur leads back to the starting material; while reaction at the carbon atom affords a pyrrole derivative, which was isolated.

It was found that if the reaction of phenylmethane-sulphonyl chloride with triethylamine in methylene chloride is carried out in the presence of triethylammonium chloride, the yield of oxythiobenzoyl chloride is increased. This was thought to provide additional evidence for step [2]. Analogous results were obtained in experiments using phenylmethane-sulphonyl bromide and excess bromide ions. The change in the product ratio appeared to be due to the halide ion and not the
triethylammonium ion since the addition of triethylammonium phenylmethanesulphonate in similar amounts had only a slight effect. It is interesting to note that in all cases the yield of oxythiobenzoyl halide was substantially greater in experiments using phenylmethanesulphonyl bromide rather than the corresponding chloride.

After the work mentioned above had been done, it was felt that further evidence was needed for step [2] or what has been called "abnormal" attack on a sulphene (6). An experiment was designed for this purpose in which the product could conceivably be derived from such a reaction. In the sequence depicted by equations [5] - [7] isolation of an alkyl halide would presumably constitute such evidence.

\[ p^-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{X} + \text{Et}_3\text{N} \rightleftharpoons p^-\text{NO}_2\text{C}_6\text{H}_4\text{CH}=\text{SO}_2 + \text{Et}_3\text{NH}^+\text{X}^- \]  \[ \text{[5]} \]

\[ p^-\text{NO}_2\text{C}_6\text{H}_4\text{CH}=\text{SO}_2 + \text{X}^- \rightleftharpoons p^-\text{NO}_2\text{C}_6\text{H}_4\text{CH-SO}_2\text{X} \]  \[ \text{[6]} \]

\[ p^-\text{NO}_2\text{C}_6\text{H}_4\text{CH-SO}_2\text{X} \rightarrow p^-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{X} + \text{SO}_2 \]  \[ \text{[7]} \]

\( X = \text{Cl} \) or \( \text{Br} \).

This reaction sequence could be forced along the desired reaction pathway in a number of ways. Reaction [6] would be aided by the addition of halide ions (in the form of the triethylammonium salt). Decomposition of the chlorosulphinate anion to the benzylhalide, equation [7] would be expected to be increased more rapidly than the reaction with more sulphene,
equation [3], when the temperature is raised, since it is a well known fact that unimolecular processes increase more rapidly than bimolecular processes when the temperature is increased. Coupling reactions of the sulphone would be reduced by using a reaction mixture which is dilute in sulphonyl halide compared to the other reactants. The presence of a p-nitro group on the aromatic ring would make the benzylic carbon more susceptible to nucleophilic attack relative to the unsubstituted sulphonyl halide and the corresponding chlorosulphinate would lose sulphur dioxide more readily than the unsubstituted compound. Substitution in this way also has the added advantage that the expected product, namely p-nitrobenzyl chloride, is a solid.

When the reaction was attempted, p-nitrobenzyl chloride was in fact isolated, by thin-layer chromatography, in 5% yield, together with 4,4'-dinitrostilbene, from the reaction of p-nitrophenylmethanesulphonyl chloride and triethylamine in the presence of a fifteen molar excess of triethylammonium chloride in refluxing methylene chloride. The corresponding reaction of p-nitrophenylmethanesulphonyl bromide in the presence of an excess of triethylammonium bromide gave a 33% yield of p-nitrobenzyl bromide. It seemed therefore that the reaction sequence postulated above might be possible.

An attempt was made to prove unequivocally that the sulphone was an intermediate in the reaction. p-Nitrophenyl-
methanesulphonyl-1,1-d$_2$ bromide was prepared from p-nitrophenylmethanesulphonyl chloride using a method similar to the preparation of phenylmethanesulphonyl-1,1-d$_2$ chloride (4). Deuterium analysis indicated the presence of 90.0% of the expected deuterium content. If the reaction did indeed go by way of a sulphone intermediate any p-nitrobenzyl bromide isolated from the reaction of the dideuterated sulphonyl bromide would have at least one of the deuteriums replaced by protium, equation [7]. However, the p-nitrobenzyl bromide isolated still contained almost two atoms of deuterium. This was shown by (i) the absence of any substantial adsorption for a benzylic proton at 4.53 p.p.m. in the n.m.r. spectrum of the product and (ii) deuterium analysis which indicated the presence of 89% of the original deuterium. That is to say that little exchange took place, and the reaction could not have gone via a sulphone to any significant extent.

p-Nitrophenylmethanesulphonyl-1,1-d$_2$ bromide was allowed to react with aniline in refluxing benzene. The p-nitrophenylmethanesulphonanilide produced was shown to be mono-deuterated at the benzylic position by deuterium analysis which indicated the presence of 50% of the original deuterium. That is to say p-nitrophenylmethanesulphonyl bromide can react by a sulphone mechanism under favourable conditions.
\[ \text{pNO}_2\text{C}_6\text{H}_4\text{CD}_2\text{SO}_2\text{Br} + \text{PhNH}_2 \rightarrow \text{pNO}_2\text{C}_6\text{H}_4\text{CD}=\text{SO}_2 + \text{PhNH}_2\text{D}^+\text{Br}^- \] [8]

\[ \text{pNO}_2\text{C}_6\text{H}_4\text{CD}=\text{SO}_2 + \text{PhNH}_2 \rightarrow \text{pNO}_2\text{C}_6\text{H}_4\text{CHDSO}_2\text{NHPH} \] [9]

Evidence that the sulphonyl bromide does react by a sulphone mechanism was also obtained by the fact that 4,4'-dinitrostilbene could be isolated from the reaction with triethylamine in the absence, or presence, of excess bromide ions.

Another control experiment consisted of refluxing \( p \)-nitrophenylmethanesulphonyl bromide with triethylammonium bromide in methylene chloride with no base added. Analysis of the product by infrared spectroscopy and thin-layer chromatography showed a mixture of starting material and \( p \)-nitrobenzyl bromide. Since the sulphonyl bromide did not give any alkyl bromide on refluxing in methylene chloride in the absence of base or bromide ions, it seemed that bromide ion was displacing the sulphonyl bromide group by a mechanism not involving a sulphone, perhaps by a direct displacement mechanism.

\[ \text{pNO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{Br} \quad \xrightarrow{\text{Br}^-} \quad \text{pNO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br} + \text{SO}_2 \] [10]

Tetraethylammonium bromide was found to react more rapidly than the triethylammonium salt. The reaction of \( p \)-nitrophenylmethanesulphonyl bromide with a twenty fold
excess of tetraethylammonium bromide in methylene chloride at room temperature for \( \frac{1}{2} \) hour yielded \( p \)-nitrobenzyl bromide in greater than 90% yield. There was no trace of any sulphonyl bromide remaining, as judged by infrared spectroscopy and thin-layer chromatography.

A further result, consistent with a displacement reaction by bromide ions, was obtained by the following experiment. When \( p \)-nitrophenylmethanesulphonyl-\( \text{\textsubscript{1,1-d\textsubscript{2}}} \) bromide was allowed to react with tetraethylammonium bromide, the alkyl bromide, which was isolated in over 95% yield, still contained, by deuterium analysis, 92% of the original deuterium. The n.m.r. and infrared spectra were identical to those of the \( p \)-nitrobenzyl bromide obtained from the reaction with added triethylamine.

The product isolated from the reaction of \( p \)-nitrophenylmethylene sulphonyl chloride with a twenty fold excess of tetraethylammonium chloride, under comparable conditions to those used for the bromide ion experiments, although obtained in a low yield, was shown to contain some starting material. In view of the fact that Winstein and co-workers (7) had found tetraethylammonium bromides and chlorides to be of comparable nucleophilicity in non-aqueous media, and that one would expect, at least on a qualitative basis, \( \text{SO}_2\text{Cl}^- \) not to be a much worse leaving group than \( \text{SO}_2\text{Br}^- \), the reaction may be more than a simple substitution reaction.
Simple reactions of sulphonyl compounds resulting in loss of sulphur dioxide have been known for some time. Included among these are the careful studies of Geiseler and co-workers (8) on the thermal decomposition in the vapour phase of some simple aliphatic primary and secondary sulphonyl chlorides and bromides. Together with the studies of Nauman (9) on the vapour phase decomposition of the methanesulphonyl chloride, these studies constitute good support for the gas phase desulphonylation reaction proceeding by a radical chain process whereby each sulphonyl halide molecule first undergoes homolysis at the sulphur-halide bond. These reactions take place at measurable rates only at temperatures above 200°.

Although less definitive, studies of the liquid phase decomposition also indicate that a free radical process is operative. For example, Herbrandson (10) found racemisation to occur when optically active 2-octanesulphonyl chloride was thermally decomposed in a number of solvents. When N,N,-dimethylformamide was used as the solvent the 2-chloro-octane obtained was optically active and resulted from inversion and partial racemisation of the active centre. Herbrandson suggested that an ionic mechanism might be operating for this reaction.

On the other hand examples exist in which the thermolysis of sulphonyl halides is thought to proceed via a non-radical
process. In the study of the thermal decomposition of trimethylmethanesulphonyl chloride in the vapour phase, and in solution, Scott and co-workers (11) concluded that the reaction might proceed by a cyclic intramolecular mechanism where the transition state was pictured as

![Diagram](image)

Another example of an internal substitution reaction in which the liberated fragment is sulphur dioxide is the thermal decomposition of thiol sulphonates (12).

\[
\text{R-S-S-R'} \rightarrow \text{R-S-R'} + \text{SO}_2
\]

\[\text{R} = \text{Ph}_2\text{CH} \text{ or PhCH}_2\]

Kice has presented arguments against a radical mechanism and against the decomposition involving a rate-determining ionisation to a well defined ion-pair intermediate. Although no clear-cut decision could be made about the
mechanism to account for the "remarkable nonstereospecific nature of the reaction", it was postulated that a carbene mechanism may be operating.

\[
\begin{align*}
\text{PhC}^+ & \xrightarrow{\Delta} \text{SO}_2 \\
\text{PhC}^+ & \xrightarrow{\Delta} \text{SR'}
\end{align*}
\]

\[
\begin{align*}
\text{PhC}: + \text{HSR'} & \rightarrow \text{PhC}: - \text{SR'(racemic)} + \text{SO}_2
\end{align*}
\]

The unimolecular decomposition of chlorosulphites is another interesting example of a thermal reaction leading to the loss of sulphur dioxide. Boozer and Lewis (13) found that the stereochemical course of the reaction seemed to depend upon the nature of the solvent used. They considered three mechanisms for the reaction, all of which involve the ionisation of the sulphur-chlorine bond as the rate determining step and ion-pairs of stable configuration as intermediates.

All of these thermal decomposition reactions are unimolecular in nature. However, the sulphonyl halides used in this study have been shown not to decompose thermally under the conditions used. The reaction only proceeds if halide
ion is added as a catalyst. Reactions that are similar in this respect can be found in the chemical literature. Lewis and Coppinger (14) have found that the decomposition of secondary alkyl chlorosulphites can be catalysed by tertiary amines and their hydrochlorides. A bimolecular displacement of the $S_N2$ type was proposed, which was consistent with the kinetics and the stereochemical course of the reaction. In the case of catalysis by the free amine, chloride ion was believed to arise from a preceding elimination reaction.

$$\text{R-O-S-Cl} \longrightarrow \text{RCl} + \text{SO}_2 \quad \text{(inversion)} \quad [11]$$

After work described in this thesis had begun a communication appeared (15) reporting that the decomposition of alkyl chloroformates could be catalysed by chloride ions.

$$\text{Cl}^- \quad \text{R-O-C-Cl} \longrightarrow \text{RCl} + \text{CO}_2 \quad [12]$$

The authors stated that the observed $S_N2$ attack by chloride ion was consistent with the previously expressed (16) interpretation of the tertiary amine catalysis of the decomposition of alkyl chloroformate, in which displacement of halide by amine at carbonyl carbon was followed by an inverting attack at the alkyl group by the displaced chloride ion.
The hydrolysis of primary alkyl chlorosulphates has also been shown to be catalysed by added nucleophiles (23).

\[
\begin{align*}
  R-O-S-Cl & \quad Y^- \quad \underset{H_2O}{\longrightarrow} \quad R-Y + H_2SO_4 + HCl \quad [13] \\

\end{align*}
\]

It appears, then, that the halide ion catalysed decomposition of sulphonyl halides in methylene chloride is not completely without precedent. Naturally, as in the case of the unimolecular decompositions, there may be a broad spectrum of mechanistic pathways.

Previous investigations (14, 15, 23) of the mechanism of decomposition reactions which are catalysed by halide ions have been concerned, almost entirely, with their kinetic aspects. It is clear that, at least, in the catalysed decomposition of chlorosulphites and chloroformates, that the analogous decomposition of sulphonyl halides has the same characteristics. A number of possible mechanisms can be visualised that would include the known facts about the reactions. Because the chloride ion-sulphonyl chloride reaction is slower than the corresponding bromide ion-sulphonyl bromide reaction (p. 7) there was the possibility that the reaction was not a simple displacement reaction, equation [14], but might proceed by a reaction pathway in which the S-X bond is partially broken in the transition state.
RSO₂⁻ + X⁻ → RX + [SO₂X]⁻ → SO₂ + X⁻ [14]

The difference between these two mechanisms may be summarized by the structure 1 and 2 which represent the transition states of the direct displacement and the "fragmentation reaction" respectively.

\[
\begin{align*}
1 & \quad \text{SO}_2^- \quad \text{X}^- \\
2 & \quad \text{SO}_2 \quad \text{X}^- \\
\end{align*}
\]

The term "fragmentation reaction" was proposed by Grob (17) in 1955. It was defined as the cleavage of a molecule represented by a-b-c-d-x into three fragments a-b, c=d, and X. The symbols (a), (b), (c), and (d) represents atoms such as carbon, oxygen, nitrogen, and phosphorus, which are capable of forming double bonds. The letter (a) denotes an atom or group of atoms which is capable of donating electrons by an inductive or mesomeric mechanism. Such reactions are clearly the reverse of condensations. There is a number of well known examples of this type of reaction; a very thorough documentation of which has appeared in a recent review article (18).

Grob (18) has included, in his list of fragmentation reactions, the decomposition of alkyl chloroformates, which he has represented as,

\[
\begin{align*}
\text{RO-CO-Cl} & \quad \xrightarrow{\text{-CO}_2^-} \quad R^+ + \text{Cl}^- \quad \xrightarrow{\text{RCI}} \\
\end{align*}
\]
Clearly then, the decomposition of sulphonyl halides to sulphur dioxide and alkyl halide, whether by an unimolecular or a bimolecular process is, by Grob's definitions, a fragmentation reaction.

By analogy to α eliminations (19) one can also have α fragmentations. In this case the electrofugal and nucleofugal groups (20) are both removed from the same atom.

\[ a-b-c-X \quad \Longrightarrow \quad a-b + :c + :X \]

Since the valence state of atom (c) is decreased by two the reaction can be observed when the lower valence state of (c) is stable, for example, when carbon monoxide or an isocyanide is produced as the unsaturated fragment when (c) is carbon. Reactions of this type include the decarboxylation of carboxylic acids and their derivatives. Some reactions of sulphonyl derivatives in which one of the products is sulphur dioxide belong to this class.

A report by Grob (21) indicated that bimolecular mechanisms of fragmentation, represented by

\[ Y: \quad \rightarrow \quad F - \quad C - \quad C - X \quad \rightarrow \quad Y - F + C = C + X^- \]

where Y is a nucleophile, were unknown. However, evidence that transition state 2 may be possible has been presented by Buncel and Millington (23) who suggested that in the solvolysis of alkyl chlorosulphates,
both the carbon-oxygen and the sulphur-chlorine bond may be weakened in the transition state. The postulate was presented with reservations since it was based purely on the size of the entropy of activation (see Part III, Section C).

Throughout this thesis the term "bimolecular concerted \( \sigma \) fragmentation" or more simply "S\(_N\)2 concerted fragmentation" will be reserved for the mechanism in which the transition state corresponds to \( \sigma \). The reaction in which the transition state is \( \sigma \) will be referred to as a "direct displacement".

Since it seemed that the new reaction of sulphonyl halides could proceed by any one of a number of reaction pathways, and the reaction may have some novel features, it was decided to inquire further into the actual mechanism of the halide ion catalysed decomposition of sulphonyl halides.
PART II

THE PREPARATION OF ALKANESULPHONYL HALIDES

Alkanesulphonyl chlorides are well known organic compounds and consequently a large number of preparations are available in the literature. One of these is the action of phosphorous trichloride or thionyl chloride upon the sulphonic acid salt, but preparations of sulphonyl chlorides by this method are only useful in the aromatic series, where the starting material is easily available.

The process of chlorosulphonation (24) of alkanes using a mixture of chlorine and sulphur dioxide in the presence of light usually gives a mixture of sulphonyl chlorides and is not suitable to laboratory scale preparation. By modifying the process of chlorosulphonation of Grignard reagents, first developed by Cherbuliez and Schnauder (25), Scott (26) was able to increase the yields of alkane sulphonyl chlorides considerably, but the preparation of phenylmethanesulphonyl chlorides proceeded in only 50% yield. Bordwell (27) found that some sulphonyl chlorides could be conveniently prepared from olefins by their reaction with thiolacetic acid. The intermediate thiolacetate, obtained in very high yield, could
be converted to the sulphonyl chloride by cleavage with chlorine gas in water at 0°. Preparation of sulphonyl chloride by this technique is generally applicable for primary, secondary, and cycloalkanesulphonyl chlorides, but not of course for phenylmethanesulphonyl chlorides.

The preparation of alkanesulphonyl chlorides is more conveniently accomplished by chlorination, in aqueous media, of alkane thiols, or some of their derivatives, which are cleaved during the chlorination process. Of these thiol derivatives sodium alkylthiosulphates and the alkylthiouronium salts appear to be the most suitable. These derivatives are easily prepared by the reaction of alkyl halides with sodium thiosulphate and thiourea respectively and are usually soluble in water. The use of alkylisothiouronium salts has proven to be hazardous in the past and several severe explosions have occurred, possibly due to the action of chlorine on the nitrogen containing portions of the isothiouria structure. To avoid this Ziegler and Sprague (28) treated the isothiouronium salt with aqueous sodium hydroxide to obtain the alkane thiol which could safely be chlorinated.

The easiest preparation of alkanesulphonyl chlorides from alkyl chlorides is via the sodium alkylthiosulphate and their subsequent chlorination in dilute acetic acid solution (28).
Preparation of the sulphonyl chlorides by this method is particularly suitable to the phenylmethane compounds because benzyl chlorides react readily with sodium thiosulphate, and since the benzyl chlorides are commercially available this method was used for the preparation of the sulphonyl chlorides.

The benzyl chlorides were allowed to react with sodium thiosulphate without prior purification and the aqueous solution of the sodium alkylthiosulphate was washed with ether to remove any organic impurities. Rapid chlorination at as low a temperature as possible is imperative to prevent any alkyl chloride being formed. Chlorine was bubbled at a very fast rate into an acidic solution, rather than a suspension (28) of the Bunte salt, containing a large quantity of crushed ice. When the solution became a permanent green the gas rate was slowed and chlorine passed into the solution for a further 5 minutes only. The solid sulphonyl chloride was usually obtained in excellent yield. Because in most cases the sulphonyl chlorides were reduced directly to the sulphinic acid for conversion to the sulphonyl bromide, they were not purified, but used as the crude product.

Compared to the alkanesulphonyl chlorides, the sulphonyl bromides are relatively unknown species. Consequently the small number of preparations available have been adapted from methods available for the corresponding sulphonyl
chlorides. The most common method of preparation is the bromination of the sodium salt of a sulphinic acid, or the acid itself, with bromine (29). Bromination of S-substituted thiouronium salts has also been used as a method of preparation (30). Aromatic sulphonyl bromides are best prepared by the reaction of phosphorus pentabromide with a sulphonic acid, or its salt (31), but recently Poshkus and co-workers (32) showed that sulphonyl bromides could easily be prepared by bromination, with bromine, or sodium bromate, of the aromatic sulphonyl hydrazide.

However, since sulphinic acid salts may be prepared very easily from sulphonyl chlorides, the preparation of alkanesulphonyl bromides by the method of Otto and Ostrop (29) seemed the most convenient. The reduction of the sulphonyl chlorides was carried out using sodium sulphite. It was found that, contrary to the experience of Smiles and Bere (33), it was not necessary to keep the reaction mixture basic with sodium hydroxide solution. Indeed with an aliphatic sulphonyl chloride the likelihood exists that the yield of the sodium sulphinate might be reduced due to sulphene formation. It was found that it was sufficient to stir the insoluble crude sulphonyl chloride rapidly in an aqueous solution of sodium sulphite at about 60°. When the reaction was judged complete, that is, no more organic material appeared to dissolve, the
aqueous solution was filtered, or washed with organic solvent, to remove impurities.

Because bromide ion catalyses the desulphonylation reaction of sulphonyl bromides, the bromination step, i.e. the conversion of sulphinate to sulphonyl bromide, was accomplished under very carefully controlled conditions. A positive bromine compound (34) was thought to be the ideal source of bromine, and N-bromoacetamide, which is the most soluble in water (34), was used because disproportionation gives bromine and a water soluble product.

After reduction, methylene chloride was added to the aqueous solution and N-bromoacetamide introduced to the reaction mixture in small portions. The only precaution necessary was to keep the temperature of the reaction medium as low as possible, usually around 0°. When addition was complete rapid work-up usually afforded an excellent yield of reasonably pure sulphonyl bromide. In the bromination of sodium 3,4-dimethylphenylmethanesulphinate the desulphonylation reaction was so facile that isolation of the pure sulphonyl bromide became impossible. Even with sodium p-methylphenylmethanesulphinate, the sulphonyl bromide was obtained in only a small yield and only in a pure state after repeated fractional crystallizations.
In some preparations, side reactions produced products that could be easily identified. The preparation of p-chlorophenylmethane sulphonyl bromide by bromination of the sodium sulphinate yielded a mixture of two compounds. The major component was the sulphonyl bromide (as shown by infrared spectroscopy) and the minor one was proven to be p-chlorobenzyl p-chlorophenylmethanethiolsulphonate \((\text{p-ClC}_6\text{H}_4\text{CH}_2\text{SO}_2\text{-S-CH}_2\text{C}_6\text{H}_4\text{E-Cl})\). This compound could have been formed by a number of reaction pathways, but must have arisen after the reduction step since organic impurities were removed by washing with methylene chloride.

