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The Thermal Decomposition Of Perchloric Acid

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THE THERMAL DECOMPOSITION OF PERCHLORIC ACID

by

Robert Gilbert

Department of Chemistry

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

Faculty of Graduate Studies
The University of Western Ontario
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ABSTRACT

The kinetics of the thermal decomposition of perchloric acid vapour in pyrex reaction vessels has been investigated between 279 and 471°C with initial perchloric acid concentrations of 1×10^{-4} to 1.5×10^{-3} mole litre⁻¹ using a flow technique. Four reaction vessels of different dimensions were used and the effect of ageing, annealing, coating and packing reaction vessels was observed. The major reaction products over this temperature range are chlorine, oxygen and water, although there was evidence for the formation of small amounts of hydrogen chloride in a side reaction. The decomposition was essentially first order at all temperatures although significant deviations from first order kinetics were observed at high conversions in the intermediate temperature region. Strong surface effects were observed, particularly at low temperatures. With certain surfaces, sigmoid shaped decomposition curves were observed and these were ascribed to self-heating resulting from the greatly increased rate of decomposition on these surfaces.

Three different kinetic models were discussed. While a chain mechanism may be involved, it is more probable that

perchloric acid decomposes unimolecularly in the gas phase and heterogeneously on sparsely populated sites on the pyrex surface. The rate constant for the gas phase decomposition is given by $k(\text{sec}^{-1}) = 1.3 \times 10^{12} \exp(-41,200/RT)$ and the specific rate constant for the heterogeneous decomposition on freshly annealed pyrex is given by $k(\text{sec}^{-1} \text{ cm}^{-2}) = 3.5 \times 10^2 \exp(-15,100/RT)$. The surface concentration of active sites depends on the history of the pyrex.

The effect on the decomposition of perchloric acid of five Harshaw catalysts (Cu-0203, Fe-0301, Al-0104, Cu-0803 and Mn-0201) was investigated. All were positive catalysts and the major reaction products were chlorine, oxygen and water. The decomposition on the first four was clearly first order and Arrhenius parameters were obtained for these. The activation energies were 54.0, 28.6, 28.8 and 39.0 kcal mole⁻¹, respectively and a compensation effect was observed.

A preliminary study of the reaction of perchloric acid with the model fuels, hydrogen, methane, ethane and ethylene was made under fuel-rich conditions. Hydrogen reacted directly with perchloric acid on the pyrex surface to give mainly hydrogen chloride and water while methane, ethane and ethylene reacted with the decomposition intermediates of perchloric acid to give carbon monoxide and hydrogen chloride as the main products.

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CHAPTER 1

INTRODUCTION

Much of the current interest in the thermal decomposition of perchloric acid has arisen for technological reasons. Many of the solid fuel rocket propellants in use today are based on ammonium perchlorate (AP) and under certain conditions the thermal decomposition of AP controls the rate of propellant burning. This has motivated an extensive study of this complicated reaction. At the present time the mechanism of the decomposition has not been fully elucidated and this is in part due to the lack of information on the possible intermediate reactions. The work described in this thesis was carried out to obtain further information on one such reaction, namely the thermal decomposition of perchloric acid.

1.1 Thermal Decomposition of Ammonium Perchlorate

It is beyond the scope of this thesis to review all the work on AP and so just a brief outline is given. More detailed presentations can be found in a number of reviews¹⁻⁴, in particular the comprehensive review by Jacobs and Whitehead¹.

AP is stable at room temperature but decomposes at measurable rates at temperatures greater than about 150°C

to give entirely gaseous products. At decomposition temperatures below approximately 300°C, AP undergoes an autocatalytic reaction which ceases after about 30% decomposition. This is usually called the low temperature reaction. The residue is quite stable at these temperatures unless rejuvenated by sublimation, recrystallisation or mechanical disturbance. At temperatures above 350°C, the high temperature decomposition occurs; this reaction is not autocatalytic and decomposition is complete. Concurrently with these decomposition reactions, AP also undergoes dissociative sublimation.

Catalysts may profoundly affect the decomposition. The shape of the decomposition-time curve may be modified; the extent of reaction may be altered and the overall rate of decomposition may be changed.

A unified reaction scheme for the decomposition of AP has been proposed¹.

The primary step (step 1) is proton transfer to give adsorbed ammonia and perchloric acid on the surface of the crystal. This step is reversible. The low temperature decomposition involves the reaction of these adsorbed

species (step 2). The adsorbed perchloric acid probably decomposes and the chlorine oxides, produced as intermediates, oxidise the ammonia. The reaction is thus in part, at least, heterogeneous. The failure of the low temperature reaction to go to completion may be caused by the accumulation of ammonia on the surface, which suppresses the reversible proton transfer process.