One of the more obvious ways by which the thiolsulphonate could have been formed is by a disproportionation reaction of the free sulphinic acid, which must be present to a certain extent in the slightly acidic medium.

\[
3\text{RSO}_2\text{H} \rightarrow \text{RSO}_2\text{-SR} + \text{RSO}_3\text{H} + \text{H}_2\text{O}
\]

This reaction has been well documented in the aryl sulphinic acid series (35) and proceeds very rapidly in acetic acid even at room temperature. Aliphatic sulphinic acids are even less stable, in fact, Autenrieth (36) reported that he was unable to isolate any sulphinic acid from reductions of sulphonyl chlorides because of their tendency to disproportionate. It wasn't until 1948 that Marvel and Johnson (37) were able to isolate the first free alkyl
sulphinic acid from the reaction of a Grignard reagent and exactly one mole of sulphur dioxide. Excess sulphur dioxide causes the magnesium sulphinate to disproportionate.

Aromatic sulphinic acids are known to yield sulphenyl bromides or disulphides, depending upon the reaction conditions (38), with hydrogen bromide (which may be present in a small amount). Either of these molecules might react with a sulphinate anion. Reaction of the disulphide would produce the thiosulphonate directly. A thiosulphonate could arise from the reaction of a sulphinyl bromide and a sulphinate anion in the following manner.

\[
\text{RS-Br} + \text{RSO}_2^- \rightarrow \text{RSO}_2-\text{S}-\text{R}
\]

\[
\text{RSO}_2-\text{S}-\text{R} \rightarrow \text{RSO}_2-\text{O}-\text{S}-\text{R} \rightarrow \text{RSO}_2-\text{SR} + \text{RSO}_3\text{H}
\]

The sulphinyl sulphone (sulphinic anhydride) first formed decomposes very readily into sulphonic acid and thiosulphonate (39).

In an attempt to reduce the extent of this side reaction in the \( p \)-chlorophenylmethanesulphonyl bromide preparation the sodium sulphinate solution was added to a suspension of \( N \)-bromoacetamide in water-methylene chloride. By keeping down the concentration of sulphinate anion in the reaction mixture it was hoped that the amount of impurities would be reduced. This procedure did seem to help a little but the ester was still produced. The route by which it was formed
is purely speculative, but in any event it was easily removed by extracting the product of the reaction with petroleum ether in which it was insoluble.

For the nitro-substituted compounds the preparation of the sulphonyl bromide via the sodium sulphinate proved to be difficult. Reduction of the sulphonyl chloride with aqueous sodium sulphite solution gave little or no yield of the corresponding sodium sulphinate presumably because of further reduction of the nitro group (40). Recently King and Durst (4) had prepared phenylmethanesulphonyl-1-d₂ chloride by chlorinating the corresponding triethylammonium sulphonate with phosphorus pentachloride. This method was adapted for the preparation of the nitro-substituted phenylmethanesulphonyl bromides. The salt was prepared by treating the crude sulphonyl chloride with an excess of triethylamine in a dioxane-water mixture. Subsequent bromination with excess phosphorus pentabromide in methylene chloride solution gave the sulphonyl bromide in excellent yield. Impurities could be removed by treatment with animal charcoal and recrystallization.

When the stereochemical course of the reaction was studied, it became necessary to prepare phenylmethanesulphonyl bromide from benzyl bromide by a stereochemically unambiguous route. Fortunately Kice (12) had demonstrated that the preparation of
phenylmethanesulphonyl chloride from benzyl chloride using sodium sulphite followed by phosphorus oxychloride was reasonably stereospecific.

Using this method benzyl-\(\text{\textsuperscript{\textcircled{R}}-d}\) bromide was refluxed in sodium sulphite solution until the mixture became homogeneous. The mixed salts that were obtained, sodium phenylmethanesulphonate and sodium bromide, were simply mixed with phosphorus pentabromide at room temperature, after they had been thoroughly dried, to yield the sulphonyl bromide. When the salts were dried too thoroughly it was necessary to heat the mixture at 50-60\(^\circ\) to start the reaction. When reaction occurred the solid mass liquified, with gas being evolved (presumably hydrogen bromide), and resolidified on cooling. The solid material was dissolved in methylene chloride and after work-up the sulphonyl bromide was obtained in good yield.

By using the same technique it was possible to prepare 2-phenylethanesulphonyl bromide from 2-phenylethyl bromide. It was found also that the nitro-substituted phenylmethanesulphonyl bromides, which had proved troublesome to prepare, could be obtained in excellent yield from the corresponding sodium sulphonate (from the benzyl chloride and sodium sulphite) by reaction with phosphorus pentabromide.
PART III

KINETICS

A. The Measurement of the Rate of the Reaction

a) By the amount of sulphur dioxide produced.

Methylene chloride was chosen as the major solvent for studying the rate of the reaction. It could be purified and dried quite simply by one distillation from calcium hydride. Excellent characteristics of this solvent are its ability to dissolve alkylammonium salts and its unreactivity towards sulphonyl halides. Important also is this solvent's ability to dissolve sulphur dioxide. By control experiments it was found that the amount of sulphur dioxide in a methylene chloride solution remained constant for a considerable length of time at room temperature. Since sulphur dioxide is one of the products of the reaction, it proved to be a simple matter to evaluate the extent of the reaction by estimating the amount of sulphur dioxide in the reaction solution.

The most commonly used method for the determination of sulphur dioxide is by absorption into water or aqueous alkali (41). Absorption by aqueous alkali has the added advantage that the base destroys any unreacted starting material. There-
fore by shaking the reaction solution with aqueous sodium hydroxide solution, sulphur dioxide forms sodium sulphite, and unreacted starting material is converted to the sodium sulphonate. The organic phase was separated. An excess of iodine solution was added to the aqueous solution immediately after acidification, to prevent any loss of sulphur dioxide. The excess iodine was back titrated with standardized sodium thiosulphate solution. The iodine solution was not standardized, but a blank titration enabled one to calculate the amount of standardized sodium thiosulphate solution that was equivalent to the sulphur dioxide produced in the reaction.

Since acetonitrile is miscible with water the extent of the reaction in that solvent could be estimated by titrating the excess iodine, after addition of the iodine solution, without separation of any organic phase.

As the reaction is a pseudo first-order one, the apparent second order rate constant could be calculated from the slope of log (100-percentage reaction) versus time. In all cases the reaction was followed to over 50% reaction and in most cases in excess of 75%. In one or two cases a straight line plot was obtained to over 90% reaction.

b) By vapour phase chromatography

Compared to the phenylmethanesulphonyl bromides other
alkylsulphonyl bromides appear to react very slowly. Consequently estimation of the rate of the reaction by titration of the sulphur dioxide may produce error due to the loss of sulphur dioxide from the reaction solution over the necessarily long reaction times. The blank values of the volumetric solutions would also have to be constantly checked. Because the organic product from the reaction of methanesulphonyl bromide with tetraethylammonium bromide is quite volatile it was thought that the extent of the reaction could be measured by vapour phase chromatography. This was found to be the case.

Methyl bromide (b.p. 3.6°C) and methylene chloride were easily separated on a 10% carbowax column at room temperature using a very low flow rate. Sulphur dioxide could also be identified on the recorder chart, but no attempt was made to estimate the amount. From time to time samples of the reaction solution were taken, using a syringe, and injected into an F. and M. model 700 vapour phase chromatograph in which the injector temperature was kept as low as possible to prevent any pyrolysis of the starting material. The amount of methyl bromide present was estimated by comparing the area under the peak (or weight of the peak) for that compound with the area of a peak produced by a standard methyl bromide solution injected under the same experimental conditions. It was shown that no pyrolysis was taking place in the instrument by the fact that no methyl bromide peak appeared when a solution
of starting material was injected onto the column.

c) **By infrared spectroscopy**

The boiling point of 2-phenylethyl bromide, the expected product from the reaction of 2-phenylethanesulphonyl bromide with bromide ions, is comparatively high (217-218°, 734 mm.) and any attempt to separate it by vapour phase chromatography would automatically lead to high injector and column temperatures. This in turn could lead to the production of the alkyl bromide by reaction pathways other than the one under study (8).

Infrared spectroscopy has been used many times to measure the rates of chemical reactions (42). It is clear that if the product or the reacting molecule has a band in the infrared that is significantly separated from the others the kinetics can be measured. The Beer-Lambert relationship has to be assumed to be essentially linear over the range of concentrations used, which is generally small, a fact that has been demonstrated in a number of cases (43). 2-phenylethyl bromide has a band at 650 cm⁻¹ whereas the other materials do not. The height of this peak was estimated after a given time from a spectrum of the reaction solution. Comparison of the peak height with that obtained from a known concentration of 2-phenylethyl bromide in methylene chloride gave, at least, a semi-quantitative estimate of the extent of the reaction.

B. **The Kinetic Order of the Reaction.**

A kinetic study of the reaction under scrutiny is greatly simplified by the fact that the amount of nucleophile in
the reaction mixture, remains constant, that is, a halide ion is produced for every one used up. One is dealing with a pseudo first-order reaction. A straight line resulted, in every kinetic run, for a plot of log (100-percent. reaction) versus time, and so the reaction is clearly first-order in sulphonyl halide.

The apparent second-order rate constant was calculated from the formula

\[ k' = \frac{2.303 \times \text{slope}}{[X^-]} \]

For a reaction to be first-order in halide ion, that is, a bimolecular reaction, the apparent second-order rate constant should not vary as the concentration of halide ion is changed. Since phenylmethanesulphonyl bromide is the most easily obtainable of the sulphonyl bromides, the reaction of it with tetraethylammonium bromide in methylene chloride was studied in greater detail. It was found that when the concentration of bromide ions was varied from 0.01 to 0.0001 molar, a hundred fold change in concentration, the rate constant increased from 5.8 to 6.8 \times 10^{-2} \text{ l. mole}^{-1} \text{ sec}^{-1} \text{ at } 35^\circ \text{ and from } 2.35 \text{ to } 3.1 \text{ l. mole}^{-1} \text{ sec}^{-1} \text{ at } 25^\circ. \text{ (Table I).}

This type of deviation from simple second-order kinetics is well documented in the chemical literature. For bimolecular nucleophilic substitution reactions involving
neutral substrates and anionic nucleophiles in dipolar aprotic solvents second-order rate constants tend to decrease with increasing concentration of nucleophilic reagent. This was attributed, for a number of years, by Ingold and his co-workers, to salt effects (44), but Winstein and co-workers (7) have shown, by developing the idea first proposed by Acree (22), that this phenomenon is in fact due mainly to ionic association.

The simplest approach to this problem (7) assumes that the free anion is very much more reactive than an associated ion (ion-pair, triplet etc.), and because the salt is more dissociated at lower concentrations the second-order rate constant should increase with decreasing salt concentration. Other effects such as interactions between ions and the reactant, and ions and the transition state may be present, but Evans and Sugden (45) have shown that most of the variation is due to ionic association of the nucleophile. These authors obtained a steady value for the second-order rate constant of the exchange reaction of lithium bromide with n-butyl bromide over a 400 fold range of salt concentration, by assuming that only dissociated ions were reactive.

Winstein (7) has stated that since dissociated ions appear to be more reactive than associated ions, the rate depression in these reactions observed when lithium perchlorate is added can be explained by a common ion repression of the
### TABLE I

The Second Order Rate Constants for the Reaction of Phenylmethanesulphonyl Bromide [0.01M] with Tetraethylammonium Bromide in Methylene Chloride.

<table>
<thead>
<tr>
<th>Tetraethylammonium Bromide [M]</th>
<th>Temperature</th>
<th>( k'_2 ) (1.mole(^{-1}).sec(^{-1})) x 10(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>35(^\circ)</td>
<td>5.8</td>
</tr>
<tr>
<td>0.002</td>
<td>&quot;</td>
<td>6.2</td>
</tr>
<tr>
<td>0.001</td>
<td>&quot;</td>
<td>6.0</td>
</tr>
<tr>
<td>0.0005</td>
<td>&quot;</td>
<td>6.9</td>
</tr>
<tr>
<td>0.00025</td>
<td>&quot;</td>
<td>6.4</td>
</tr>
<tr>
<td>0.0001</td>
<td>&quot;</td>
<td>6.8</td>
</tr>
<tr>
<td>0.01</td>
<td>25(^\circ)</td>
<td>2.35</td>
</tr>
<tr>
<td>0.001</td>
<td>&quot;</td>
<td>2.45</td>
</tr>
<tr>
<td>0.00012</td>
<td>&quot;</td>
<td>3.1</td>
</tr>
<tr>
<td>0.001</td>
<td>0(^\circ)</td>
<td>0.104</td>
</tr>
</tbody>
</table>
dissociation of the lithium halide. The apparent second-
order rate constant of the reaction of phenylmethanesulphonyl
bromide with tetraethylammonium bromide is decreased from
$3.1 \times 10^{-2}$ to $1.91 \times 10^{-2}$ mole$^{-1}$sec$^{-1}$ in the presence of
0.01 molar lithium perchlorate, presumably because of the
decrease in the amount of free halide ions in solution.

The concentration of the free halide ions can be cal-
culated from the dissociation constant, and the second-order
rate constant calculated from this amount in solution is
essentially independent of the nature of the cation. The
extent of ion-pairing decreases with ionic size (7) and in
acetone the ion-pairing of the tetraalkylammonium halides
is relatively unimportant. However, in the less polar
methylenecarbonate (dielectric constant at $25^\circ$ is 8.9
against 20.5 for acetone (46)) one would expect ion-pairing
to a greater degree. Unfortunately no dissociation constants
are available for the tetraalkylammonium salts in methylene
carbonate, but the value of $7.2 \times 10^{-6}$ for triethylmethy-
ammonium iodide in methylene carbonate obtained by Beard and
Plesch (48) should give one a qualitative idea of the amount
of association that must be present in the higher concentra-
tions of salt used.

The values obtained at low concentrations of bromide
ions ([0.0001] and [0.0005] molar) are probably not very
accurate since the kinetic measurements are subject to a number of errors. A 1 percent hydrolysis of the sulphonyl bromide would double the effective bromide ion concentration. Some sulphur dioxide will probably be lost from the reaction solution over the necessarily long reaction times. It was not possible to obtain a steady value for the apparent second-order rate constant when a dissociation constant of $10^{-5}$ was assumed. That is, the values obtained from the kinetic measurements do not fit a simple ion pair description, presumably because of the above mentioned errors in measuring the rate constants at low salt concentrations; but it is probably safe to say that the reaction is first order in bromide ion and that the overall reaction is bimolecular.
### TABLE II

The Effect of the Cation on the Reaction Rate of Phenylmethanesulphonyl Bromide with Alkylammonium Salts in Methylene Chloride at 25°

<table>
<thead>
<tr>
<th>Salt. [molar conc.]</th>
<th>$k_2/1. \text{mole}^{-1}\text{sec}^{-1}$</th>
<th>Relative rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Et}_3\text{N}^+\text{HBr}^-[0.01]$</td>
<td>$1.5 \times 10^{-4}$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{Et}_4\text{N}^+\text{Br}^-[0.01]$</td>
<td>$2.35 \times 10^{-2}$</td>
<td>155</td>
</tr>
<tr>
<td>$\text{Et}_4\text{N}^+\text{Br}^-[0.001]$</td>
<td>$2.45 \times 10^{-2}$</td>
<td>163</td>
</tr>
<tr>
<td>$\text{Bu}_4\text{N}^+\text{Br}^-[0.001]$</td>
<td>$2.6 \times 10^{-2}$</td>
<td>173</td>
</tr>
</tbody>
</table>

The rates of tetrabutyl and tetraethylammonium bromides are about the same, and this is not surprising since it has been stated (49) that the effect of alkyl group upon the dissociation constant is negligible for substitution of n-propyl and above. A small increase in rate in substituting the larger n-butyl for ethyl might be expected because of less ion pairing, and is found to be the case.

The triethylammonium cation is smaller and one would expect greater association from purely coulombic forces, and therefore a slower rate, for triethylammonium bromide. In addition to this there is the hydrogen bonding effect. It has been shown by Allerhand and von Schleyer (50) that halide
ions can act as very strong proton acceptors in a variety of solvents, including methylene chloride even when a haloform is the proton donor. Taylor and Kraus (51) have shown that even picrate ion has a tendency to form hydrogen bonds with labile hydrogen from the accompanying cation, leading to incomplete dissociation in nitrobenzene. In dimethylformamide, which solvates cations more effectively than nitrobenzene, triethylammonium picrate is completely dissociated, but partially substituted ammonium bromides are weak electrolytes (52). The great affinity of bromide ion for a proton in dipolar aprotic media would lead to greater association and hence a slower rate for triethylammonium bromide, in methylene chloride as the solvent.

C. The Interpretation of Thermodynamic Data.

Originally the measurement of the rates of the reaction of phenylmethanesulphonyl bromides was undertaken to determine the linear free energy relationship between the rate of the reaction and the substituent, and to use this as a criterion for the determination of the mechanism. Since the rate differences are small (Table III) the possibility existed that the rates were obtained near to the isokinetic temperature (53), in which case it would be hazardous to draw any conclusions from the rate data at one temperature. Measurements were made at different temperatures, but due to the nature of the
**TABLE III**

The Effect of Substituents of the Reaction Rate of Phenylmethanesulphonyl Bromides with Tetraethylammonium Bromide in Methylene Chloride

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Temperature</th>
<th>$k_2'(1 \text{ mole}^{-1} \text{ sec}^{-1}) \times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted</td>
<td>25°</td>
<td>2.45</td>
</tr>
<tr>
<td>p-nitro</td>
<td>&quot;</td>
<td>3.85</td>
</tr>
<tr>
<td>m-nitro</td>
<td>&quot;</td>
<td>3.5</td>
</tr>
<tr>
<td>p-chloro</td>
<td>&quot;</td>
<td>3.15</td>
</tr>
<tr>
<td>m-chloro</td>
<td>&quot;</td>
<td>1.7</td>
</tr>
<tr>
<td>p-methyl</td>
<td>&quot;</td>
<td>5.3</td>
</tr>
<tr>
<td>Unsubstituted</td>
<td>35°</td>
<td>6.0</td>
</tr>
<tr>
<td>p-nitro</td>
<td>&quot;</td>
<td>8.4</td>
</tr>
<tr>
<td>m-nitro</td>
<td>&quot;</td>
<td>9.9</td>
</tr>
<tr>
<td>p-chloro</td>
<td>&quot;</td>
<td>10.1</td>
</tr>
<tr>
<td>m-chloro</td>
<td>&quot;</td>
<td>5.1</td>
</tr>
</tbody>
</table>
solvent and the reaction, the temperature range was not large, and in some cases only 10°. Nevertheless the enthalpies, entropies and the free energies of activation were calculated from the rate constants obtained at different temperatures (54). The results appear in Table IV.

**TABLE IV**

Activation Parameters for the Reaction of Substituted Phenylmethanesulphonyl Bromides with Tetraethylammonium Bromide

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\Delta H^\ddagger$ (kcal.mole$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (e.u.)</th>
<th>$\Delta G_{25}^\ddagger$ (kcal.mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted</td>
<td>18.8</td>
<td>-3</td>
<td>19.7</td>
</tr>
<tr>
<td>p-nitro</td>
<td>13.7</td>
<td>-19</td>
<td>19.4</td>
</tr>
<tr>
<td>m-nitro</td>
<td>20.6</td>
<td>+4</td>
<td>19.4</td>
</tr>
<tr>
<td>p-chloro</td>
<td>20.7</td>
<td>+4</td>
<td>19.5</td>
</tr>
<tr>
<td>m-chloro</td>
<td>19.2</td>
<td>-2</td>
<td>19.9</td>
</tr>
</tbody>
</table>

A plot of $\Delta H^\ddagger$ versus $\Delta S^\ddagger$ produced a reasonably straight line, but the possibility exists that it may have been derived from random error and that no isokinetic relationship exists (55).

The plot of the results listed in Table IV gave a slope of 302° ± 30°, very close to the mean experimental temperature. It has been calculated (56) that a 3% error in rate constant
and a 30° difference in temperature would result in a $\Delta H^*$ value accurate to ± 1 kcal. and a statistical error in $\Delta S^*$ of ± 2.6 e.u. In view of the fact that the rate constants for the $m$-nitro substituted and the unsubstituted sulphonyl bromide reactions are known to an accuracy of about 3% and the temperature range used was 35°, the enthalpy and entropy of activation must be known to about the same accuracy.

Since the spread of the points, ignoring $p$-chloro and $m$-chloro, is greater than random error, the plot of $\Delta H^*$ versus $\Delta S^*$ is real and an isokinetic relationship exists.

One of the more useful features of the isokinetic relationship is that it can be expected to apply only to a series of reactions in which the structural change does not change the mechanism of the reaction or the nature of the transition state. Therefore there is probably a constant reaction mechanism for the desulphonation reaction of the substituted phenylmethanesulphonyl bromides. As the isokinetic temperature is close to the mean reaction temperature any quantitative generalizations concerning the effect of structure upon the reaction rate must be discussed with considerable caution. The actual values of the activation parameters however, may be discussed.

A conspicuous feature of the values obtained is the high (more positive) entropies of activation. Highly negative entropies of activation in the region of -20 to -30 e.u. (in
aqueous solvents) are generally associated with bimolecular reactions in solution (56). A non-polar medium such as methylene chloride would also be expected to decrease the entropy. It is interesting to note that the magnitude of this activation parameter has been used as a criterion of fragmentation by Buncel and Millington (23), when discussing the hydrolysis of primary alkyl chlorosulphates. The simultaneous fission of the two bonds with the formation of three fragments would result in an increased (in a positive direction) $\Delta S^+$ due to the gain in translational, rotational and vibrational degrees of freedom. The authors carry on to say that possibly a fragmentation process in the chlorosulphate hydrolysis reaction may be the reason for the relatively more positive entropy of activation that is observed, and that the high values obtained for other reactions such as the solvolysis of alkyl chloroformates (57) may be interpreted on the basis of multiple bond fission. Since the size of this parameter is influenced by many factors (56) and has a high degree of error, any hypothesis which uses the values of $\Delta S^+$ as a criterion of mechanism must be approached with caution. However, the concept is of interest. As one of the purposes of this thesis is to determine the mechanism of the desulphonation reaction it is interesting to speculate that the reaction may be a fragmentation process.
Since the entropy of activation is a measure of the freedom from restraint of motion among the reactants, the fact that the reaction of p-nitrophenylmethanesulphonyl bromide with bromide ions has a relatively low value can be easily rationalized. Resonance of the p-nitro group in the transition state, through the phenyl ring would result in the loss of some degrees of freedom and would produce a more negative value for $\Delta s^\#$. Contribution from a corresponding resonance structure is impossible for the m-nitro compound and hence a more positive entropy term is observed because of a smaller loss of degrees of freedom.

D. The Hammett Plot

Since it appears that the rates of the desulphonylation reaction have been measured near to the isokinetic temperature (Section C) any Hammett-type correlations for this reaction should be treated with restraint.

A considerable amount of information concerning the rates of reactions of nucleophiles at benzylic carbon has been available in the chemical literature for some time. Attempted correlations with the Hammett equation have been unsuccessful. Non-linear plots of two types are observed, (i) Hammett plots of the reactivity of p-substituted benzyl halides with anions are U-shaped with the unsubstituted compound at the rate minimum (58), (ii) the rates of the
m-substituted benzyl halides are consistently lower than would have been predicted on the basis of σ values and are in a number of cases below that of the unsubstituted compounds.

The substituent effects observed in S_N2 reactions at benzylic carbon are generally small and the differences in rate observed for the reaction under study, although measured near to the isokinetic temperature, are comparable. The shape of the Hammett plot (Fig. 1) at 25° and 35° is that expected for a reaction having a bimolecular mechanism which progresses from more "S_N1 like" with p-methyl as the substituent, to more "S_N2 like" with the p-nitro substituent. As expected the m-chloro compound reacts more slowly than the unsubstituted substrate. However, the m-nitro compound reacts at a rate comparable to that of the para substituted analogue. Careful study of the literature revealed that these phenomena are not without precedent. In the reaction of benzyl halides with sodium thiosulphate in aqueous acetone Fuchs and Carlton (60) showed that the Hammett plot gave a curve for the para substituents and a curve for the meta substituted compounds. The m-nitro compound was anomalous in that it reacted at a faster rate than the unsubstituted compound.

The shape of the plots obtained when bimolecular reactions are subjected to Hammett-type correlations has been rationalized by Swain and Langsdorf (59). These authors
pointed out that although the Hammett equation assumes that the reaction and substituent constants are independent \( \rho \) could be a function of \( \sigma \). That is, a strongly electron donating group not only stabilizes, by resonance, a transition state having a \( \mathcal{S}^+ \) charge, but also increases the capacity of the molecule as a whole for positive charge. The converse is true for an electron withdrawing group which should increase the capacity of the molecule for negative charge. What the authors are saying is that as one progresses from strongly electron donating to strongly electron withdrawing substituents the mechanism of a bimolecular substitution reaction progresses from more \( S_N^1 \) like to more \( S_N^2 \) like. A U-shaped curve, which is experimentally found, is predicted.

The Hammett plots obtained in the present case, therefore, although showing small changes in reaction rate, are consistent with those obtained for the well documented bimolecular substitution reactions. It seems then, although the differences in rate should be treated with the necessary caution, that the interpretation of the substituent effects presented by Swain and Langsdorf (59) are more or less applicable to the reaction under study, and the shape of the Hammett plot is evidence that the reaction is a bimolecular one.
Fig. 1

The Hammett Plot of

$RCH_2SO_2Br + Et_4N^+Br^- \rightarrow RCH_2Br + SO_2$

$\Delta_{\text{p}-\text{NO}_2}$

$\Delta_{\text{m}-\text{NO}_2}$

$\Delta_{\text{p}-\text{Cl}}$

$\Delta_{\text{m}-\text{Cl}}$

$\Delta_{\text{p}-\text{Me}}$

$\Delta_{\text{H}}$

$\log \frac{k}{k_0}$

$0.8$

$0.6$

$0.4$

$0.2$

$0.0$

$\sigma$

$\Delta = 35^\circ$

$\theta = 25^\circ$

$CH_2SO_2Br + Br^- + \Delta_{\text{p}-\text{NO}_2}$
E. **Solvent Effects**

According to the classical theory of Hughes and Ingold (16) on the effects of change of solvent, the rate of a reaction of the type

\[ Y^- + RX \rightarrow Y^- - R - X \rightarrow RY + X^- \]

should decrease with increasing polarity of the solvent. However, this qualitative treatment ignores specific interactions such as association, dissociation and hydrogen bonding. These effects would be expected to play a large part in controlling the reaction rate in dipolar aprotic solvents (61). Consideration of the way in which these specific interactions effect the reaction rate can often be very illuminating.

Dissociation of the salt in dipolar aprotic solvents determines the rate of a reaction to a certain extent (7). As the dielectric constant, or the solvent ionizing power \( Z \), increases, the amount of association should decrease, and the rate increase. This is borne out by the fact that the rate of the reaction under study, using tetraethylammonium bromide, is increased from 2.45 to 7.9 x 10^{-2} \( \text{l.mole}^{-1}\text{sec}^{-1} \) as the solvent is changed from methylene chloride to acetonitrile (\( Z \) values 64.2 and 71.3 respectively (46)). Conversely, when the solvent polarity was decreased, as in a methylene chloride-ether mixture (2:1 v/v), the rate dropped from 3.8 to 2.5 x 10^{-2} \( \text{l.mole}^{-1}\text{sec}^{-1} \) for p-nitrophenylmethanesulphonyl bromide, as expected. (Table V)
### TABLE V

**Solvent Effects on the Reaction Rate of**

\[
\text{RCH}_2\text{SO}_2\text{Br} \xrightarrow{\text{Br}^-} \text{RCH}_2\text{Br} + \text{SO}_2 \text{ at } 25^\circ
\]

<table>
<thead>
<tr>
<th>R</th>
<th>Cation [molar]</th>
<th>Solvent</th>
<th>(k_2 \text{ l.mole}^{-1}\text{sec}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>Et(_4)N(^+) [0.001]</td>
<td>CH(_2)Cl(_2)</td>
<td>2.45 \times 10^{-2}</td>
</tr>
<tr>
<td>Ph</td>
<td>Et(_3)NH(^+) [0.001]</td>
<td>CH(_2)Cl(_2)</td>
<td>1.5 \times 10^{-4}</td>
</tr>
<tr>
<td>Ph</td>
<td>Et(_4)N(^+) [0.001]</td>
<td>CH(_3)CN</td>
<td>7.9 \times 10^{-2}</td>
</tr>
<tr>
<td>Ph</td>
<td>Et(_3)NH(^+) [0.05]</td>
<td>CH(_3)CN</td>
<td>1.67 \times 10^{-2}</td>
</tr>
<tr>
<td>pNO(_2)C(_6)H(_4)</td>
<td>Et(_4)N(^+) [0.001]</td>
<td>CH(_2)Cl(_2)</td>
<td>3.8 \times 10^{-2}</td>
</tr>
<tr>
<td>pNO(_2)C(_6)H(_4)</td>
<td>Et(_4)N(^+) [0.01]</td>
<td>CH(_3)OH</td>
<td>No reaction; less than 8 \times 10^{-6}</td>
</tr>
<tr>
<td>pNO(_2)C(_6)H(_4)</td>
<td>Et(_4)N(^+) [0.007]</td>
<td>CH(_2)Cl(_2)/Et(_2)O</td>
<td>2.5 \times 10^{-2}</td>
</tr>
<tr>
<td>pNO(_2)C(_6)H(_4)</td>
<td>Et(_4)N(^+) [0.02]</td>
<td>CH(_2)Cl(_2)/isoPrOH</td>
<td>2.3 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Changing the solvent from methylene chloride to acetonitrile had a more striking effect when triethylammonium bromide was used as the source of bromide ions. The rate increased approximately 100 fold. The effect, though large, could have been anticipated. Cations with a labile proton available for hydrogen bonding (see Section B) such as R\(_3\)NH\(^+\) form strongly hydrogen bonded structures with suitable anions in non-polar solvents (62). The hydrogen bonding should decrease as the ionizing power of the solvent is increased. Together with the greater solvation of the smaller cation (63).
the amount of 'free' anions in solution should increase, and hence the rate of the reaction should increase.

In an effort to prove an aspect of the mechanism (see PART VI) the reaction was attempted using methanol as the solvent. When p-nitrophenylmethanesulphonyl bromide and tetraethylammonium bromide were mixed in methanol and allowed to stand at 25°, the only product, as judged by n.m.r. spectroscopy and thin layer chromatography, was the solvolysis product methyl p-nitrophenylmethanesulphonate. No desulphonylation product (p-nitrobenzyl bromide) was detected. Under comparable conditions, without any salt added, the same amount of solvolysis took place. It was estimated by comparison of the benzylic protons of the sulphonyl bromide and sulphonate that 53% reaction had taken place, corresponding to a second-order solvolysis rate of about $8 \times 10^{-6}$ l.mole$^{-1}$ sec$^{-1}$ at 25°. When a mixture of methylene chloride and isopropyl alcohol (4:1 v/v) was used as the solvent some p-nitrobenzyl bromide formed together with the solvolysis product. The apparent second-order rate constant for bromide ion attack was found to be $2.3 \times 10^{-3}$ l.mole$^{-1}$sec$^{-1}$ an approximate ten fold decrease in rate from the reaction in methylene chloride.

Since Parker (61) has stated that the rates of $S_N^2$ reactions of anionic nucleophiles are increased by $10^3$ to $10^7$ in the change from protic to dipolar aprotic solvents these
effects are to be expected. They did show however that specific interactions do play an important role in reactions of this type.

F. The Scope of the Reaction

Since the catalysed desulphonylation reaction has been studied so far using only the phenylmethyl system, other compounds were prepared to get some idea of what effect the change in the R group would have on the rate of the reaction, and on the scope of the reaction:

\[ RCH_2SO_2Br + Br^- \rightarrow RCH_2Br + SO_2 \]

The results of such a study are listed in Table VI.

TABLE VI

The Effect of Change of Substrate on the Bromide Ion Catalysed Desulphonylation of Sulphonyl Bromides

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Rate of Reaction (1.mole(^{-1}).sec(^{-1}))</th>
<th>Relative Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylmethanesulphonyl bromide</td>
<td>(2.35 \times 10^{-2})</td>
<td>8400</td>
</tr>
<tr>
<td>Methanesulphonyl bromide</td>
<td>(1.0 \times 10^{-5})</td>
<td>36</td>
</tr>
<tr>
<td>2-Phenylethanesulphonyl bromide</td>
<td>(2.8 \times 10^{-6})</td>
<td>1</td>
</tr>
</tbody>
</table>

The most impressive thing about these results is the marked accelerating effect of the phenyl group. Other studies (20, 64) on the effect of substrate in bimolecular reactions
have indicated that the benzyl group does enhance the rate of reaction by stabilizing, through overlap, the orbital by which the entering and leaving group are bound. However, when R is methyl the rate is usually comparable to that of R equal to benzyl (presumably due to less steric interference). Why the reaction is so facile when the substrate is phenylmethane-sulphonyl bromide (or why the others are so slow) are questions that are unanswered at the moment.

Compounds other than the phenylmethane ones do react, although slowly, since it was shown that no alkyl bromides were produced in the absence of bromide ions. The reaction is therefore a general one, for sulphonyl bromides at least.
PART IV
THE CARBON KINETIC ISOTOPE EFFECT

The work described in this section was accomplished with the direct guidance and collaboration of Dr. J. B. Stothers and Mr. A. J. McNamara.

Since, in principle, kinetic isotope effects provide information concerning the nature of the transition state, carbon isotope effects could provide additional information about nucleophilic substitution at saturated carbon. This topic has been the subject of detailed mechanistic study over the last 30 years, but about which controversy still exists. Nucleophilic displacement reactions have been discussed in terms of a two step ($S_{N2}$) and a one step ($S_{N1}$) mechanism together with various degrees of the two extremes. The bonding changes in going from reactants to activated complex are clearly different for the two mechanisms and so isotope effect measurements would be expected to furnish additional information about this intriguing problem.

Fry (65) suggested that the kinetic isotope effect for an $S_{N1}$ process is lower than that for an $S_{N2}$ process because of specific effects such as solvation and resonance inter-
action all of which tend to increase the transition state
term in the Bigeleisen equation, which can be represented
by (66):-

\[
\frac{k_{12}}{k_{13}} = TIF \left(1 - \text{TST} + \text{IST}\right)
\]

TIF = temperature independent term
TST = transition state term
IST = initial state term.

and one should be able to distinguish between \(S_{N1}\) and \(S_{N2}\)
mechanisms by carbon isotope effects. Stothers and Bourns
(67) had expressed the same idea on the basis of their results
from the solvolysis of 1-bromo-1-phenylethane, and rational-
ized their low isotope effect for an \(S_{N1}\) process in terms of
charge declocalization by the phenyl ring.

As has been indicated in a previous part of this thesis
(Part III) nucleophilic displacement reactions of benzyl com-
pounds fall into the borderline region between the two extremes.
The mechanism can be shifted to more "\(S_{N1}\) like" or more
"\(S_{N2}\) like" by introducing appropriate substituents into the
ring. The steric environment of the central atom is kept
constant, while the electrical environment can be changed.
The effect of substituents on the carbon isotope effect for
the bimolecular reactions of benzyl halides, with various
nucleophiles, has been studied in these laboratories by
Stothers and McNamara (68). The scrutiny of these reactions could provide valuable insight into the nature of substituent effects in bimolecular processes, and study of the reaction discussed in this thesis is an extension of the work of Stothers and McNamara, besides giving useful information concerning the nature of the reaction pathway.

For a process exhibiting a primary isotope effect the difference in isotopic abundance of an atom at the reaction centre in the reactant and product, is a function of the extent of the reaction. The isotope fractionation is a maximum initially and decreases to zero for complete conversion to product. The reaction must of course be allowed to produce sufficient product to allow its separation from the unreacted starting material. Generally from five to fifteen percent reaction has been used.

Since the $^{12}$C/$^{13}$C ratio for the carbon atom at the reaction centre in the starting material and product must be compared, this atom must be isolated from the rest of the molecule in a form suitable for analysis, which in this case would be carbon dioxide for mass spectrometric analysis. It is essential for isotope effect studies that the overall yield of the degradation process be high to avoid extraneous isotopic fractionation. Fortunately the conversion of the α-carbon atom of the benzylic system to carbon dioxide in very high
yield has been developed by Stothers and his co-workers. The method employed involves the oxidation of the side chain to form the corresponding benzoic acid, which can then be decarboxylated using a modified Schmidt reaction (69).

The mass spectrometer used was an isotope ratio, 15-inch Nier type, with which the signal corresponding to the 45 mass is compared with the signals of the 44 and 46 masses. After correction for contributions of the $^{17}O$ and $^{18}O$ nuclei, (66) the isotopic ratio was converted to $k_{12}k_{13}$ expression derived by Stevens and Attree (70) which takes into account the extent of the reaction.

The desulphonylation reaction of phenylmethanesulphonyl bromides is particularly suitable for a study of this sort because the small amount of product, after the necessarily small extent of reaction, can easily be separated from the starting material simply by converting the latter to a water soluble compound by a sulphene reaction. The phenylmethanesulphonyl bromide was reacted with tetraethylammonium bromide under conditions used for the measurement of the rates to avoid any concentration effects. After the required extent of reaction the solution was quenched by pouring it into a mixture of methylene chloride, triethylamine and water. The organic solvent was present to facilitate the reaction of the starting material with the essentially water insoluble base
to form the water-soluble triethylammonium sulphonate.

Using Swain's (59) rate data the reaction of triethylamine with the benzyl bromide would be negligible under the conditions used. After the organic solution had been washed and dried the solvent was removed as much as possible by distillation through a spinning band column (for the unsubstituted material) or a 12" Vigreux column. In all cases the infrared spectrum of the remaining solution showed no trace of sulphonyl bromide. The sample in a small amount of methylene chloride was supplied to Mr. A.J. McNamara, who oxidized it directly, using a large excess of potassium permanganate, in high yield, to the corresponding benzoic acid. The $k_{12}$ ratios obtained are presented in Table VII.

For the purposes of a qualitative discussion it is convenient to discuss the transition state in terms of the force constants of the vibrational modes associated with the reaction centre (65).

$$
A + Y^- + R \rightarrow X \rightarrow [Y-----R-----X] \rightarrow Y - R + X^- + A
$$
TABLE VII

The Carbon-13 Kinetic Isotope Effects in the Reaction of Phenylmethanesulphonyl Bromides with Tetraethylammonium Bromide in Methylene Chloride at 25°.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Reaction Time (min.)</th>
<th>% Reaction</th>
<th>k_{12}</th>
<th>k_{13}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCH$_2$SO$_2$Br</td>
<td>113</td>
<td>15.1</td>
<td>1.0352</td>
<td>±0.0016</td>
</tr>
<tr>
<td>mC$_6$H$_4$CH$_2$SO$_2$Br</td>
<td>150</td>
<td>14.3</td>
<td>1.0453</td>
<td>±0.0001</td>
</tr>
<tr>
<td>pC$_6$H$_4$SO$_2$Br</td>
<td>88</td>
<td>15.0</td>
<td>1.0312</td>
<td>±0.0013</td>
</tr>
<tr>
<td>mNO$_2$C$_6$H$_4$SO$_2$Br</td>
<td>77</td>
<td>15.0</td>
<td>1.0414</td>
<td>±0.0008</td>
</tr>
<tr>
<td>pNO$_2$C$_6$H$_4$CH$_2$SO$_2$Br</td>
<td>59</td>
<td>12.8</td>
<td>1.0544</td>
<td>±0.0007</td>
</tr>
</tbody>
</table>
The symbols $k_1$, $k_2$, $k_3$ and $k_5$ are stretching force constants involving $X$, $R$ and $Y$. The $A\cdots R$ bonding represents all other bonding changes in $R$ such as resonance stabilization and solvation, in going from the reactants to the transition state; the force constant $k_4$ summarizes these effects.

When $k_2$ and $k_3$ are large the transition state is of the $S_N^2$ type and, when small, the $S_N^1$ type. Intermediate situations may be represented by various combinations of values for $k_2$ and $k_3$. For a unimolecular reaction the $A\cdots R$ interaction is large and hence $k_4$ is large while the opposite ($k_4$ is small) is true for the bimolecular case.

The observed isotope effect is generally lower than that which is predicted by the three centre equation of Bigeliesen and Wolfberg (72), and to rationalize this in terms of the available stretching modes Westheimer (71) presented the following argument. In the transition state there are two stretching modes for $Y\cdot R\cdot Y$, one for which there is no restoring force, which is the reaction co-ordinate, and a symmetric stretching vibration. The symmetric vibration represents bonding in the activated complex that is not present in the reactants.

If $k_2$ and $k_3$ are equal, no motion of $R$ is involved in the symmetric stretching vibration and the frequency will be independent of the mass of $R$, but if $k_3 > k_2$ or $k_2 > k_3$
the frequency and hence the isotope effect will depend upon
the isotopic mass of R. It follows, that for a symmetrical
intermediate (S_N^2, k_2 = k_3) the transition state term (TST)
will be zero since the frequency will be isotope independent
and there will be little or no contribution from the A----R
interactions.

For a reaction in which k_2 > k_3 or k_3 > k_2 the situation
changes. There will be contributions to the TST from the
symmetric stretching mode resulting in a reduced isotope
effect. In a S_N^1 reaction there is no symmetric stretching
frequency in the transition state, but there may be a large
A----R term resulting in a large isotope dependent term in
the TST. The outcome is a lowering of the isotope effect.
Since the A----R interaction term may be large it is possible
that the magnitude of the carbon 13 isotope effect could be
used as a criterion for distinguishing between S_N^2 (large
isotope effect) and S_N^1 (small isotope effect) mechanisms.

Consistent with the interpretation obtained from rate
studies, that the desulphonylation reaction is bimolecular,
is the fact that the presence of a ^{13}C atom at the benzylic
position slowed the reaction by more than 3%. (Table VII).
These values are of the same order of magnitude obtained
for other well documented bimolecular substitution reactions
at benzylic carbon. For example, in the reaction of benzyl
bromide with methoxide ion in methanol at 0° the k_{12}/k_{13} ratio
is 1.0531 (104) while the ratio for the reaction of benzyl chloride with methoxide ion in methanol at 25° was found to be 1.0464 (68).

In 1955, a postulate was advanced by Hammond (73) which related the energy content of the reactants, intermediates and products to the expected geometry of the transition state. Stated simply a transition state is more like the product or the reactant depending on whether the intermediate is of high or low energy, e.g. for a $S_N1$ reaction having an intermediate carbonium ion of high energy the transition state will be more like the carbonium ion.

The transition state for a reaction

\[ X + YX \rightarrow XY + X \]

should be symmetrical. However if in a polar displacement such as

\[ Z + YX \rightarrow ZY + X \]

$Z$ is a better nucleophile than $X$, the postulate predicts that the transition state resembles the reactants more than the products. A better nucleophile need not "push" so hard to reach a free energy maximum. For the desulphonylation reaction $Br^-$ would be expected to be a better nucleophile than $SO_2Br^-$ since the negative charge would be more diffuse in the latter, and in the transition state $2$ bromide ion should only be
loosely bonded, and the C-S bond will be shorter than the C-Br bond.