At higher temperatures, the ammonia will desorb and a situation develops in which the ammonia and perchloric acid molecules are both desorbing into the gas phase rather than reaction at the surface (steps 3 and 4). At low ambient pressures, they diffuse sufficiently rapidly out of the heated reaction zone before substantial decomposition of perchloric acid can occur. The ammonia and perchloric acid then recombine on any cold surface to complete the sublimation process (step 6). As the ambient pressure increases, the rate of diffusion of ammonia and perchloric acid through the gas phase decreases and their residence time in the reactor is sufficiently long for decomposition of perchloric acid and the subsequent oxidation of ammonia to occur (step 5).

Different catalysts may affect the mechanism in different ways. A catalyst may change the position of the proton transfer equilibrium or affect the heterogeneous decomposition of the perchloric acid.

1.2 Physical Properties of Perchloric Acid

The general properties of HClO_4 ⁵⁻⁹ have been reviewed by a number of people, notably by Pearson⁵.

Anhydrous perchloric acid is a colourless, mobile liquid with a freezing point of -100°C . It is thermally unstable and at room temperature decomposes within a few hours. It is in fact notoriously explosive but apparently this is due to chlorine oxide impurities¹⁰. It is stable in aqueous solution and forms an azeotropic mixture of 72.4% by weight of the acid. There is evidence for the formation of six different hydrates but only the monohydrate, a white crystalline solid isomorphous with AP, is well characterised. The stability of the aqueous solution is associated with the dissociation of the essentially covalent perchloric acid molecule to give a stable perchlorate ion. In the gas phase, perchloric acid is monomeric and in the vapour from 72% acid, there is no association between the acid molecules and water. This makes 72% acid a useful, safe source of perchloric acid molecules, although of course water molecules are also present.

The perchloric acid molecule is tetrahedral in shape with a Cl-O bond length of 1.408 Å and a Cl-OH bond length of 1.630 Å¹¹. The HO-ClO₃ bond is the weakest. Using the heats of formation available for gaseous perchloric acid, gaseous hydroxyl and chlorine trioxide radicals, Levy¹⁰ calculated the bond dissociation energy, $D(\text{HO-ClO}_3)$,

to 48.3 kcal mole⁻¹. Heath and Majer¹² in a mass spectrometric study of the vapour of 72% perchloric acid obtained a value of 46 ± 5 kcal mole⁻¹ from a measurement of the appearance potential of the ClO_3^+ ions:

The value used for the ionization potential, $I(\text{ClO}_3)$, was that of Dibeler¹³.

Fisher¹⁴ calculated the bond dissociation energy, $D(\text{H-OCLO}_3)$, to be approximately 112 kcal mole⁻¹ using a value of 59 kcal mole⁻¹ for the heat of formation of the ClO_4 radical, obtained in his mass spectrometric study of dichlorine heptoxide.

The bond dissociation energy, $D(\text{HOO}_2\text{Cl-C})$ is not known but from a consideration of the Cl-O bond strength in other molecules, Heath and Majer¹² estimated a value of about 60 kcal mole⁻¹.

1.3 Thermal Decomposition of Gaseous Perchloric Acid

The literature, on the thermochemistry and thermal decomposition of perchloric acid up to 1963, has been reviewed by Pearson and Cummings¹⁵. In addition, the reviews cited in Section 1.2 contain discussions of the decomposition. The more recent literature has been discussed by Pearson¹⁶ in his review "Perchlorate Oxidizers". Much of the work in the thermal decomposition is, however, described only in technical reports, which are not readily

available. This work will therefore be described in some detail and the results critically discussed.

Perchloric acid may decompose in the vapour phase to form either chlorine or hydrogen chloride⁵ according to the equations:

The enthalpy change for equation 1.1 is $-28 \text{ kcal mole}^{-1}$ and for equation 1.2 it is $-21 \text{ kcal mole}^{-1}$.

The first investigation of the thermal decomposition of perchloric acid was reported by Sibbett and Lobato¹⁷ in 1960. They studied the decomposition of the anhydrous acid vapour at 200°C and 220°C with initial acid pressures of 8.8 to 373.3 torr. They suggested that the reaction could be represented entirely by equation 1.1, although analyses of the reaction products by mass spectrometry, infra-red spectrometry and by gas chromatographic techniques were not considered to be completely successful. This equation corresponds to a product gas containing 18.2% water, 18.2% chlorine and 63.6% oxygen (percentages are by volume). The product gas analysed as 75-85% oxygen, 10-13% chlorine, 6-10% water and 1-2% hydrogen chloride. Hydrogen and chlorine balances could not be achieved. It was suggested that the hydrogen chloride was formed

photochemically by the secondary reaction of chlorine and water, and that some of the water and chlorine remained adsorbed in the surface.