An extension of the postulate was forwarded by Swain and Thornton (74) to account for the effect of substituents on the transition state. In essence, this rule predicts that as the $\sigma$ value of the substituent increases the bonds being broken and formed in the transition state shorten for nucleophilic substitution at benzylic carbon. This would tend to make $k_3$ and $k_2$ more equal and hence the transition state will become more symmetrical. The net effect would be an increase in the isotope effect.

Although the isotope effect does generally increase as the $\sigma$-value increases there is no linear relationship for the Hammett plot such as that observed in some sulphur isotope effects (76). It is possible to visualize that, as one increases the $\sigma$ value of the substituent, the force constants would progress from $k_3 > k_2$, $k_3 = k_2$, $k_3 < k_2$. In other words the kinetic isotope effect would pass through a maximum as envisioned by Bigeleisen (75) for 3-centre proton transfer reactions. It is possible for the present case that the maximum occurs with the p-nitro substituent and the other substituents shift the effect to either side of this maximum. For this idea to be correct other effects besides electron withdrawing ability, such as differences in solvation
or steric effects would have to be present that would modify the $\sigma$ value of the substituent, and hence the symmetry of the transition state.

Even though these ideas are speculative it is clear that isotope effect studies can provide much useful information about reaction mechanisms even with no more than a qualitative consideration of isotope theory. In this case it has been shown that the reaction is indeed bimolecular and that with more powerful electron withdrawing groups the transition state becomes more symmetrical.
PART V

THE STEREOCHEMISTRY OF THE REACTION

Although it has been shown by a Hammett plot and carbon kinetic isotope effects that the reaction is bimolecular, there still remains the possibility that the primary attack by the nucleophile is on sulphur and not the α carbon atom. At the present time there are no quantitative data regarding the rate of nucleophilic attack at sulphonyl sulphur, but in a recent paper Rice (77) indicated that nucleophilic attack at sulphinyl sulphur is very rapid. It appeared possible that the observed bimolecularity of the reaction could arise from attack of halide ion at sulphonyl sulphur producing the intermediate 3 which could then undergo an intramolecular

![Chemical structure](image)

rearrangement to produce the observed products. The latter process would be an example of the so-called "S, i mechanism". There are a number of examples in the literature, mostly
concerning displacement of -OH by halide ion, of this type of reaction. In all cases the carbon atom at which substitution was taking place retained its stereochemical configuration. For theoretical reasons and from a large amount of experimental evidence it has been stated that "Substitution by mechanism $S_N^2$ involves inversion of configuration, independently of all constitutional details" (16). Obviously the two mechanisms, $S_N^2$ displacement at the benzylic carbon or nucleophilic attack at sulphonyl sulphur with concomitant collapse can be distinguished by observing the stereochemical course of the reaction.

The relative configurations of the reactants must be known before the stereochemical course of the reaction can be determined. An indication of how to do this was provided in a publication by Kice (12) who prepared optically active phenylmethanesulphonyl-l-$d$-chloride and related its stereochemistry to the starting benzyl chloride. The work described in this Part involves the preparation of a sulphonyl bromide having an optically active primary carbon atom in the $\alpha$ position and its reaction with bromide ions.

The preparation of a compound containing an optically active primary carbon atom was accomplished by a partial asymmetric reduction of benzaldehyde-$\alpha$-$d$, which had been prepared in excellent yield and purity by the method of Seebach and co-workers (78) who developed a method for the
synthesis of l-deuterioaldehydes using 1,3 dithiane compounds as indicated in the following scheme.

\[
\begin{align*}
\text{SH} & \quad \text{H}^+ \quad \text{SH} \quad + \quad \text{H} \quad \text{Ph} \\
\downarrow \quad \text{BuLi} \quad \downarrow \quad \text{D}_2\text{O} \quad \downarrow \quad \text{H}_9\text{O} \quad \text{H}_9\text{Cl}_2 \\
\text{Li} \quad \text{Ph} & \quad \rightarrow \quad \text{D} \quad \text{Ph} \quad \rightarrow \quad \text{D} \quad \text{Ph}
\end{align*}
\]

The benzaldehyde-\(\text{H}-\text{D}\) was reduced using optically active isobornylxymagnesium bromide as the catalyst (79). The benzyl-\(\text{H}-\text{D}\) alcohol prepared in this way was claimed by Streitwieser to be nearly optically pure, but Horeau and Nouaille (80) in a recent publication proved Streitwieser's specimen to be only 14% optically pure. Since the optical rotation was to be measured with a Jasco Optical Rotatory Dispersion Recorder which can measure small rotations quite accurately this would be of little consequence in demonstrating the stereochemical course of the reaction.

Based on the accepted mechanism of the Meerwein-Ponndorf reduction, Streitwieser and his co-workers (81)
assigned the R configuration to (-)-benzyl \( \alpha \)-d-alcohol. This assignment was confirmed by Brewster's analysis (82).

Phosphorus tribromide reacts with benzyl \( \alpha \)-d alcohol to yield the benzyl bromide with inversion of configuration (79) and the benzyl bromide may be treated with sodium sulphite to yield sodium phenylmethanesulphonate, again with inversion of configuration (12). From past experience it was a simple matter to convert the sulphonate to the corresponding sulphonyl bromide in a reaction with phosphorus pentabromide that does not affect the optical centre. Hence, the absolute stereochemistry of the starting material is known and the stereochemistry of the expected product, benzyl \( \alpha \)-d bromide, can be determined from its sign of rotation.

The expected product can be racemised by the nucleophile in the solution. Therefore, the rate of racemisation of optically active benzyl \( \alpha \)-d bromide by bromide ions under conditions used to study the reaction of optically active phenylmethanesulphonyl bromide with bromide ions was determined. The rate of loss of optical activity of benzyl \( \alpha \)-d-bromide upon reaction with tetraethylammonium bromide in methylene chloride at 25° was followed using a Jasco instrument set at a fixed wavelength of 400nm. An excellent pseudo first order plot was obtained which gave a second order rate constant of \( 5.12 \times 10^{-2} \) l.mole\(^{-1}\)sec\(^{-1}\).
For consecutive first-order reactions (83) the concentration of B at time t

\[ \begin{array}{c}
A \xrightarrow{k_1} B \xrightarrow{k_2} C \\
\end{array} \]

that is,

\[ \begin{array}{c}
\text{Br}^- \\
\text{PhCHDSO}_2\text{Br} \xrightarrow{} \text{PhCHDBr} \xrightarrow{} \text{PhCHDBr(rac,)} \\
\end{array} \]

is given by the equation

\[ B = \frac{A_0 k_1}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right) \]

where \( A_0 \) = concentration of A at time \( t = 0 \). Since \( k_1, k_2 \) and \( A_0 \) are known the amount of B, i.e. optically active benzyl-\( \alpha \)-d bromide, in the reaction mixture after time \( t \), should be easily obtained. Provided the mixture of racemic and optically active benzyl-\( \alpha \)-d bromide can be separated clearly from the starting material, the rotation, and hence the stereochemistry of the optically active benzyl bromide, produced by the desulphonylation reaction, can be determined.

The reaction of \( R(-) \)-phenylmethanesulphonyl-1-d bromide with tetraethylammonium bromide was allowed to proceed to about 50% reaction. The time allowed was greater than that for maximum concentration of B but it was felt that errors in the work-up could be minimized by having a greater concentration of B + C. After quenching the reaction by pouring
into water, separation of the materials was achieved, following work-up, simply by crystallizing the starting material out of pentane. The benzyl-α-δ bromide remained in solution. This method had the added advantage in that it allowed recovery of the phenylmethanesulphonyl-1-δ bromide and it was possible to show that its stereochemistry did not change under the reaction conditions. The rotation of R(-)-phenylmethanesulphonyl-1-δ bromide before and after the reaction at 400 μ was -2.5° and -2.6° respectively.

The mixed benzyl-α-δ bromides (opt. active and racemic) obtained by careful distillation were shown by the absence of any sulphonyl absorption in the infrared spectrum to contain no starting material. The spectrum was identical with an authentic sample of benzyl-α-δ bromide. The material gave a positive plane curve with [α]_400 of + 0.51° which corresponded, by calculation using equation (16) to S(+) benzyl-α-δ bromide in approximately 60% optical purity.

After this work had begun Mosher and his co-workers (84) prepared S(+) benzyl-α-δ alcohol from benzaldehyde-α-δ by reduction with actively fermenting yeast. The alcohol prepared in this way was shown by Horeau (80) to be 100% optically pure. Using this method S(+) benzyl-α-δ alcohol was prepared having an [α]_400 + 2.1°. The S(+) phenylmethanesulphonyl-1-δ bromide was obtained via the benzyl-α-δ bromide in good yield having 93.5% of the expected deuterium and
\[ \alpha \]_{400} + 6.2^\circ. The infrared spectrum was identical with that of R(-)-phenylmethanesulphonyl-1-d bromide. The optically active benzyl bromide obtained from the desulphonylation reaction was again shown, by the method described above to have only 60% of the optical activity expected from 100% inversion at the substituted carbon.

\[
\begin{align*}
R(-)Ph^*CHDSO_2Br & \xrightarrow{\text{Et}_4NB} \quad S(+)Ph^*CHDBr \text{ at least 60}\% \\
S(+)Ph^*CHDSO_2Br & \longrightarrow \quad R(-)Ph^*CHDBr \text{ at least 60}\%
\end{align*}
\]

It can be stated that at least 60% of the product is that of inversion. This can be due to one or two things. More than one process may be taking place during the reaction. There is another possible explanation however. When one looks more closely at the preparation of the sulphonyl bromide it can be seen that there is some possibility for partial racemization. The sodium sulphonate is prepared by refluxing a heterogeneous mixture of the benzyl-\text{\textalpha}-d bromide in water. As the reaction proceeds the sulphite group replaces the bromide, forming bromide ions. It is possible, although this point has not been checked, that partial racemization could occur from attack of bromide ion on the optically active benzyl-\text{\textalpha}-d bromide. i.e: The conversion of benzyl-\text{\textalpha}-d bromide to sulphonyl bromide does not proceed with 100% inversion.
If both the phenylmethanesulphonyl-\(\text{L-}\text{d}\) bromide and the corresponding benzyl-\(\alpha\text{-d}\) bromide could be converted into the same compound by routes not affecting the optical purity of the compounds involved, a comparison of the optical rotation of each derivative would give a direct measure of the relative optical purities. \(S\text{(–)}\)-benzyl-\(\alpha\text{-d}\) bromide was converted into \(R\text{(–)}\)-benzyl-\(\alpha\text{-d}\) ethyl sulphone containing 99\% of the expected deuterium (compared to the corresponding phenylmethanesulphonyl-\(\text{L-}\text{d}\) bromide) using the method developed by Kice (12). The sulphone had a negative plain curve with \([\alpha]\)\text{400} = -0.90\(^\circ\) confirming, by comparison with the results of Kice (12) that the absolute stereochemistry of the compounds used in this section are as represented.

When \(R\text{(+)}\)-phenylmethanesulphonyl bromide was converted to benzyl \(\alpha\text{-d}\) ethyl sulphone by reduction with zinc and reaction with ethyl bromide the product was racemic. In view of the fact that a control experiment using phenylmethanesulphinic \(\text{L,1-}\text{d}\) acid showed that no exchange of deuterium took place, and that Kice (12) obtained optically active benzyl \(\alpha\text{-d}\) ethyl bromide from optically active phenylmethanesulphinic \(\text{L-}\text{d}\) acid using the same technique, this result is surprising. It is probably not real, but probably due to a slight change in the experimental conditions used, and to the small amounts of materials used.

Other well known methods for the determination of optical
purity (85), namely, the enzymatic method and the isotopic
dilution method are impractical or impossible in this case.
Recently Raben and Mislow (86) have developed a method for
the determination of optical purity through the use of n.m.r.
spectroscopy. These authors have adapted the method to
compounds that owe their optical activity to deuterium substi-
tution. In essence the method consists of converting a mix-
ture of the enantiomers into a mixture of diastereomers with
a reagent that is optically pure, under conditions that would
exclude racemization or epimerization. The ratio of the
diastereomers, which is equal to the ratio of the enantiomers,
is determined by n.m.r. The method works because of the mag-
netic non-equivalence of the protons close to the new added
asymmetric centre.

To determine the optical purity of phenylmethanesulpho-
nyl-1-d bromide by this method, one must find a derivative
which can be prepared without racemizing the optical centre,
in which the benzylic protons (in the non deuterated material)
are split into a multiplet. Menthol phenylmethanesulphonate
4 was prepared for this purpose.

\[
\text{(D)}\quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \quad \text{C} \quad \text{SO} \quad \text{O} \\
\text{H} \\
\text{H}
\]
Unfortunately the methylene protons appeared as a singlet. Even in benzene, which Roberts and co-workers (87) showed increased the chemical shift between such protons, the methylene signal still appeared as a somewhat broadened singlet.

All that can be stated at the moment regarding the stereocchemical course of the reaction is that 60%, and probably more, of the product is formed by inversion and at least part of this "partial racemization" may be accounted for by the fact that the phenylmethanesulphonyl-1-\textsuperscript{d} bromide is not as optically pure as the reference benzyl \(\alpha\)-\textsuperscript{d} bromide. It is concluded that the major reaction, at the very least, is \(S_N^2\) in nature, rather than \(S_{\text{N,i}}\).
PART VI

THE MECHANISM OF THE REACTION

In the preceding parts, the reaction under study has been shown by rate studies, stereochemistry and carbon isotope effects to be of the $S_N^2$ type. This evidence together with the fact that the reaction rate is unaffected by the presence of styrene or benzoyl peroxide (the rate constants are $2.5\times10^{-2}$ and $2.15\times10^{-2}\text{ l.mole}^{-1}\text{sec}^{-1}$ respectively in methylene chloride at $25^\circ$, compared to $2.45\times10^{-2}\text{ l.mole}^{-1}\text{sec}^{-1}$ in the absence of these materials), clearly distinguishes the reaction from the pyrolytic decomposition of alkanesulphonyl halides, which has been found to show some properties of a free radical chain process (10).

There remains, however, the question of whether the leaving anion is simply $\overset{5}{\text{S}}\overset{2}{\text{O}}_2X$, which subsequently decomposes into $\text{SO}_2$ and $X^-$ (equations [17] and [18]), or whether the S-X bond is partially broken in the transition state $\overset{2}{2}$. This has been called a bimolecular concerted $\overset{\alpha}{\text{ fragmentation}}$ in the general introduction, but will be referred to here more simply as an $S_N^2$ fragmentation.
\[
\begin{align*}
\text{PhCH}_2\text{SO}_2\text{X} + X^- & \xrightleftharpoons[k_1]{k_2} \text{PhCH}_2\text{Br} + \text{SO}_2\text{X} \\
\text{SO}_2\text{X} & \rightarrow \text{SO}_2 + X^-
\end{align*}
\]

[17] [18]  

The apparent second order rate constant of the reaction of phenylmethanesulphonyl chloride with tetraethylammonium chloride in methylene chloride at 25° is \(1.1 \times 10^{-4} \text{ l.mole}^{-1} \text{ sec}^{-1}\). This is more than 200 times slower than the reaction of the corresponding sulphonyl bromide with bromide ions under identical conditions. Since tetraethylammonium bromide and chloride were found to be almost identical in their rate of reaction with benzyl tosylate and benzyl phenylmethanesulphonate in methylene chloride under conditions used for the desulphonylation reaction, judged by the ratios of product and starting material in the n.m.r. spectrum, it is suggested that the difference in reactivity does not derive from a difference in nucleophilicity towards benzylic carbon between chloride and bromide ions in this system. These results suggest that the reaction may be more than a simple substitution reaction since \(\text{SO}_2\text{Cl}^-\) would not be expected to be much worse a leaving group than \(\text{SO}_2\text{Br}^-\).

In order to get some idea of the scope of the reaction the series of compounds listed in Table VIII were prepared or obtained (see Experimental) and treated with tetraethylammonium bromide in methylene chloride. By work-up and analysis, by n.m.r. spectroscopy or by thin layer chromatography,
it was possible to arrive at a maximum rate for the reaction. After the isolated product had been analysed, the "fragmentation" product was added in a small amount, since no "fragmentation" product was detected, and the mixture worked up as before. Renewed analysis enabled one to state that if a certain amount of reaction had taken place it would have been possible to detect the product.

**TABLE VIII**

The Maximum Rate of the Reaction of Some Sulphonyl Compounds with Tetraethylammonium Bromide in Methylene Chloride at 25°C.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Maximum Rate (1.mole⁻¹sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhNO₂C₆H₄CH₂SO₂-OPh</td>
<td>less than 2 x 10⁻⁷</td>
</tr>
<tr>
<td>PhCH₂SO₂CH₂Ph</td>
<td>less than 2 x 10⁻⁷</td>
</tr>
<tr>
<td>PhCH₂SO₂-CH₂C-Ph</td>
<td>less than 2 x 10⁻⁷</td>
</tr>
<tr>
<td>PhCH₂SO₂-CF₃</td>
<td>less than 2 x 10⁻⁷</td>
</tr>
</tbody>
</table>

In all cases listed in Table VIII there was no reaction observed.

Among the groups attached to sulphonyl sulphur in this non-reacting group was an electron donating group (CH₂Ph), a strongly electron-withdrawing group, and a group which shows
electron releasing resonance and inductive electron withdrawal (O-Ph) similar to the halides. To account for these observations in terms of the reaction proceeding by direct displacement (eg. [17]) would require one to explain why \( \text{SO}_2\text{Br} \) is a better leaving group than either \( \text{SO}_2\text{CF}_3 \), \( \text{SO}_2\text{CH}_2\text{CPh} \), \( \text{SO}_2\text{CH}_2\text{Ph} \) and \( \text{SO}_2\text{-OPh} \) by more than five orders of magnitude in each case. One would at least expect \( \text{SO}_2\text{CF}_3 \) to be a better leaving group than \( \text{SO}_2\text{Br} \) due to the strong electron withdrawing nature of the trifluoromethyl group compared to bromine (Hammett para \( \sigma \) values 0.54 and 0.23 respectively).

Instead of inventing a new mechanistic effect it is easier to interpret these observations on the basis of a concerted fragmentation process going through the transition state 2. The observed rate order, \( \text{Br} \succ \text{Cl} \gg \text{CF}_3 \) etc. would then reflect the normal order of these groups as leaving anions (nucleofugal groups) (88).

It is possible to argue that benzyl trifluoromethyl sulphone failed to react because \( k_{-1} \) is much greater than \( k_2 \) (equation [17]). As a specific test for such a scheme, the reaction was carried out in the presence of an excess of \( p \)-nitrobenzyl bromide. If such a process was operating it would be expected to give detectable quantities of \( p \)-nitrobenzyl trifluoromethyl sulphone and benzyl bromide. In fact after a relatively long reaction time the \( p \)-nitrobenzyl bromide was accounted for quantitatively with no
sign of any p-nitrobenzyl trifluoromethyl sulphone or benzyl bromide being produced as judged by n.m.r. spectroscopy. This possible interpretation is therefore disproved.

The reaction of benzyl trifluoromethyl sulphone with tetraethylammonium bromide was also carried out using refluxing ethanol as the solvent. Under these conditions it would be expected that if any benzyl bromide were formed it would be trapped by the solvent, forcing the equilibrium to the right, and therefore decreasing the amount of starting material. Since all of the starting material was accounted for, the mechanism was disproved, if one assumes that nucleophilic attack on benzylic carbon would occur in ethanol as the solvent under these conditions (see Part III, Section E).

Another mechanism that can be suggested, that accounts for the observed bimolecularity, is one which involves a preliminary ionization [19] with a rapid equilibrium to the far left, followed by bromide ion attack on the ion pair [20].

\[
\begin{align*}
R\text{SO}_2\text{Br} & \rightleftharpoons R^+\text{SO}_2\text{Br}^- & [19] \\
R^+\text{SO}_2\text{Br}^- + \text{Br}^- & \rightarrow R\text{Br} + \text{SO}_2 + \text{Br}^- & [20]
\end{align*}
\]

This is the limiting case of the \(S_{N2}\) fragmentation reaction. However, if the reaction does follow this pathway the ion-pair would have to show some remarkable properties.
Klages and Malecki (89) have recently prepared a material which they called "tosyl perchlorate" and formulated it as

\[
\text{pCH}_3\text{PhSO}_2^+\text{ClO}_4^- \quad \rightleftharpoons \quad \text{pCH}_3\text{PhSO}_2^-\text{OClO}_3
\]

This material is highly reactive and is quite indiscriminate in the way it reacts. For example it reacts with benzene to form a sulphone and with ether to form a sulphonate ester.

\[
\text{pCH}_3\text{C}_6\text{H}_4\text{SO}_2^+\text{ClO}_4^- \quad \overset{\text{C}_6\text{H}_6}{\rightarrow} \quad \text{pCH}_3\text{C}_6\text{H}_4\text{SO}_2^-\text{Ph}
\]

\[
\text{pCH}_3\text{C}_6\text{H}_4\text{SO}_2^+\text{ClO}_4^- \quad \overset{\text{Et}_2\text{O}}{\rightarrow} \quad \text{pCH}_3\text{C}_6\text{H}_4\text{SO}_2^-\text{OEt}
\]

The reaction of p-nitrophenylmethanesulphonyl bromide with tetraethylammonium bromide when carried out in a mixture of methylene chloride and ether (2:1) gave only p-nitrobenzyl bromide as the product. There was no detectable amount of the ethyl sulphonate. Furthermore when the same sulphonyl bromide was allowed to react with bromide ions in a mixture of methylene chloride and isopropanol the product contained almost equimolar amounts of p-nitrobenzyl bromide and the isopropyl sulphonate ester.

\[
\text{pNO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{Br} \quad \overset{\text{Br}^-}{\underset{k_{\text{Br}}}{\rightleftharpoons}} \quad \text{pNO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br} + \text{SO}_2 + \text{Br}^- \\
\overset{k_{\text{OH}}}{\underset{\text{isoPrOH}}{\rightleftharpoons}} \quad \text{pNO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2^-\text{OCH(CH}_3\text{)}_2
\]
Under the conditions of the reaction the rates of the desulphonylation reaction \( k_{Br} \) and the alcoholysis \( k_{OH} \) were approximately \( 2.3 \times 10^{-3} \) and \( 1.8 \times 10^{-5} \) l.mole\(^{-1}\)sec\(^{-1}\) respectively. On the basis of the ionization mechanism (eq. [19]), and assuming that all of the reactions of bromide ion with the ion-pair lead to benzyl bromide, this would mean that the reaction of the ion-pair with bromide ion is more than 100 times faster than that of the ion-pair with isopropyl alcohol. It is probable, also, that bromide ion would attack the sulphur (the exchange reaction) which would increase this ratio many-fold. The properties found for tosyl perchlorate suggest that ion pairs of this type would be distinctly unspecific in their reactions with moderately reactive nucleophiles and therefore equation [19] does not seem to be a suitable reaction upon which to base the observations.

The available facts are best explained, lacking evidence to the contrary, by a mechanism involving a nucleophilic attack on the \( \alpha \) carbon atom and passing through a transition state depicted by structure 2.
The halide ion catalysed desulphonylation of alkane-sulphonyl halides is an example of an $S_N^2$ fragmentation.
EXPERIMENTAL

Infrared spectra were obtained using Beckman IR-5, IR-10 or IR-7 spectrophotometers equipped with sodium chloride optics. All values quoted for the infrared positions except where otherwise stated were determined with the IR-7 instrument. The n.m.r. spectra were obtained using a Varian A-60 instrument with tetramethylsilane as the internal standard. Vapour phase chromatography was carried out using a F. and M. Laboratory Chromatograph Model 700. Melting points are uncorrected and were determined on a Kofler hot stage. The drying of organic extracts was carried out over anhydrous magnesium sulphate.

Petroleum ether, unless otherwise stated, refers to that fraction of boiling range 35-60°. Pentane was Eastman-Kodak "Yellow Label", distilled once prior to use. Phenylmethanesulphonyl chloride was Eastman-Kodak "White Label" and was used as such unless otherwise stated. Triethylamine was B.D.H. "Laboratory Reagent" and was distilled once from calcium hydride before use. The alkylammonium salts were supplied by Eastman-Kodak and were recrystallized from methylene chloride-ether before use. Thin layer chromatography was performed using Camag Kieselgel DF5. Deuterium oxide (99.7% D₂O) was supplied by Atomic Energy of Canada Ltd.
Microanalyses were performed by Dr. Alfred Bernhardt, Microanalytische Laboratorium, Mulheim (Ruhr), Germany and A.B. Gygli, Toronto. Deuterium analyses were carried out by J. Nemeth, Urbana, Illinois, U.S.A. using the falling drop method.

I. PRELIMINARY EXAMINATION

1. Reaction of \( p \)-nitrophenylmethanesulphonyl chloride with triethylamine in the presence of excess triethylammonium chloride.

\( p \)-Nitrophenylmethanesulphonyl chloride (1.17 g, 5 mmoles, Section II A.) recrystallized from \( \text{CCl}_4 \) m.p. 89-92° reported m.p. 90-91°(28) and triethylammonium chloride (10.4 g, 75 mmoles) were weighed in a dry-box and transferred to a flame-dried flask. Methylene chloride (250 ml) was distilled directly into the flask from calcium hydride. Freshly distilled triethylamine (1 ml) in methylene chloride (5 ml) was added slowly down the condenser into the refluxing solution. After being refluxed for 30 mins. the solution was washed with dilute sulphuric acid, twice with water, and dried. Removal of the solvent yielded a yellow oil (348 mg). Thin-layer chromatography, using benzene as the solvent, showed the presence of \( p \)-nitrobenzyl chloride and 4,4'-dinitrostilbene in the oil. The fast-running fraction, corresponding to
p-nitrobenzyl chloride, was separated from the thin-layer plates and the silica extracted with acetone. Removal of the solvent yielded a yellow solid (55 mg). The compound was recrystallized from ether-petroleum ether, m.p. 71°, mixed m.p. with authentic sample (B.D.H.) 71°. The infrared spectrum was superimposable with the spectrum of authentic p-nitrobenzyl chloride.

2. Reaction of p-nitrophosphynmethanesulphonyl bromide with triethylamine in the presence of excess triethylammonium bromide.

a) Similar to the reaction above, the reaction of p-nitrophosphynmethanesulphonyl bromide (772 mg, 2.75 mmoles), and triethylamine (0.5 ml) in the presence of triethylammonium bromide (4.8 g, 26.5 mmoles) in methylene chloride (250 ml) yielded a pale yellow solid (109 mg, 33%) upon separation of the front running fraction, from thin layer chromatography. The compound was recrystallized from ether-petroleum ether, m.p. 95-97°, reported m.p. 99-100° (105). The infrared spectrum was superimposable with that of an authentic sample of p-nitrobenzyl bromide (Aldrich).

b) A yellow solid (237 mg, 37%) was obtained as the fast running fraction when p-nitrophosphynmethanesulphonyl-1,1-d_2 bromide was treated with triethylamine in the presence of 15 fold excess of triethylammonium bromide as above. It was
shown to be mainly \( p \)-nitrobenzyl-\( 1,1-d_2 \) bromide by the following evidence.

(i) Only a small peak, attributed to approximately 5\% undeuterated \( p \)-nitrobenzyl bromide at 4.53 p.p.m. was visible in the n.m.r. spectrum (CDCl\(_3\)).
(ii) Deuterium analysis indicated 26.75\% atom excess D.

Calculated for \( C_7H_4D_2Br \): 33.33\% atom excess D.

(iii) m.p. 93-97\° after one recrystallization from ethanol, mixed m.p. with natural abundance isomer 95-96\°. The infra-red spectrum (CHCl\(_3\), 0.1 mm) showed strong absorption at; 1607, 1525, 1350, 1110, and 856 cm\(^{-1}\).

3. Reaction of \( p \)-nitrophenylmethanesulphonyl bromide with aniline.

a) A solution of \( p \)-nitrophenylmethanesulphonyl bromide (230 mg,) and aniline (1.0 ml) in dry benzene (25 ml) was allowed to stand at room temperature for 1 hour. The solution was washed with dilute hydrochloric acid, water, and dried. The solvent was removed under reduced pressure. A pale yellow solid (154 mg, 52\%) remained. The compound afforded white needles upon recrystallization from methylene chloride, m.p. 128-130\° (vac. capillary). Calculated for \( C_{13}H_{12}N_2O_4S \): C, 53.43; H, 4.14; N, 9.59; S, 10.95\%. Found: C, 53.47; H, 4.15; N, 9.78; S, 10.64\%.

The n.m.r. spectrum (CDCl\(_3\)) showed sharp singlets at 4.42 p.p.m. and 5.30 p.p.m.; relative areas 2:1; as well
as the aromatic absorption.

b) When \( p \)-nitrophenylmethanesulphonyl-1,1-d\(_2\) bromide (282 mg, 10. mmole) was treated with aniline (10. ml) under identical conditions, a white solid (235 mg, 80\%) was obtained m.p. 128-130\(^\circ\); mixed m.p. 128\(^\circ\) with natural abundance isomer. Calculated for \( \text{C}_{13}\text{H}_{11}\text{DN}_{2}\text{O}_{4}\text{S} \): 8.33 atom % excess D. Found: 7.62 atom % excess D. The n.m.r. spectrum (CDCl\(_3\)) had a broad band at 4.42 p.p.m. assigned to the benzylic proton.

4. Reaction of \( p \)-nitrophenylmethanesulphonyl bromide with triethylammonium bromide in the absence of triethylamine.

a) A solution of \( p \)-nitrophenylmethanesulphonyl bromide 420 mg, 2 mmoles) and triethylammonium bromide (25.3 g, 20 molar excess) in methylene chloride (150 ml) was refluxed for 30 mins. The methylene chloride was washed 3 times with water and dried. Evaporation of solvent under reduced pressure gave a pale yellow solid (330 mg) whose infrared spectrum (IR-5) showed that sulphonyl bands at 1371 and 1162 cm\(^{-1}\) had diminished relative to the nitro group absorption at 1532 and 1352 cm\(^{-1}\). The product was shown to be a mixture of mainly \( p \)-nitrobenzyl bromide and starting material by thin-layer chromatography (benzene as eluent).

As a control experiment, \( p \)-nitrophenylmethanesulphonyl bromide (200 mg) was dissolved in methylene chloride (15 ml)
and heated at 80° in a sealed tube for 80 hours. Removal of the solvent in vacuo afforded a pale yellow solid (196 mg) whose infrared spectrum (IR-5) and thin-layer chromatography indicated starting material with no p-nitrobenzyl bromide present.

5. Reaction of p-nitrophenylmethanesulphonyl bromide with tetraethylammonium bromide.

A solution of p-nitrophenylmethanesulphonyl bromide (150 mg) and tetraethylammonium bromide (1.7 g) in methylene chloride (30 ml) was stirred at room temperature (26°) for 1 hour. The methylene chloride was washed three times with water and dried. Removal of the solvent in vacuo yielded a yellow solid (100 mg, 86%) whose infrared spectrum (IR-5) showed no peaks at 1370 or 1162 cm⁻¹ indicating that no starting material remained. Thin-layer chromatography confirmed that the product was essentially p-nitrobenzyl bromide.

b) p-Nitrophenylmethanesulphonyl-1,1-d₂ bromide (140 mg, 0.5 mmole) and tetraethylammonium bromide (210 mg, 1.0 mmoles) were dissolved in methylene chloride (10 ml) and allowed to stand at room temperature for 20 hours. The solution was washed twice with water and dried. Removal of the solvent in vacuo yielded a pale yellow solid (105 mg, 99%) which was recrystallized from ether-petroleum ether, m.p. 97-99°;
mixed m.p. with natural abundance isomer 96-98°. Calculated for C\textsubscript{7}H\textsubscript{4}D\textsubscript{2}BrNO\textsubscript{2} 33.33 atom % excess D. Found: 27.60 atom % excess D. The infrared spectrum (CHCl\textsubscript{3}) was identical with that of p-nitrobenzyl-\textsubscript{1,1-d\textsubscript{2}} bromide obtained from the reaction in the presence of triethylamine.

6. Reaction of p-nitrophenylmethanesulphonyl chloride with tetraethylammonium chloride.

A solution of p-nitrophenylmethanesulphonyl chloride (150 mg) and tetraethylammonium chloride (1.61 g, 15 molar excess) in methylene chloride (30 ml) was refluxed for one hour. Removal of the solvent \textit{in vacuo} yielded a yellow oily solid (48 mg only), the infrared spectrum of which indicated that the starting material was present in approximately 50% of the total (sulphonyl bonds at 1165 and 1390 cm\textsuperscript{-1}). A repeat experiment gave the same low yield of product.

II. PREPARATIONS OF SULPHONYL HALIDES


The method of Zeigler and Sprague (28) was modified in the following way.

A mixture of the benzyl chloride (0.1 moles) and sodium thiosulphate (26 g, 1.05 moles) was refluxed in 50% aqueous methanol (80 ml) for 12 hours. The resulting clear solution
was poured into enough cold water to keep the Bunte salt in solution (approximately 600 ml) and washed once with ether. Glacial acetic acid (25 ml) and a large quantity of crushed ice was added to make the total volume about one litre. Chlorine gas (Matheson, lecture bottle) was passed into the mixture through a glass tube (outside diameter 8 mm) while the solution was stirred rapidly with a mechanical stirrer. Ice was added from time to time to keep the solution as cold as possible. When the mixture became a permanent green-yellow the gas flow was slowed to a moderate speed and stirring continued for another 5 minutes. The mixture was extracted 3 times with methylene chloride. The combined extracts were washed once with 2% sodium bisulphite solution, twice with water and dried. Removal of the solvent under reduced pressure gave the sulphonyl chloride as a crude oil or solid. This material was used as such, without further purification, for the preparation of the corresponding sulphonyl bromides.

2. Phenylmethanesulphonyl bromide

The following procedure was found to be more convenient, and resulted in better yields, in the author's hands, than the method of Holmberg (47) or Durst (3).

Phenylmethanesulphonyl chloride (27.5 g, 0.15 moles) and sodium sulphite (39 g, 0.31 moles) were stirred in water
(200 ml) at 50°. When all of the sulphonyl chloride had reacted the solution was filtered and washed once with a small amount (30 ml) of methylene chloride. Methylene chloride (250 ml) was added and the solution cooled in an ice-salt bath. N-bromoacetamide (Arapahoe Chemicals Inc.) was added in small portions, with stirring, at such a rate to keep the temperature below 10°, until a permanent brown colour remained. The organic phase was washed with water, 2% sodium bisulphite solution, water, and dried. Removal of the solvent under reduced pressure yielded a white solid (25.5 g, 76%), m.p. 78-81°. One recrystallization from methylene chloride-petroleum ether, afforded white needles, m.p. 80-81°; reported m.p. 79-80° (47).

3. **p-Nitrophenylmethanesulphonyl bromide**

Crude p-nitrophenylmethanesulphonyl chloride (7 g) was dissolved in dioxane. The addition of water (35 ml) caused clouding of the solution, and more dioxane was added to just redissolve the precipitated material. Triethylamine (15 ml) was added, with stirring over a period of 5 minutes. The solvent was evaporated in vacuo and the resulting product dissolved in water (100 ml) and washed twice with ether. The water was removed under reduced pressure and the residue dissolved in chloroform. The solution was dried and phosphorus pentabromide (B.D.H., 40 g) was added at room temperature,
with stirring, over a period of 15 minutes. The solution was allowed to stand at room temperature for a further 30 minutes. Careful addition of crushed ice destroyed the excess phosphorus pentabromide. The chloroform solution was washed with water, 2% sodium bisulphite solution, twice more with water and dried. Evaporation of the solvent yielded a pale yellow solid, which was recrystallized from methylene chloride-petroleum ether. Pale yellow cubic crystals were obtained (7.10 g, 85%) m.p. 107-112°. The compound was recrystallized 3 times from methylene chloride-pentane, m.p. (vac. capillary) 110.5-113.5°. Calculated for C\textsubscript{7}H\textsubscript{6}BrNSO\textsubscript{4}: C, 30.01; H, 2.16; Br, 28.52; N, 5.00; S, 11.45%. Found: C, 30.26; H, 2.31; Br, 28.61; N, 4.90; S, 11.36%. The n.m.r. spectrum (CDCl\textsubscript{3}) showed a band at 4.98 p.p.m. (singlet) attributed to the benzylic proton as well as aromatic adsorption. Major infrared peaks below 1700 cm\textsuperscript{-1} (CH\textsubscript{Cl}\textsubscript{3}, 10%, 0.1 mm); 1610 (m), 1532 (vs), 1371 (vs), 1352 (vs), 1318 (m), 1162 (vs), 1134 (m), 880 (m); 864 (m), 858 (m), 689 (m), 648 cm\textsuperscript{-1} (m).

4. m-Nitrophenylmethanesulphonyl bromide

a) from the sulphonyl chloride.

The procedure was identical to that described above. Starting from impure m-nitrophenylmethanesulphonyl chloride (20.5 g) a yellow solid was obtained, a solution of which
was decolourized with charcoal and the compound recrystallized from chloroform-petroleum ether, to obtain very pale yellow cubic crystals (17.2 g, 71%) m.p. (vac. capillary) 98-100°. Calculated for \( \text{C}_7\text{H}_6\text{BrNSO}_4 \): C, 30.01; H, 2.16; Br, 28.52; N, 5.00; S, 11.45%. Found: C, 30.36; H, 2.33; Br, 28.44; N, 5.03; S, 11.36%. The benzylic protons showed up as a singlet at 5.07 p.p.m. in the n.m.r. spectrum (CDCl\(_3\)).

Major infrared peaks below 1700 cm\(^{-1}\) (CHCl\(_3\), 5%, 0.2 mm): 1538 (vs), 1368 (vs), 1356 (vs), 1252 (m), 1160 (vs), 1134 (m), 905 (m), 868 (m), 815 (m), 808 (m), 687 (m), 620 cm\(^{-1}\) (m).

b) from the sodium sulphinate.

A mixture of m-nitrobenzyl chloride (1.7 g, 1.0 moles) and sodium sulphite (1.3 g) was refluxed in water (25 ml) for 4 hours. The solution was completely homogeneous after this length of time. The solution was washed once with methylene chloride (20 ml) and the water was removed under reduced pressure. After the solid (3 g) had been thoroughly dried at 100° it was mixed with phosphorus pentabromide (10 g). The mixture was heated at 60° for 5 minutes to start the reaction. Methylene chloride (50 ml) was added and the solution was washed 3 times with water, and dried. Removal of the solvent under reduced pressure afforded a brown solid (2.0 g, 71%) which was recrystallized from methylene chloride-pentane, m.p. 98-101°.
5. \textit{p-Nitrophenylmethanesulphonyl-1,1-\textsubscript{d}_2} bromide

The procedure used was similar to that used by Durst (3) for the preparation of phenylmethanesulphonyl-1,1-\textsubscript{d}_2 chloride. \textit{p-Nitrophenylmethanesulphonyl} chloride (24.2 g) was dissolved in dry dioxane (100 ml) containing deuterium oxide (50 ml). Freshly distilled triethylamine (30 ml) was added with stirring, over a period of 5 minutes and the resulting dark red solution allowed to stand at room temperature for a further 5 minutes. Evaporation of the solvent under reduced pressure produced a brown residue which was treated with 2:1 water-ether (200 ml) in order to dissolve as much as the material as possible. The insoluble brown residue was filtered off (3.8 g, m.p. 105-110°). The aqueous layer was washed once more with ether and the water removed under reduced pressure. The yellow, solid residue was dissolved in chloroform and phosphorus pentachloride (45 g.) was added in small portions over a period of 15 minutes. Stirring was continued for 15 minutes more at room temperature. The chloroform solution was washed with sodium bisulphite solution and water, and dried. A yellow crystalline material (17.2 g) was obtained after removal of the chloroform. Three more treatments of the crude sulphonyl chloride with deuterium oxide and triethylamine in dioxane yielded a yellow crystalline material. (10.1 g).
Using the procedure as described above but with phosphorus pentabromide rather than pentachloride, \( p \)-nitrophenylmethanesulphonyl-1,1-d\(_2\) bromide (9.2 g) was obtained which was recrystallized from chloroform-petroleum ether, m.p. 111-114\(^\circ\). Calculated for C\(_7\)H\(_4\)D\(_2\)BrNO\(_4\): 33.33 atom % excess D. Found: 30.00 atom % excess D. The n.m.r. spectrum showed a small band, at 4.98 p.p.m. besides aromatic absorption. The infrared spectrum showed bands at 2232 cm\(^{-1}\) and 2141 cm\(^{-1}\) ascribable to C-D stretching. Major peaks in the infrared spectrum below 1700 cm\(^{-1}\) (CHCl\(_3\), 10%, 0.1 mm.) were; 1607 (m), 1527 (vs), 1369 (vs), 1354 (vs), 1316 (m), 1162 (vs), 1110 (m), 862 (m), 854 (s), 697 (m), 635 cm\(^{-1}\) (m).

6. \( p \)-Chlorophenylmethanesulphonyl bromide

A solution of crude \( p \)-chlorophenylmethanesulphonyl chloride (45 g, 0.2 moles) and sodium sulphite (56 g, 0.45 moles) in water (250 ml) was stirred at 70\(^\circ\). When all of the sulphonyl chloride had reacted (about 15 minutes) the solution was filtered and washed twice with methylene chloride. The sodium sulphinate solution was added dropwise to a cooled mixture of N-bromoacetamide (62 g, 0.45 moles) in a 1:1 mixture (500 ml) of methylene chloride and water. The rate of the addition was controlled to keep the temperature of the solution below 10\(^\circ\). After the solution was washed with 2% sodium bisulphite solution and water, and dried, removal
of the solvent afforded a white solid (38.8 g). Fractional crystallization from carbon tetrachloride and then from petroleum ether (60-80°) to remove the less soluble impurity gave p-chlorophenylmethanesulphonyl bromide showing no evident impurity by infrared and n.m.r. spectroscopy, m.p. 64-65°. Calculated for C₇H₆BrClO₂S: C, 31.19; H, 2.24; Br, 29.64; Cl, 13.15; S, 11.90%. Found: C, 31.29; H, 2.36; Br, 29.74; Cl, 13.20; S, 12.04%. N.m.r. bands (CCl₄) at 4.83 p.p.m. (singlet) and 7.41 p.p.m. (singlet). Infrared (CCl₄, 5%, 0.2 mm) peaks below 1600 cm⁻¹ included: 1597 (m), 1492 (s), 1374 (vs), 1163 (vs), 1098 (s), 1017 (m), 838 cm⁻¹ (m). The less soluble impurity from above was recrystallized from carbon tetrachloride m.p. 130.5°. Calculated for C₁₄H₁₂Cl₂O₂S₂: C, 48.42; H, 3.48; S, 18.04%. Found: C, 48.99; H, 3.34; S, 17.79%. N.m.r. bands (CDCl₃) 4.08 p.p.m. (singlet), 4.24 p.p.m. (singlet), and 7.30 p.p.m. (multiplet); relative areas 1:1:4.

Infrared (CHCl₃, 5%, 0.2 mm) peaks below 1600 cm⁻¹ included: 1597 (m), 1492 (s), 1331 (vs), 1142 (s), 1131 (s), 1122 (s), 1095 (s), 1017 (m), and 838 cm⁻¹ (m).

7. m-Chlorophenylmethanesulphonyl bromide

The crude oil (31.5 g, 0.14 moles) obtained from the preparation of m-chlorophenylmethanesulphonyl chloride was
stirred with sodium sulphite (35 g, 0.28 moles) in water (250 ml) at 70° until no more reaction appeared to take place (30 min.). The solution was filtered and washed twice with methylene chloride. After addition of the sodium sulphinate solution to a mixture of N-bromoacetamide (39 g, 0.28 moles) in a 2:1 mixture (450 ml) of methylene chloride: water, the resulting solution was worked up as in the previous experiment to yield a white solid (25.4 g). The compound was recrystallized from carbon tetrachloride, m.p. 81-82°. Calculated for C₇H₆BrClO₂S: C, 31.19; H, 2.24; Br, 29.64; Cl, 13.15; S, 11.90%. Found: C, 31.36; H, 2.41; Br, 29.74; Cl, 13.20; S, 12.00%. N.m.r. bands (CCl₄) at 4.83 p.p.m. (singlet) and 7.43 p.p.m. (multiplet). Major infrared (CHCl₃, 5%, 0.2 mm) below 1500 cm⁻¹ included: 1478 (m), 1408 (m), 1370 (vs), 1161 (vs), 896 cm⁻¹ (m).

8. p-Methylphenylmethanesulphonyl bromide

Impure p-methylphenylmethanesulphonyl chloride (25 g, 0.1 moles) was reduced to the sodium sulphinate with sodium sulphite (26 g, 0.21 moles) in water (250 ml) at 60°. The solution was filtered and washed once with methylene chloride. The aqueous phase was rapidly stirred mechanically with methylene chloride (300 ml) and crushed ice. N-bromoacetamide was added in small portions until a permanent brown
colour was obtained. Crushed ice was also added from time to time to keep the temperature at, or near, 0°. The organic phase was washed with 2% sodium bisulphite solution, water and dried. Removal of solvent under reduced pressure furnished a white solid (17.0 g). Recrystallization from pentane gave white needles, m.p. 55-57°, the n.m.r. spectrum of which indicated it to be free of impurities. Calculated for C₈H₇BrO₂S: C, 38.54; H, 3.64; Br, 32.07; S, 12.86%. Found: C, 38.84; H, 3.66; Br, 32.10; S, 12.92%. Major infrared peaks (CCl₄, 10%, 0.1 mm) below 1600 cm⁻¹ included: 1513 (m), 1372 (vs), 1202 (m), 1172 (m), 1160 (vs), 1133 (m), 872 (m), 823 (m) 690 cm⁻¹ (m). The n.m.r. spectrum (CCl₄) showed bands at 2.38 p.p.m. (singlet), 4.82 p.p.m (singlet) and 7.30 p.p.m. (multiplet).

10. 2-Phenylethanesulphonyl bromide

Sodium 2-phenylethanesulphonate (3 g) (19) and phosphorus pentabromide were ground together and heated at 120° for 20 minutes. The mixture was allowed to stand at room temperature for a further 30 minutes and poured into a mixture of ice, water, and ether. The aqueous phase was extracted twice with ether and the combined organic phases dried. Removal of the solvent under reduced pressure gave a brown solid (2.6 g, 87%), which was recrystallized from chloroform - petroleum ether to yield white fine needles,
m.p. 56-58°; reported m.p. 59-60° (90).

11. **Methanesulphonyl bromide**

Methanesulphonyl chloride (Eastman, 11.5 g, 0.1 moles) and sodium sulphite (26 g, 0.21 moles) were stirred in water (200 ml) at 50° for 1 hour. The solution, which was completely homogeneous, was washed once with methylene chloride. Methylene chloride (100 ml) was added. Addition of N-bromoacetamide to the cooled solution was controlled, so that the temperature did not rise above 10°. When a permanent brown colour was obtained the methylene chloride solution was washed with 2% sodium bisulphite solution, and water, and dried. Removal of the solvent under reduced pressure at room temperature produced a colourless oil. Distillation yielded a clear colourless oil (7.9 g, 50%), b.p. 82-83°, (17 mm); reported b.p. 44-46° (1 mm) (92). The infrared spectrum (CCl₄, IR-10) was similar to that of methanesulphonyl chloride showing very strong sulphonyl absorption at 1365 and 1160 cm⁻¹.
III MEASUREMENT OF THE RATE OF THE REACTION

A. By titration of the sulphur dioxide produced.

1. Preparation of Solutions.

   Sodium thiosulphate:

   Allied Chemical Reagent grade was dissolved in water and sodium carbonate (0.1 g per litre) added. The solution was standardized in the normal manner (93) after 24 hours.

   Iodine:

   Iodine (B.D.H. Analar) was dissolved in a small amount of water together with potassium iodide (93). The solution was made up to the required volume and was not standardized, although it was usually approximately the same normality as the sodium thiosulphate solution used in a particular experiment.

2. General Procedure for Rate Determinations

   a) In methylene chloride solution

   To a solution (25 ml, 0.02 M) of the sulphonyl halide in methylene chloride was added a solution (25 ml) of the halide salt. Timing was started at the beginning of the transfer. The solution was thoroughly mixed and placed in a water bath whose temperature was controlled by a "Haake Unitherm" thermostat to $\pm 0.05^\circ$. After an appropriate time interval the reaction mixture was poured into a solution of sodium
hydroxide (1 g) in water (150 ml). The solution was thoroughly shaken and the organic phase removed. After acidification with concentrated sulphuric acid, iodine solution (50 ml) was added by pipette. The excess iodine was titrated with sodium thiosulphate solution using B.D.H. "Iodine Indicator". The percentage reaction was calculated and the best straight line for log (100-% reaction) versus time calculated using a computer and a least mean-square programme. The pseudo first order rate constant was calculated from the slope and the apparent second order rate constant obtained from this by introducing a term for the bromide ion concentration. The standard deviation of the rate constant was calculated (103) from the deviation of log (100-% reaction) given by the computer programme.

a) In acetonitrile solution

To the sulphonyl halide dissolved in acetonitrile in a standard volumetric flask was added a solution of the halide salt in acetonitrile. The solution was made up to the mark and timing was started. The flask was immersed in a constant temperature waterbath. After an appropriate time interval an aliquot (50 ml) was transferred to an aqueous solution of sodium hydroxide (1 g, in 200 ml). The mixture was thoroughly shaken. Iodine solution (50 ml) was added after acidification with concentrated sulphuric acid, and
after allowing the solution to stand at room temperature for 5 minutes the excess iodine was titrated against sodium thiosulphate using B.D.H. "Iodine Indicator".

The values quoted in the following tables are representative of the values obtained. In all cases more than one kinetic run was carried out.
a) Reactions in methylene chloride

1. The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.01 M)

SOLUTIONS: TEMPERATURE: 35.0 ± 0.05°C

Phenylmethanesulphonyl bromide: 1.175 g in 250 ml
Tetraethylammonium bromide: 1.051 g in 250 ml
SODIUM THIOSULPHATE: 0.05 N BLANK: 25.00 ml

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\[ k_2 = 5.8 \pm 0.4 \text{ l.mole}^{-1}\text{sec}^{-1} \]
2. **The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.002 M)**

**SOLUTIONS:**

- Phenylmethanesulphonyl bromide: 1.175 g in 250 ml
- Tetraethylammonium bromide: 0.410 g in 500 ml

**SODIUM THIOSULPHATE:** 0.050 N  **BLANK:** 25.00 ml

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\[ k_2 = 6.2 \pm 0.38 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
3. **The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M).**

**SOLUTION:**  
**TEMPERATURE:**  35.0° ± 0.05°

Phenylmethanesulphonyl bromide: 1.175 g dissolved in 250 ml  
Tetraethylammonium bromide: 0.210 g dissolved in 500 ml  

**SODIUM THIOSULPHATE:** 0.050 N  
**BLANK:** 24.60 ml

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\[ k_2 = 6.0 + 0.36 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
4. **The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.0005 M)**

**SOLUTIONS:**
- Phenylmethanesulphonyl bromide: 1.175 g, in 250 ml
- Tetraethylammonium bromide: 0.105 g, in 500 ml

**TEMPERATURE:** 35.0 ± 0.05°

**SODIUM THIOSULPHATE:** 0.050 N  **BLANK:** 25.00 ml

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\[ k_2 = 6.9^{+} - 0.5 \text{ l.mole}^{-1}\text{sec}^{-1} \]
5. **The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.00025 M)**

**SOLUTIONS:**

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<tbody>
<tr>
<td>Phenylmethanesulphonyl bromide:</td>
<td>1.175 g, in 250 ml</td>
</tr>
<tr>
<td>Tetraethylammonium bromide:</td>
<td>0.0525 g, in 500 ml</td>
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**SODIUM THIOSULPHATE: 0.050 N**  **BLANK: 25.00 ml**

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\[ k_2 = 6.4 ± 0.5 \times 10^{-2} \text{ l.mole}^{-1} \text{sec}^{-1} \]
6. The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.0001 M)

SOLUTIONS: 
Temperature: 35.0 ± 0.05°

Phenylmethanesulphonyl bromide: 1.175 g, in 250 ml
Tetraethylammonium bromide: 0.0210 g, in 500 ml

SODIUM THIOSULPHATE: 0.0249 N  BLANK: 49.55 ml

<table>
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\[ k_2 = 6.8 \pm 0.1 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
7. **The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.0123 M)**

**SOLUTIONS:**

**TEMPERATURE:** $25.0 \pm 0.05^\circ$

Phenylmethanesulphonyl bromide: 1.175 g, in 250 ml

Tetraethylammonium bromide: 1.2957 g, in 250 ml

**SODIUM THIOSULPHATE:** 0.0255 N  \hspace{1cm} **BLANK:** 47.20 ml

<table>
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$k_2 = 2.35 \pm 0.3 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1}$
8. The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M)

SOLUTIONS:  
TEMPERATURE: 25.0 $^\pm$ 0.05$^\circ$

Phenylmethanesulphonyl bromide 2.351 g, in 500 ml
Tetraethylammonium bromide 0.210 g, in 500 ml

SODIUM THIOSULPHATE: 0.0251 N  BLANK: 48.25 ml

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<tr>
<td>11.0</td>
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<td>1.5835</td>
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</tbody>
</table>

$k_2 = 2.45 \pm 0.13 \times 10^{-2}$ l.mole$^{-1}$sec$^{-1}$
9. The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.00012 M)

SOLUTIONS:  
TEMPERATURE: 25.0° ± 0.05°

Phenylmethanesulphonyl bromide: 2.351 g, in 500 ml
Tetraethylammonium bromide: 0.0128 g, in 250 ml
SODIUM THIOSULPHATE: 0.0255 N  BLANK: 44.30 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.7005</td>
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<td>73.8</td>
<td>18.30</td>
<td>66.27</td>
<td>1.5280</td>
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</tbody>
</table>

\[ k_2 = 3.1 \pm 0.1 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
10. The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M)

**SOLUTIONS:**

<table>
<thead>
<tr>
<th></th>
<th>TEMPERATURE: 0.0 °C + 0.1 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylmethanesulphonyl bromide:</td>
<td>1.175 g, in 250 ml</td>
</tr>
<tr>
<td>Tetraethylammonium bromide:</td>
<td>0.210 g, in 500 ml</td>
</tr>
</tbody>
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**SODIUM THIOSULPHATE:** 0.0256 N  **BLANK:** 48.50 ml

<table>
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<th>TIME (hr)</th>
<th>TITRE (ml)</th>
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<th>LOG (100-% REACTION)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
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<td>1.9721</td>
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<tr>
<td>20</td>
<td>45.50</td>
<td>7.70</td>
<td>1.9652</td>
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<tr>
<td>28</td>
<td>44.20</td>
<td>11.04</td>
<td>1.9492</td>
</tr>
<tr>
<td>52</td>
<td>41.40</td>
<td>18.09</td>
<td>1.9134</td>
</tr>
<tr>
<td>76</td>
<td>38.60</td>
<td>25.25</td>
<td>1.8736</td>
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<td>114</td>
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<td>32.96</td>
<td>1.8264</td>
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<td>162</td>
<td>30.70</td>
<td>45.66</td>
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<tr>
<td>186</td>
<td>28.50</td>
<td>51.30</td>
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</table>

\[ k_2 = 1.04 \pm 0.03 \times 10^{-3} \ \text{mole}^{-1}\text{sec}^{-1} \]
11. The reaction of phenylmethanesulphonyl bromide with triethylamine hydrobromide (0.05 M)

SOLUTIONS:  
TEMPERATURE: 35.0 ± 0.05°

Phenylethanesulphonyl bromide: 1.175 g, in 250 ml
Triethylamine hydrobromide: 4.553 g, in 250 ml

SODIUM THIOSULPHATE: 0.050 N  
BLANK: 25.00 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-%REACTION)</th>
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</thead>
<tbody>
<tr>
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<td>10.00</td>
<td>1.9542</td>
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<tr>
<td>1.0</td>
<td>22.30</td>
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<td>1.6021</td>
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</table>

\[ k_2 = 7.7 + 0.7 \times 10^{-4} \text{ l.mole}^{-1}\text{sec}^{-1} \]
12. **The reaction of phenylmethanesulphonyl bromide with triethylamine hydrobromide (0.001 M)**

**SOLUTIONS:**

- Phenylmethanesulphonyl bromide: 1.175 g, in 250 ml
- Triethylamine hydrobromide: 0.8926 g, in 250 ml

**SODIUM THIOSULPHATE:** 0.0260 N  **BLANK:** 48.90 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
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<th>LOG (100-% REACTION)</th>
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</thead>
<tbody>
<tr>
<td>25.0</td>
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<td>14.29</td>
<td>1.9331</td>
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<td>54.5</td>
<td>39.35</td>
<td>24.79</td>
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<td>72.5</td>
<td>33.60</td>
<td>39.73</td>
<td>1.7801</td>
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<td>141.5</td>
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<td>191.5</td>
<td>23.90</td>
<td>64.91</td>
<td>1.5452</td>
</tr>
</tbody>
</table>

\[ k_2 = 1.5 \pm 0.2 \times 10^{-4} \text{ l.mole}^{-1}\text{sec}^{-1} \]
13. The reaction of phenylmethanesulphonyl bromide with tetra n-butylammonium bromide.

SOLUTIONS: 

TEMPERATURE: 25.0 ± 0.05°C

Phenylmethanesulphonyl bromide: 1.175 g, in 250 ml
Tetra n-butylammonium bromide: 0.1321 g, in 250 ml

SODIUM THIOSULPHATE: 0.0255 N BLANK: 48.60 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
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</thead>
<tbody>
<tr>
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<td>1.8067</td>
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<td>30.40</td>
<td>46.38</td>
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</table>

\[ k_2 = 2.6 \pm 0.14 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
14. The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.00011 M) in the presence of tetraethylammonium perchlorate (0.013 M)

**SOLUTIONS:**

<table>
<thead>
<tr>
<th></th>
<th><strong>TEMPERATURE:</strong> 25.0 ± 0.05°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylmethanesulphonyl bromide: 2.351 g, in 500 ml</td>
<td></td>
</tr>
<tr>
<td>Tetraethylammonium bromide: 0.01175 g</td>
<td></td>
</tr>
<tr>
<td>Tetraethylammonium perchlorate: 1.485 g</td>
<td></td>
</tr>
</tbody>
</table>

**SODIUM THIOSULPHATE:** 0.0255 N  **BLANK:** 44.30 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
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</thead>
<tbody>
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<td>16.05</td>
<td>1.9241</td>
</tr>
<tr>
<td>47.5</td>
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<td>68.0</td>
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<td>40.00</td>
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<td>80.0</td>
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<tr>
<td>91.1</td>
<td>24.40</td>
<td>50.72</td>
<td>1.6927</td>
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</tbody>
</table>

$$k_2 = 1.9 + 0.06 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1}$$
15. The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.0012 M) in the presence of benzoyl peroxide (0.0017 M)

SOLUTIONS:  
TEMPERATURE: 25.0 ± 0.05°  
Phenylmethanesulphonyl bromide: 1.175 g in 250 ml  
Benzoyl peroxide: 0.205 g  
Tetraethylammonium bromide: 0.1261 g in 250 ml

SODIUM THIOSULPHATE: 0.0253 N  BLANK: 47.10 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
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</thead>
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<td>43.35</td>
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<td>1.9563</td>
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<td>1.8720</td>
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<td>34.70</td>
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<td>1.8347</td>
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<td>31.95</td>
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<tr>
<td>9.0</td>
<td>26.25</td>
<td>53.26</td>
<td>1.6697</td>
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</table>

\[ k_2 = 2.15 \pm 0.05 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
16. The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M) in the presence of styrene (0.02 M).

**SOLUTIONS:**

<table>
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<tr>
<th></th>
<th>TEMPERATURE: 25.0 ± 0.05°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylmethanesulphonyl bromide: 1.175 g</td>
<td>in 250 ml</td>
</tr>
<tr>
<td>Styrene:</td>
<td>1.042 g</td>
</tr>
<tr>
<td>Tetraethylammonium bromide: 0.105 g in 250 ml</td>
<td></td>
</tr>
</tbody>
</table>

**SODIUM THIOSULPHATE:** 0.0253 N  
**BLANK:** 48.80 ml

<table>
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<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
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<th>LOG (100-% REACTION)</th>
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</thead>
<tbody>
<tr>
<td>0.0</td>
<td>48.10</td>
<td>1.77</td>
<td>1.9923</td>
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<tr>
<td>2.0</td>
<td>42.40</td>
<td>16.19</td>
<td>1.9668</td>
</tr>
<tr>
<td>3.0</td>
<td>39.75</td>
<td>22.89</td>
<td>1.9336</td>
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<td>1.8119</td>
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<td>31.70</td>
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<td>1.7540</td>
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<td>8.0</td>
<td>28.65</td>
<td>50.97</td>
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</table>

\[ k_2 = 2.5 \pm 0.27 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
17. The reaction of \( p \)-nitrophenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M)

**SOLUTIONS:**
- **TEMPERATURE:** 35.0 ± 0.05°
- \( p \)-Nitrophenylmethanesulphonyl bromide: 1.400 g in 250 ml
- Tetraethylammonium bromide: 0.210 g in 500 ml

**SODIUM THIOSULPHATE:** 0.0246 N  **BLANK:** 49.25 ml

<table>
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<td>1.8944</td>
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<tr>
<td>1.0</td>
<td>37.85</td>
<td>28.20</td>
<td>1.8561</td>
</tr>
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<td>1.5</td>
<td>32.20</td>
<td>42.13</td>
<td>1.7624</td>
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<td>26.95</td>
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<td>1.6521</td>
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</table>

\[ k_2 = 8.4 \pm 0.8 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
18. The reaction of $p$-nitrophenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M)

SOLUTIONS: TEMPERATURE: 25.0 ± 0.05°

$p$-Nitrophenylmethanesulphonyl bromide: 2.800 g in 500 ml
Tetraethylammonium bromide: 0.210 g in 500 ml

SODIUM THIOSULPHATE 0.0255 N BLANK: 47.30 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
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</thead>
<tbody>
<tr>
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<td>1.8969</td>
</tr>
<tr>
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<td>1.8722</td>
</tr>
<tr>
<td>2.0</td>
<td>34.65</td>
<td>31.63</td>
<td>1.8348</td>
</tr>
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<td>6.0</td>
<td>23.75</td>
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</table>

$k_2 = 3.85 \pm 0.3 \times 10^{-2} \text{ 1.mole}^{-1}\text{sec}^{-1}$ (6 runs)
19. The reaction of m-nitrophenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M)

SOLUTIONS: TEMPERATURE: 35.0 ± 0.05°

m-Nitrophenylmethanesulphonyl bromide: 1.400 g in 250 ml
Tetraethylammonium bromide: 0.210 g in 500 ml

SODIUM THIOSULPHATE: 0.0251 N BLANK: 49.30 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
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</thead>
<tbody>
<tr>
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<td>41.70</td>
<td>19.09</td>
<td>1.9080</td>
</tr>
<tr>
<td>1.0</td>
<td>36.75</td>
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<td>1.8355</td>
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<td>31.00</td>
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<td>3.5</td>
<td>20.90</td>
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</tbody>
</table>

\[ k_2 = 9.9 \pm 0.6 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
20. The reaction of \( m \)-nitrophenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M)

**SOLUTIONS:**

- \( m \)-Nitrophenylmethanesulphonyl bromide: 1.400 g in 250 ml
- Tetraethylammonium bromide: 0.105 g in 250 ml

**TEMPERATURE:** 25.0 ± 0.05°

**SODIUM THIOSULPHATE:** 0.0255 N  **BLANK:** 48.10 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
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</thead>
<tbody>
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<td>1.9916</td>
</tr>
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<td>1.9358</td>
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<td>47.25</td>
<td>1.7222</td>
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</table>

\[ k_2 = 3.5 + 0.2 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
21. The reaction of \( m \)-Nitrophenylmethanesulphonyl bromide with Tetraethylammonium bromide (0.001 M)

**SOLUTIONS:**

- \( m \)-Nitrophenylmethanesulphonyl bromide: 1.400 g in 250 ml
- Tetraethylammonium bromide: 0.106 g in 250 ml

**TEMPERATURE:** 0.0 ± 0.1°C

**SODIUM THIOSULPHATE:** 0.0253 N  **BLANK:** 46.80 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.1</td>
<td>43.10</td>
<td>9.23</td>
<td>1.9580</td>
</tr>
<tr>
<td>38.7</td>
<td>39.40</td>
<td>18.72</td>
<td>1.9100</td>
</tr>
<tr>
<td>67.1</td>
<td>35.75</td>
<td>27.94</td>
<td>1.8577</td>
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<td>196.2</td>
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<td>1.6341</td>
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</table>

\( k_2 = 1.16 \pm 0.09 \times 10^{-3} \text{ l.mole}^{-1} \text{sec}^{-1} \)
22. The reaction of \( p \)-chlorophenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M)

SOLUTIONS:  
\[ \text{TEMPERATURE: } 35.0 \pm 0.05^\circ \]
\[ p \)-Chlorophenylmethanesulphonyl bromide: 1.348 g in 250 ml \]
\[ \text{Tetraethylammonium bromide: 0.210 g in 500 ml} \]

SODIUM THIOSULPHATE: 0.0247 N  
BLANK: 48.95 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100- % REACTION)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>18.73</td>
<td>1.9100</td>
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<tr>
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<td>35.80</td>
<td>32.61</td>
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<td>31.10</td>
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<td>1.7461</td>
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<td>1.6538</td>
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<td>1.6045</td>
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<td>21.55</td>
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<td>1.5055</td>
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</table>

\[ k_2 = 10.1 \pm 0.2 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
23. The reaction of $p$-chlorophenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M)

**SOLUTIONS:**

- **TEMPERATURE:** 25.0 $^\circ\text{C}$
- $p$-Chlorophenylmethanesulphonyl bromide: 1.348 g in 250 ml
- Tetraethylammonium bromide: 0.210 g in 500 ml

**SODIUM THIOSULPHATE:** 0.255 N  **BLANK:** 50.65 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG(100-% REACTION)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>47.70</td>
<td>7.52</td>
<td>1.9661</td>
</tr>
<tr>
<td>2.0</td>
<td>42.30</td>
<td>21.28</td>
<td>1.8961</td>
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<td>39.60</td>
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<td>1.8563</td>
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<td>4.0</td>
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<td>1.7495</td>
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<td>1.7230</td>
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<td>8.0</td>
<td>26.95</td>
<td>60.39</td>
<td>1.5978</td>
</tr>
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</table>

$k_2 = 3.15 + 0.27 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1}$
The reaction of m-chlorophenylmethanesulphonyl bromide

tetraethylammonium bromide (0.001 M)

SOLUTIONS:  
TEMPERATURE: 35.0 ± 0.05°

m-Chlorophenylmethanesulphonyl bromide: 1.348 g in 250 ml
Tetraethylammonium bromide: 0.210 g in 500 ml

SODIUM THIOSULPHATE: 0.0247 N  BLANK: 47.00 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>40.15</td>
<td>16.99</td>
<td>1.9192</td>
</tr>
<tr>
<td>1.5</td>
<td>36.75</td>
<td>25.45</td>
<td>1.8725</td>
</tr>
<tr>
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<td>33.00</td>
<td>34.72</td>
<td>1.8147</td>
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<td>38.71</td>
<td>1.7874</td>
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<td>43.90</td>
<td>1.7490</td>
</tr>
<tr>
<td>3.5</td>
<td>28.30</td>
<td>46.37</td>
<td>1.7292</td>
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<td>4.5</td>
<td>23.80</td>
<td>57.54</td>
<td>1.6280</td>
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</table>

\[ k_2 = 5.1 \pm 0.3 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
25. The reaction of \textit{m}-chlorophenylmethanesulphonyl bromide

with tetraethylammonium bromide (0.001 M)

\textbf{SOLUTIONS:}

\textbf{TEMPERATURE:} \(25.0 \pm 0.05^\circ\)

\textit{m}-Chlorophenylmethanesulphonyl bromide: 1.348 g in 250 ml

Tetraethylammonium bromide: 0.210 g in 500 ml

\textbf{SODIUM THIOSULPHATE:} 0.0252 N \quad \textbf{BLANK:} 46.35 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
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</thead>
<tbody>
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</tr>
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<td>38.75</td>
<td>19.13</td>
<td>1.9078</td>
</tr>
<tr>
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<td>34.10</td>
<td>30.82</td>
<td>1.8400</td>
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<td>31.20</td>
<td>38.13</td>
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<tr>
<td>10.5</td>
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</tr>
<tr>
<td>11.5</td>
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<td>1.6878</td>
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</table>

\[k_2 = 1.7 \pm 0.1 \times 10^{-2} \text{ l.mole}^{-1} \text{sec}^{-1}\]
26. The reaction of \( p \)-methylphenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M)

**SOLUTIONS:**

- \( p \)-Methylphenylmethanesulphonyl bromide: 1.246 g in 250 ml
- Tetraethylammonium bromide: 0.210 g in 500 ml

**TEMPERATURE:** 25.0 ± 0.05°C

**SODIUM THIOSULPHATE:** 0.0256 N  **BLANK:** 49.05 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>18.86</td>
<td>1.9092</td>
</tr>
<tr>
<td>0.25</td>
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<td>20.91</td>
<td>1.8981</td>
</tr>
<tr>
<td>0.5</td>
<td>39.40</td>
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</tr>
<tr>
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</tr>
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<td>35.35</td>
<td>35.15</td>
<td>1.8119</td>
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<tr>
<td>3.5</td>
<td>26.90</td>
<td>56.83</td>
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</table>

\[ k_2 = 5.3 \pm 0.4 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
27. The reaction of phenylmethanesulphonyl chloride with tetraethylammonium chloride (0.01 M)

SOLUTIONS:  TEMPERATURE:  25.0 ± 0.05°

Phenylmethanesulphonyl chloride:  0.9333 g in 250 ml
Tetraethylammonium chloride:  1.657 g in 500 ml

SODIUM THIOSULPHATE:  0.0254 N  BLANK:  49.00 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>12.45</td>
<td>1.9422</td>
</tr>
<tr>
<td>49</td>
<td>39.80</td>
<td>23.37</td>
<td>1.8842</td>
</tr>
<tr>
<td>75</td>
<td>36.55</td>
<td>31.62</td>
<td>1.8349</td>
</tr>
<tr>
<td>98</td>
<td>33.85</td>
<td>38.49</td>
<td>1.7890</td>
</tr>
<tr>
<td>122</td>
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<tr>
<td>149</td>
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<td>1.7041</td>
</tr>
<tr>
<td>169</td>
<td>28.35</td>
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<td>1.6770</td>
</tr>
<tr>
<td>193</td>
<td>26.70</td>
<td>56.65</td>
<td>1.6370</td>
</tr>
</tbody>
</table>

\[ k_2 = 1.15 ± 0.05 \times 10^{-4} \text{ mole}^{-1} \text{sec}^{-1} \]
b) Reactions in acetonitrile

1. The reaction of phenylmethanesulphonyl bromide with triethylamine hydrobromide: (0.05 M)

SOLUTION:  
TEMPERATURE: 25.0 \( \pm \) 0.05\(^\circ\)  
Phenylmethanesulphonyl bromide: (1.175 g) and  
Triethylamine hydrobromide: (0.5450 g) dissolved in 500 ml

SODIUM THIOSULPHATE: 0.0255 N  
BLANK: 49.10 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
</tr>
</thead>
<tbody>
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<td>2.0</td>
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<td>1.5234</td>
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<tr>
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<td>70.71</td>
<td>1.4667</td>
</tr>
<tr>
<td>4.0</td>
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</tbody>
</table>

\[ k_2 = 1.85 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]

with 0.4204 g triethylamine hydrobromide

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.9356</td>
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<tr>
<td>1.0</td>
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<td>1.8779</td>
</tr>
<tr>
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<td>35.90</td>
<td>33.70</td>
<td>1.8215</td>
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<tr>
<td>2.0</td>
<td>33.40</td>
<td>40.07</td>
<td>1.7776</td>
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</tbody>
</table>

\[ k_2 = 1.45 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]

\[ k_2 \text{ (average)} = 1.65 \pm 0.2 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]
2. The reaction of phenylmethanesulphonyl bromide with tetraethylammonium bromide (0.001 M)

SOLUTION:  
TEMPERATURE:  25.0 ± 0.05°

Phenylmethanesulphonyl bromide: (1.175 g) and
Tetraethylammonium bromide: (0.105 g) dissolved in 500 ml

SODIUM THIOSULPHATE: 0.0255 N  BLANK: 47.60 ml

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>TITRE (ml)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>3.5</td>
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</table>

$k_2 = 7.9 \pm 0.2 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1}$
B. By Vapour Phase Chromatography

a) The reaction of methanesulphonyl bromide with tetraethylammonium bromide.

A solution of redistilled methanesulphonyl bromide (295 mg, 1.86 mmoles) and tetraethylammonium bromide (210 mg, 1.0 mmoles) in methylene chloride (10 ml) was allowed to stand in a waterbath at 25°. From time to time a 5 μ litre sample was removed with a syringe and injected into a F. and M. Laboratory Chromatograph model 700. It was possible to separate the components of the mixture using a 10% carbowax column. The amount of methyl bromide produced in the reaction was estimated by cutting out and weighing the peak corresponding to that compound and comparing it to a peak produced under the same instrumental conditions from a known solution of methyl bromide (Eastman, 40 mg in 10 ml methylene chloride). It was shown that a comparable solution of methanesulphonyl bromide in methylene chloride, with no tetraethylammonium bromide added, did not produce any significant methyl bromide after 100 hours.
COLUMN: 10% Carbowax 20M on Chromosorb 3(AW) 80-100 mesh

OVEN TEMPERATURE: 25°

FLOW RATE: 25 ml per min.  
SAMPLE: 5 μ litre

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>% REACTION</th>
<th>LOG (100-% REACTION)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.8</td>
<td>6.7</td>
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</tr>
<tr>
<td>7.7</td>
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<tr>
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<td>72.2</td>
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<td>121.2</td>
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<td>1.777</td>
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</tbody>
</table>

\[ k_2 = 1.0 \times 10^{-5} \pm 0.4 \text{ l.mole}^{-1} \text{sec}^{-1} \]

C. **By Infrared Spectroscopy**

a) The reaction of 2-phenylethanesulphonyl bromide with tetraethylammonium bromide.

A solution of 2-phenylethanesulphonyl bromide (1.000 g) and tetraethylammonium bromide (420 mg, 2.0 mmoles) in methylene chloride (10 ml) was allowed to stand in a constant temperature waterbath at 25°. From time to time an infrared spectrum of the reaction mixture was taken using potassium bromide cells on a Beckman IR-5 (CsBr optics) instrument.
The spectrum obtained was compared to spectra of authentic samples of PhCH$_2$CH$_2$SO$_2$Br, PhCH$_2$CH$_2$Br, and Et$_4$N$^+$Br$^-$ in methylene chloride (10%, 0.1 mm.). It was noted that PhCH$_2$CH$_2$Br has a band at 650 cm$^{-1}$ whereas the other materials did not. By estimation of the peak height of that band, after concentration corrections, it was possible to calculate the approximate extent of the reaction.

The 650 cm$^{-1}$ band height for a 10% solution of 2-phenylethyl bromide (Eastman) was 0.15.

$$100\% \text{ reaction} = 0.15 \times \frac{185}{249}$$

<table>
<thead>
<tr>
<th>TIME (hr)</th>
<th>BAND HEIGHT</th>
<th>% REACTION</th>
<th>$k_2$(1.mole$^{-1}$sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.024</td>
<td>21</td>
<td>$3.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>312</td>
<td>0.038</td>
<td>34</td>
<td>$1.9 \times 10^{-6}$</td>
</tr>
<tr>
<td>672</td>
<td>0.072</td>
<td>78</td>
<td>$3.1 \times 10^{-6}$</td>
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</tbody>
</table>

$$k_2 = 2.8 + 0.9 \times 10^{-6} \text{ 1.mole}^{-1}\text{sec}^{-1}$$

The Relative Nucleophilicity of Bromide and Chloride Ions In Methylene Chloride.

1. Preparation of benzyl phenylmethanesulphonate.

Triethylamine (6 ml) was added dropwise to a solution of phenylmethanesulphonyl chloride (3.8 g, 0.02 moles) and benzyl alcohol (Matheson, 10 ml, 0.097 moles) in methylene chloride (50 ml). After the solution had stood for 2 minutes
it was washed with dilute sulphuric acid, 4 times with water, and dried. The removal of the solvent in vacuo yielded a yellow solid (4.1 g), which was recrystallized from methylene chloride-pentane to give white plates m.p. 77-78°. Calculated for C_{14}H_{14}SO_3: C, 64.11; H, 5.38; S, 12.20%. Found: C, 63.95; H, 5.46; S, 12.12%. The benzylic protons appeared in the n.m.r. spectrum (CDCl₃) at 4.21 p.p.m. (singlet) and 4.99 p.p.m. (singlet). Major peaks in the infrared spectrum (IR-10, 0.1 mm, CHCl₃) below 1600 cm⁻¹ appeared at 1345 (s), 1160 (s), 905 (s), 925 (s), 875 (m), 690 cm⁻¹ (m).

a) Reaction with tetraethylammonium bromide

To a solution of benzyl phenylmethanesulphonate (131 mg, 0.5 mmoles) in methylene chloride (25 ml) was added tetraethylammonium bromide (105 mg, 0.5 mmoles). The solution was allowed to stand in a waterbath at 25° for 90 minutes and then washed twice with water, and dried. Careful removal of the solvent by distillation, and by blowing nitrogen over the solvent left an oily white solid (67 mg). The n.m.r. spectrum (CDCl₃) indicated, from the relative areas of bands at 4.98 p.p.m., and 4.20 p.p.m., and 4.42 p.p.m. a mixture of starting material and benzyl bromide in the ratio of 36:100. The product (67 mg) therefore contained starting material (37 mg) which corresponded to 72% reaction.
b) Reaction with tetraethyammonium chloride.

A solution of benzyl phenylmethanesulphonate (131 mg, 0.5 mmole) and tetraethyammonium chloride (83 mg, 0.5 mmole) in methylene chloride (25 ml) was allowed to react for 90 minutes in a waterbath at 25°. Similar work-up to above gave an oily white solid (56 mg), the n.m.r. spectrum of which indicated a mixture of starting material (band at 4.98 p.p.m. relative area 25) and benzyl chloride (band at 4.50 p.p.m., relative area 94). The product therefore contained starting material (31 mg) which corresponded to 76% reaction.

2. Preparation of benzyl tosylate.

Benzyl tosylate was prepared from benzyl alcohol and \( p \)-toluenesulphonyl chloride by the method of Kochi and Hammond (94) in 70% yield m.p. 56-57°; reported m.p. 58.5-58.9° (94). The n.m.r. spectrum (CDCl\(_3\)) showed bands at 2.34 p.p.m. (singlet) and 4.90 p.p.m. (singlet) relative areas (3:2) besides complex aromatic absorption.

a) To a solution of benzyl tosylate (131 mg, 0.5 mmole) in methylene chloride (25 ml) was added tetraethyammonium bromide (105 mg, 0.5 mmole). The solution was allowed to stand in a waterbath at 25° for 1 hour after which time it was washed twice with water, and dried. Careful removal of
the solvent yielded an oily white solid (105 mg). The n.m.r. spectrum indicated, by the relative areas of the bands corresponding to the benzylic protons of the starting material and product at 4.95 and 4.40 p.p.m. respectively, that there was equal amounts of both compounds in the mixture. This corresponds to 44% reaction.

b) Reaction with tetraethylammonium chloride.

Using the same n.m.r. technique as above a mixture of benzyl tosylate (131 mg, 0.5 mmoles) and tetraethylammonium chloride (86 mg, 0.5 mmoles) in methylene chloride (25 ml) at 25° was shown to produce 46% reaction after 1 hour. A white oily solid (90 mg) was isolated after work-up, the n.m.r. spectrum of which showed bands at 5.00 p.p.m. (singlet, benzylic protons of benzyl tosylate) and 4.53 p.p.m. (singlet, benzylic protons of benzyl chloride); relative areas 58:33.

IV CARBON-13 KINETIC ISOTOPE EFFECT

The benzy]l bromide separated from a known percentage reaction of the phenylmethanesulphonyl bromide with tetraethylammonium bromide (see below) was given to Mr. A.J. McNamara as the crude product. This was oxidized directly to the benzoic acid with potassium permanganate and decarboxylated with sulphuric acid (69) to yield carbon dioxide derived
exclusively from the carbon at which displacement had occurred. All carbon dioxide samples were analyzed on a mass-spectrometer. The $^{12}\text{C}/^{13}\text{C}$ ratios were obtained from the mass 44/mass 45 ion current ratios after a suitable correction for the contribution to mass 45 for the molecular species $^{12}\text{C}^{16}\text{O}^{17}\text{O}$. (66).

Each sample in a given series was compared with a standard, the standard being a sample of carbon dioxide derived from the benzyl bromide that was obtained from a 100% reaction of the sulphonyl bromide with tetraethylammonium bromide.

1. Isolation of the benzyl bromide.

   a) The phenylmethanesulphonyl bromide (20 mmoles) was dissolved in methylene chloride in a 2 litre volumetric flask. Tetraethylammonium bromide (420 mg, 2 mmoles) was added and the volume made up to the mark at which time the stopwatch was started. After the solution was shaken for 2 minutes, to make sure that all the salt had dissolved, it was allowed to stand in a waterbath at 25° for a calculated time corresponding to about 15%. The solution was transferred to a separatory funnel that already contained triethylamine (20 ml), methylene chloride (300 ml) and water (1500 ml). After thoroughly mixing the solution the organic layer was separated and washed with dilute sulphuric acid (5 ml conc. $\text{H}_2\text{SO}_4$ in 1500 ml water), and twice with water. The methylene chloride was dried, and distilled from a waterbath at 50-55° through a 12 inch Vigreux
column. The sample was supplied, usually in methylene chloride (about 3 ml), to Mr. A.J. McNamara. The infrared spectrum of all solutions supplied showed no sign of any sulphonyl bromide being present.

b) Preparation of standard alkyl bromide.

The phenylmethanesulphonyl bromide (5 mmoles) was dissolved in methylene chloride (50 ml) and tetraethylammonium bromide (2.10 g, 10 mmoles) added. After a period of about 3 days the solution was washed 3 times with water and dried. The sample was presented to be oxidized, after removal of the solvent by distillation, in a small amount of methylene chloride.

V STEREOCHEMICAL COURSE OF THE REACTION

1. Preparation of benzaldehyde-α-δ.

This compound was prepared from freshly distilled benzaldehyde (Fisher, Certified Reagent) as described by Seebach (78), who kindly supplied the procedure prior to publication.

2. Preparation of R(-)-benzyl-α-δ alcohol.

Benzaldehyde-α-δ (25 g) was converted to hydrogen benzyl -α-δ phthalate, (20.0 g) using the procedure of Streitwieser and Wolfe (79), having [α]D + 0.22° (0.1, C18, acetone). The ester was reduced with lithium aluminium hydride (12 g) and
yielded benzyl-\(\alpha\)-\(d\) alcohol (8.7 g, b.p. 60° (2 mm)), having 
\([\alpha]_D^{25} = -1.1° \ (0.01, \text{neat}), \ n_D^{25} = 1.5370. \) The n.m.r. spectrum 
indicated that approximately one proton was present in the 
benzylic position, by an ill defined triplet at 4.43 p.p.m. 
(relative area 1 proton to aromatic absorption at 7.20 p.p.m.). 

3. Preparation of S-(+)-benzyl-\(\alpha\)-\(d\) alcohol.

The following procedure is that described by Mosher 
and co-workers (84) with slight modifications.

Benzaldehyde-\(\alpha\)-\(d\) (6.3 g), dissolved in ethanol (3 ml), 
was added, over a period of 2 hours, to a rapidly fermenting 
mixture of dextrose (U.S.P., Drug Trading Co., 340 g) and 
bakers' yeast (Fleishman's, 80 g) in water (1.5 l). After 
6 hours more yeast (40 g, in 100 ml water) was added and the 
mixture left for 30 hours. A clear distillate (3 l) was 
collected from steam distillation of the mixture, using a 
12" Vigreux column to break up the foam produced. Anhydrous 
potassium carbonate (1500 g) was added and the solution was 
extracted 6 times with methylene chloride (50 ml portions). 
After the solution was dried, most of the solvent was removed 
by simple distillation and the residue fractionated on a 
spinning band column to yield a clear liquid (3.0 g) having 
\([\alpha]_D^{25} + 2.1° \ (0.1, \text{c}^4, \text{CH}_2\text{Cl}_2). \)

4. Preparation of S-(+)-benzyl-\(\alpha\)-\(d\) bromide.

The procedure of Kice (12) was modified in the following 
way. R-(−)-benzyl-\(\alpha\)-\(d\) alcohol (1.97 g) was placed in a small
round-bottomed flask (5 ml), fitted with a reflux condenser
topped by a drying tube, and frozen in a Dry Ice - acetone
bath. Freshly distilled phosphorus tribromide (2 ml, Eastman
"Yellow Label") was added down the condenser in one portion.
The mixture was stirred after allowing it to warm slowly to
room temperature. After pentane (10 ml) was added the
solution was successively washed with water, 10% sodium
carbonate solution and water, and dried. Removal of the
solvent was affected by distillation from a waterbath at
50°. Upon distillation of the residue, under reduced pressure,
in a alembic, a colourless liquid (2.38 g, 77%) was obtained,
which had \([\alpha]_D\) + 0.74, \([\alpha]_{400}\) + 1.60° (0.1, \(c\), \(C_9H_2Cl_2\)).
The n.m.r. spectrum showed bands at 4.38 p.p.m. (triplet)
and 7.28 p.p.m. (singlet) relative areas 1:5.
5. Preparation of R-(-)-benzyl-\(\alpha\)-d bromide.

Using the same procedure as above S-(+) -benzyl-\(\alpha\)-d
alcohol (1.05 g) gave benzyl-\(\alpha\)-d bromide (1.21 g, 73%) having
\([\alpha]_D\) -0.72°, \([\alpha]_{400}\) - 3.0° (0.1, \(c\), \(C_{12}H_{2}Cl_2\)).
6. Preparation of R-(-)-phenylmethanesulphonyl-1-d bromide.

A solution of S-(+) -benzyl-\(\alpha\)-d bromide (2.93 g, 17.0
mmoles) and sodium sulphite (2.16 g, 17.4 mmoles) in water
(25 ml) was refluxed for 2 hours. The homogeneous solution
that was obtained was washed once with methylene chloride.
The water was removed under reduced pressure to give a white
solid (4.67 g) which was dried under high vacuum at 100° for 1 hour. The salts were thoroughly mixed with phosphorus pentabromide (10 g) and heated at 50° for a few minutes to start the reaction, which can be observed when the mixture solidifies liquify and gas is evolved. After cooling and resolidifying, methylene chloride (50 ml) was added and the solution washed successively with water, 2% sodium bisulphite solution, and two more times with water. The solvent was removed under reduced pressure, after the solution had been dried, to obtain an oily white solid, which was recrystallized from methylene chloride-pentane (2.13 g, 53%) m.p. 79-81°, mixed m.p. with natural abundance isomer 80-81°. Calculated for C_7H_6DBrO_2S: 14.28% atom excess D. Found: 13.50% atom excess D. The n.m.r. spectrum (CDCl_3) showed an ill-defined triplet at 4.90 p.p.m. and a singlet at 7.44 p.p.m.; relative areas 1:5. The infrared spectrum (CHCl_3, 10%, 0.1 mm) had major bands below 1600 cm\(^{-1}\) at: 1495 (m), 1455 (m), 1364 (vs), 1185 (m), 1156 (vs), 1144 (s), 817 (m), 698 cm\(^{-1}\). [\(\alpha\)]\(_D\) -0.4°, [\(\alpha\)]\(_{400}\) -2.0° (0.1, Cl, CH\(_2\)Cl\(_2\)).

7. Preparation of S(+)-phenylmethanesulphonyl-1-d bromide.

Using the same procedure as above R(-)-benzyl-\(\alpha\)-d bromide (1.90 g, 11.0 mmol) gave a white solid (1.8 g, 69%) m.p. 78-80° which had [\(\alpha\)]\(_D\) + 2.7° [\(\alpha\)]\(_{400}\) + 6.2° (0.1, Cl, CH\(_2\)Cl\(_2\)). Calculated for C\(_7\)H\(_6\)DBrO\(_2\)S: 14.28% atom excess D. Found: 13.35% atom excess D. The infrared spectrum was
identical to that of the R isomer.


A solution of R-(-)-benzyl-\(\alpha\)-d bromide (247 mg) in methylene chloride (2.0 ml) gave a deflection of 150 mm at 400 m\(\mu\), for a path length of 1.0 cm, using the 0.025° scale on the Jasco O.R.D. recorder. A portion (1 ml) of the solution was mixed with a portion (1 ml) of a solution of tetraethylammonium bromide (10.00 mg) in methylene chloride (25.0 ml). Timing was started immediately. After the solution had been mixed it was transferred to a cell fitted with a circulating pump in a constant temperature bath at 25°. The rate of loss of optical rotation was measured at 400 m\(\mu\). The apparent second order rate constant was calculated from the graph of log (100-% reaction) versus time.
Height of original R-(−)-benzyl-κ-đ bromide solution = 150 mm. Height at 0% reaction after dilution with Et₄NBr solution = 75 mm.

<table>
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<th>TIME (hr)</th>
<th>HEIGHT OF LINE (mm)</th>
<th>LOG (100-% REACTION)</th>
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</tr>
<tr>
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</tr>
</tbody>
</table>

\[ k_2 = 5.1 \times 10^{-2} \text{ l.mole}^{-1}\text{sec}^{-1} \]


A mixture of R(−)-phenylmethanesulphonyl-đ-d bromide (900 mg, \([\alpha]_{400} = 2.5^\circ\)) and tetraethylammonium bromide (81.0 mg) in methylene chloride (50.0 ml) was placed in a waterbath at 25° for 1 hour. The solution was poured into water and thoroughly shaken, and the organic phase was washed twice more with water, and dried. Most of the solvent was removed by distillation through an 8" Vigreux column. After the solution had been transferred to an Erlenmeyer flask the total volume was
5 ml. Pentane (50 ml) was added and the solution was cooled in a Dry Ice-acetone bath. The white crystals (480 mg) that were formed were filtered and shown to be starting material by the infrared spectrum (IR-10) m.p. 77-79°, [α]_400 \textsuperscript{\circ} -2.6°. Careful distillation of the filtrate yielded an oily residue which was distilled under reduced pressure, in an alembic, to afford a colourless oil (200 mg), whose infrared spectrum (IR10) indicated it to be benzyl-α-d bromide. [α]_400 + 0.51°.

10. Reaction of S- (+)-phenylmethanesulphonyl-1-d bromide with tetraethylammonium bromide.

Tetraethylammonium bromide (56.70 mg) was allowed to react with S(+) -phenylmethanesulphonyl-1-d bromide (900 mg, [α]_400 + 6.25°) in methylene chloride (50.0 ml) for 120 minutes at 25.0°. The reaction mixture was worked up as above to yield recovered starting material (335 mg, [α]_400 + 5.9°) and benzyl-α-d bromide (320 mg, [α]_400 - 0.71°).

11. Preparation of S-(-)-benzyl-α-d ethyl sulphone from benzyl-α-d bromide.

Potassium hydroxide (0.5 g), in ethanol (10 ml) was added to ethane thiol (Eastman, 1 ml) in ethanol (10 ml) while stirring under nitrogen. R-(-)-benzyl-α-d bromide (151 mg) in ethanol (3 ml) was added slowly while the solution was rapidly stirred. After 10 minutes at room temperature the solution was heated at 50° for 1 hour. The
mixture of precipitated salt and solution was poured into water and the aqueous phase extracted 5 times with methylene chloride. The organic fractions were washed twice with water, and dried. The solvent was removed by distillation and the residue distilled, under reduced pressure, in an alembic to yield a foul smelling liquid (121 mg, 94%). The alkyl sulphide was dissolved in glacial acetic acid (5 ml) and hydrogen peroxide (Fisher 30%, 1 ml) was added to the solution in one portion. After the solution had been at room temperature for 30 minutes it was heated at 70° for a further 90 minutes. The solution was poured into water, extracted 4 times with methylene chloride and the organic phases washed twice with water and dried. Removal of the methylene chloride under reduced pressure afforded a white crystalline material (115 mg, 79%), which was recrystallized from carbon tetrachloride to give white plates m.p. 80-81°, mixed m.p. with natural abundance isomer 80-81°; reported m.p. 79-80° (12). Calculated for C₉H₁₁DO₂S: 8.33% atom excess D. Found: 7.70% atom excess D. [α]₄₀₀ - 0.9°.


Triethylamine (5 ml) was added dropwise, with stirring to a solution of phenylmethanesulphonyl chloride (40 g) and dl-menthol (Eastman "Practical", 4.0 g) in methylene chloride (50 ml). After a period of 5 minutes the solution was washed
with dilute sulphuric acid, twice with water, and dried. The solvent was removed under reduced pressure giving a pale yellow solid (5.3 g), which was recrystallized from carbon tetrachloride-petroleum ether, m.p. 57-58°. Calculated for C_{17}H_{26}O_3S: C, 65.78; H, 8.44; S, 10.31%. Found: C, 65.66; H, 8.16; S, 10.32%. The benzylic proton appeared in the n.m.r. (CCl₄) at 4.16 p.p.m. (singlet) and 3.94 p.p.m. in benzene. Major bands in the infrared spectrum (IR10, 0.1 mm, 10% CHCl₃) below 1600 cm⁻¹: 1452 (m), 1340 (s), 1170 (s), 1138 (m), 940 (m), 910 (vs), 890 cm⁻¹ (s).

VI SCOPE OF THE REACTION

1. The reaction of phenyl p-nitrophenylmethanesulphonate with tetraethylammonium bromide.

   a) Preparation of phenyl p-nitrophenylmethanesulphonate.

   Triethylamine (2 ml) was added dropwise to a stirred solution of p-nitrophenylmethanesulphonyl chloride (1.2 g) and phenol (2 g, 5 molar excess) in methylene chloride (30 ml). After the solution had been allowed to stand at room temperature for 5 minutes it was washed successively with 10% sodium hydroxide solution, dilute hydrochloric acid, twice with water, and dried. The solvent was removed under reduced pressure to yield a white crystalline material (1.1 g, 79%) which was recrystallized from methylene chloride-pentane, m.p. 136-137°.
Calculated for C\textsubscript{13}H\textsubscript{11}NO\textsubscript{5}S: C, 53.22; H, 3.78; N, 4.78; S, 10.93%. Found: C, 53.25; H, 4.23; N, 4.86; S, 10.75%. The benzylic proton appeared in the n.m.r. spectrum (CDCl\textsubscript{3}) at 4.60 (singlet). The infrared spectrum (IR5, 0.1 mm 10% CHCl\textsubscript{3}) showed major peaks below 1600 cm\textsuperscript{-1} at; 1520 (s), 1380 (m), 1350 (s), 1187 (m), 1170 (m), 1145 (s), 865 cm\textsuperscript{-1} (vs).

b) A solution of phenyl p-nitrophenylmethanesulphonate (50 mg) and tetraethylammonium bromide (360 mg) in methylene chloride (10.0 ml) was allowed to stand at 25° for 166 hours. The solution was washed twice with water, and dried. A white solid (49 mg) was obtained after careful removal of the methylene chloride by distillation, the n.m.r. spectrum of which showed no band at 4.52 p.p.m. corresponding to p-nitrobenzyl bromide. A solution of p-nitrobenzyl bromide (1.0 ml, of a solution p-nitrobenzyl bromide (10 mg) in methylene chloride (100 ml)) was added and the mixture washed twice with water, and dried. Careful removal of the solvent again yield a white solid (49 mg) whose n.m.r. spectrum showed a small peak at 4.52 p.p.m. (singlet) corresponding to the added p-nitrobenzyl bromide.

2. The reaction of dibenzylsulphone with tetraethylammonium bromide.

A solution of dibenzylsulphone (246 mg, 1 mmole; m.p. 151-152° from the peracetic acid oxidation of the corresponding
sulphide) (95) and tetraethylammonium bromide (420 mg, 2 mmoles) in methylene chloride (10.0 ml) was allowed to stand at 25° for 333 hours. The solution was washed twice with water, and dried. Careful removal of the solvent by distillation left a small amount of solution (approx. 1 ml) thin-layer chromatography of which in benzene:ether (9:1) indicated entirely starting material with no trace of benzyl bromide. The solvent was completely removed under reduced pressure to leave a white solid (244 mg) to which a solution of benzyl bromide was added (5 mg, in methylene chloride (10.0 ml). Identical work-up left a solution (1 ml), thin-layer chromatography of which, under the same conditions, indicated the presence of a fast running fraction corresponding to benzyl bromide).

3. The reaction of benzyl phenacyl sulphone with tetraethylammonium bromide.

Benzyl phenacyl sulphone (274 mg, 1 mmole; prepared from the corresponding sulphide by oxidation with potassium permanganate) (9b) and tetraethylammonium bromide (420 mg, 2 mmoles) were dissolved in methylene chloride (10.0 ml) and allowed to stand at 25° for 320 hours. The solution was washed three times with water, and dried. The solvent was removed by careful distillation until a small amount (1 ml) of solution remained. Thin-layer chromatography in benzene-ether (9:1) indicated that the product was entirely starting
material. The remaining solvent was removed under reduced pressure to yield a white solid (253 mg). Benzyl bromide in methylene chloride was added (5 mg, in 10 ml) and the solution was worked up as above. Thin-layer chromatography on the concentrated solution showed the presence of benzyl bromide.

4. The reaction of benzyl trifluoromethyl sulphone with tetraethylammonium bromide.

Benzyl trifluoromethyl sulphone was prepared starting from benzyl iodide (97) and trifluoromethylsilver (AgSCF₃) (98) using the method of Orda and co-workers (100) m.p. 100-102°; reported m.p. 102-103° (100).

a) In methylene chloride.

A solution of benzyl trifluoromethyl sulphone (224 mg, 1 mmole) and tetraethylammonium bromide (420 mg, 1 mmole) in methylene chloride (10.0 ml) was allowed to stand at 25° for 240 hours. The methylene chloride was washed 3 times with water, and dried. The concentrated solution (1 ml) obtained after careful removal of the solvent by distillation was subjected to thin-layer chromatography in benzene:ether (9:1) which showed that the product was entirely starting material with no trace of benzyl bromide. The remainder of the solvent was removed under reduced pressure to yield a white solid (210 mg), m.p. 100-102°, whose infrared spectrum (IR10, 10% CHCl₃) was identical with that of benzyl trifluoromethyl sulphone.
A solution of benzyl bromide (5 mg) in methylene chloride (10 ml) was added and the mixture worked up as above. Thin-layer chromatography of the concentrated solution under identical conditions showed the presence of benzyl bromide.

b) In ethyl alcohol.

A mixture of benzyl trifluoromethyl sulphone (224 mg, 1 mmole) and tetraethylammonium bromide (420 mg, 2 mmoles) was refluxed in dry ethanol (25 ml) (101) for 4 hours. The solution was poured into water (100 ml) and extracted 4 times with methylene chloride (20 ml, portions). The combined extracts were washed twice with water, and dried. Most of the solvent was removed by careful distillation. Thin-layer chromatography on the concentrated solution (1 ml) again showed that no benzyl bromide was present and that the product was exclusively starting material. This was also shown by the infrared spectrum (IR10, CHCl₃, 10%) of the white solid (195 mg, m.p. 100-102°) which was identical with an authentic spectrum of benzyl trifluoromethyl sulphone. The fact that benzyl bromide would have been identified if it had been produced was shown by working up a solution containing benzyl bromide, as above.

As a control experiment benzyl trifluoromethyl sulphone (224 mg) was refluxed in dry ethanol (25 ml) for 4 hours. Identical work-up to the above yielded a white solid (196 mg:
m.p. 100-102°) whose infrared spectrum (IR-10, CHCl₃, 10%) was identical with that of the starting material.

5. The reaction of phenyl phenylmethanesulphonate with sodium phenoxide.

   a) Preparation of phenyl phenylmethanesulphonate.

Triethylamine (10 ml) was added to a solution of phenylmethanesulphonyl chloride (5 g, 26 mmoles) and phenol 6 g, 64 mmoles) in methylene chloride (50 ml). After the solution had remained at room temperature for 5 minutes it was washed successively with 1% sodium hydroxide solution (200 ml) dilute sulphuric acid, twice with water, and dried. The methylene chloride was removed under reduced pressure to yield a white solid (5.8 g, 89%) which was recrystallized from methylene chloride - petroleum ether, m.p. 86.5-87.5°. Calculated for C₁₃H₁₂SO₃; C, 62.90; H, 4.87; S, 12.89%. Found: C, 62.67; H, 4.81; S, 12.86%. The n.m.r. spectrum showed the benzylic protons as a singlet at 4.43 p.p.m. as well as complex aromatic bands. The infrared spectrum (IR10, 0.1 mm CHCl₃) showed major bands below 1600 cm⁻¹ at: 1585 (m), 1485 (s), 1370 (s), 1180 (m), 1165 (m), 1140 (s), 865 cm⁻¹ (s).

   b) A solution of phenol (3.6 g) and sodium (0.7 g) in methanol (30 ml) was added to a solution of phenyl phenylmethanesulphonate (248 mg, 1 mmole) in methanol (20 ml). The mixture was refluxed for 8 hours after which time the solution was added to methylene chloride (100 ml) and washed
with 1% sodium hydroxide solution (300 ml), 3 times with water, and dried. The solvent was removed under reduced pressure to yield a yellow solid (186 mg) the infrared spectrum of which (IR-10, CHCl₃, 10%) indicated that it was starting material. Thin-layer chromatography in benzene ether (9:1) confirmed that it was exclusively phenyl phenylmethanesulphonate with no trace of phenyl benzyl ether present. The yellow solid was recrystallized from methylene chloride - petroleum ether to give white needles, m.p. 85-86°.

VII MISCELLANEOUS REACTIONS.

1. General Procedure for the preparation of some esters pf p-nitrophenylmethanesulphonic acid.

Triethylamine (1 ml) was added to a solution of p-nitrophenylmethanesulphonyl chloride (235 mg, 1 mmole) in a dry alcoholic solvent (10 ml). After 5 minutes the solvent was removed under reduced pressure. Methylene chloride (25 ml) was added to the residue and the solution washed with dilute sulphuric acid, twice with water, and dried. The solvent was removed under reduced pressure.

   a) Methyl p-nitrophenylmethanesulphonate.

   This compound was prepared in 93% yield. Recrystallization from methylene chloride-pentane gave pale yellow plates, m.p. 113-115°; reported m.p. 113° (102). The non-aromatic protons appeared in the n.m.r. spectrum (CDCl₃)
at 3.82 p.p.m. (singlet) and 4.42 p.p.m. (singlet), relative area 3:2. The infrared spectrum (IR-10, 0.1 mm. CHCl₃) showed major bands below 1600 cm⁻¹; at 1523 (m), 1350 (s), 1170 (m), 990 cm⁻¹ (m).

b) Isopropyl p-nitrophenylmethanesulphonate.

This compound was prepared in 95% yield. It was recrystallized from methylene chloride - pentane, m.p. 88-91°. Calculated for C₁₀H₁₃NO₅S: C, 46.33; H, 5.06; N, 5.40; S, 12.35%. Found: C, 45.91; H, 5.22; N, 5.69; S, 12.29%.

N.m.r. bands (CDCl₃) at 1.33 p.p.m. (doublet, J = 6.2 cycles sec⁻¹), 4.41 p.p.m. (singlet), 4.88 p.p.m. (multiplet) as well as aromatic absorption. Infrared (IR-10, 0.1 mm CHCl₃) peaks below 1600 cm⁻¹ included; 1525 (s), 1350 (vs), 1173 (s), 1095 (m), 915 (vs), 860 cm⁻¹ (m).

2. The methanolysis of p-nitrophenylmethanesulphonyl bromide.

p-Nitrophenylmethanesulphonyl bromide (140 mg, 0.5 mmole) was dissolved in dry methanol (50 ml) and placed in a waterbath at 25° for 1 hour. The solution was poured into water (400 ml) and extracted 4 times with methylene chloride (25 ml). The extracts were dried, and the solvent was removed by distillation to yield a white solid (128 mg). Besides aromatic proton absorption the n.m.r. spectrum (CDCl₃) showed bands at 3.82 p.p.m. (singlet), 4.43 p.p.m. (singlet) and 5.05 p.p.m. (singlet), relative areas 172:93:106. This
represents 53% reaction.

3. The reaction of p-nitrophenylmethanesulphonyl bromide with tetraethylammonium bromide in methanol.

A solution of p-nitrophenylmethanesulphonyl bromide (140 mg, 0.5 mmoles) and tetraethylammonium bromide (105 mg, 0.5 mmoles) in methylene chloride (50 ml) was allowed to stand in a waterbath at 25°. After 1 hour the solution was poured into water (400 ml) and extracted 4 times with methylene chloride (25 ml portions). The extracts were dried and the solvent removed by distillation. The n.m.r. spectrum (CDCl₃) of the oily white solid that was obtained (120 mg) showed, as well as aromatic absorption, bands at 3.82 p.p.m. (singlet), 4.43 p.p.m. (singlet) and 5.05 p.p.m. (singlet) relative area 170:101:101. This indicated that the product was that obtained from 50% methanolysis.

4. The reaction of p-nitrophenylmethanesulphonyl bromide with tetraethylammonium bromide in methylene chloride-ether.

A solution of p-nitrophenylmethanesulphonyl bromide (140 mg, 0.5 mmoles) and tetraethylammonium bromide (105 mg, 0.5 mmoles) in a mixture of methylene chloride (50 ml) and dry ether (25 ml) was allowed to stand in a waterbath at 25° for 1 hour. The solution was washed 3 times with water, and dried. Removal of the solvent by distillation afforded a yellow semi-solid (118 mg), whose infrared (IR-10, CHCl₃) and n.m.r. spectrum (CDCl₃) indicated a mixture of starting
material and $p$-nitrobenzyl bromide. Besides aromatic absorption the n.m.r spectrum showed bands at 4.53 p.p.m. (singlet) and 5.08 p.p.m. (singlet), relative areas 115:140. From this the extent of the reaction was calculated to be 45% corresponding to an apparent second order rate constant of $2.5 \times 10^{-2}$ l.mole$^{-1}$sec$^{-1}$.

5. The reaction of $p$-nitrophenylmethanesulphonyl bromide with tetraethylammonium bromide in methylene chloride-isopropanol.

Tetraethylammonium bromide (210 mg, 1 mmole) and $p$-nitrophenylmethanesulphonyl bromide (140 mg, 0.5 mmole) were dissolved in methylene chloride (40 ml) and isopropanol (10 ml) that had been distilled from calcium (101). After the solution had stood in a waterbath at 25° for 2 1/2 hours it was washed 3 times with water, and dried. Removal of the solvent, by distillation, yielded a yellow oil (115 mg) whose n.m.r. spectrum ($CDCl_3$) indicated the presence of starting material (benzylic protons at 5.08 p.p.m.) $p$-nitrobenzyl bromide (benzylic protons at 4.53 p.p.m.) and isopropyl $p$-nitrophenylmethanesulphonate (benzylic protons at 4.41 p.p.m.), relative areas 10:10:10, that is, 33% alcoholysis and 33% desulphonylation.

6. The reaction of benzyl trifluoromethyl sulphone with tetraethylammonium bromide in the presence of $p$-nitrobenzyl bromide.
Benzyl trifluoromethyl sulphone (112 mg, 0.5 mmoles) and p-nitrobenzyl bromide (304 mg, 1.5 mmoles) were dissolved in methylene chloride (20 ml). A portion (10 ml) of the solution was washed twice with water (50 ml) and dried. The solvent was removed by distillation to yield a white solid (211 mg). Tetraethylammonium bromide (210 mg, 1.0 mmole) was added to the remainder of the solution (10 ml). This solution was allowed to stand at room temperature for 18 hours after which time it was washed twice with water (50 ml) and dried. Removal of the solvent by distillation yielded a white solid (209 mg), the n.m.r. spectrum (CDCl₃) of which was identical with that obtained from the material isolated from the solution that had no bromide ions added to it.
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