Anhydrous perchloric acid was used, a fresh sample was made for each run. The apparatus was entirely pyrex and without taps. The decomposition was followed by overall pressure measurement, initially by a pressure transducer and then by a differential manometer linked through a Bourdon gauge. The reaction was started by raising an oil-bath around the reaction bath. Unfortunately this method makes it difficult to obtain a time origin and to follow the early part of the reaction. At 200°C, it appears pressure measurements began after about 25 to 30% decomposition. The method of obtaining kinetics by initial rates could not be used.

The kinetics were complex. Assuming the stoichiometric equation given to be true, first order and second order integrated rate graphs were drawn for two different initial acid concentrations. At 200°C the reaction appeared to be second order up to 70-80% decomposition and subsequently first order up to 95% decomposition. The two second order rate constants which were obtained at the different initial acid concentrations agreed to about 8% and the two pseudo-first order constants agreed to about 5%. The effect of surface was investigated at 200°C by packing the reaction vessel with pyrex beads thus approx-

imately doubling the surface area. The kinetics showed the same form. The second order rate constant increased by about 50% and the first order rate constant increased by a factor of about 5. The first order constant thus appeared to be more sensitive to surface.

Incident light was also shown to affect the kinetics, increasing the second order rate constant markedly and reducing the first order constant slightly. A quantitative study was not made of the effect of temperature but for a run at 220°C with an initial acid pressure of 373 torr the second order rate constant had increased slightly while the first order rate constant had trebled.

They suggested that perchloric acid reacts bimolecularly to form a complex which decomposes unimolecularly.

The $\text{Cl}_2\text{O}_7 \cdot \text{H}_2\text{O}$ complex was considered to be much more stable than chlorine heptoxide which is known to decompose rapidly at 120°C.

The small temperature coefficient of the initial second order rate constant was explained by the fact that this rate constant also contains the equilibrium constant for the formation of $\text{Cl}_2\text{O}_7 \cdot \text{H}_2\text{O}$. The surface effect was said to be due to the first order step involving free radical chain initiation on the surface.

However, it is not clear that the mechanism proposed, even though it contains bimolecular and unimolecular steps would result in an overall rate which would apparently change from second to first order. The explanation of the small temperature coefficient for the second order rate constant implies $k_2 < k_1$ and so the reaction would therefore be expected to be always second order.

Sibbett and Geller^{18,19} extended this study to a temperature range of approximately 160-260°C. The data could be fitted to second order kinetics for the initial part of the reaction and to first order kinetics for the final part of the reaction for the entire temperature range. As the temperature was increased the region of apparent second order kinetics decreased. The effect of three different surface to volume ratios were observed at 200°C. The rate constants obtained from the first and second order regions were apparently proportional to the surface area although neither plots of rate constant against surface area passed through the origin. For certain runs the rate of chlorine production was measured spectrophotometrically. This was compared to the rate derived from the overall rate of pressure increase assuming equation 1.1 to represent the stoichiometry. Although there was a large amount of scatter in the spectrophotometric data, there was a general agreement with the computed chlorine production rate.

A number of reaction schemes and rate equations were considered. The rate equation used was,

$$-\frac{dA}{dt} = 2k_1 A^2 + \frac{k_2 AB}{1 + K_B B} \quad (1.4)$$

where A is the concentration of perchloric acid, B is the concentration of water, k_1 and k_2 are rate constants and K_B is an equilibrium constant. The rate equation was integrated numerically using a computer. The overall pressure increase could be obtained using the stoichiometric equation. The value of k_1 was taken as the observed initial second order rate constant. To obtain values for k_2 and K_B , the second term in equation 1.4 was integrated separately between the limits of time zero and time t. Although this second term is clearly dominant towards the end of the decomposition, it is preceded by a period in which the first term is dominant. It is therefore difficult to see the physical significance of this integration. Using the values of k_1 , k_2 and K_B obtained by this method, quite a good fit was obtained.

Sibbett and Geller wrote the following reaction scheme.

They obtained the above rate equation by considering two different Langmuir-Hinshelwood-Rideal mechanisms. However only one of these appears to be a valid derivation.

If both the reaction steps are heterogeneous and the water and perchloric acid adsorb on different sites, the following rate equation results,

$$-\frac{dA}{dt} = \frac{2k'_1 K_A^2 A^2}{(1 + K_A A)^2} + \frac{k'_2 K_A K_B A B}{(1 + K_A A)(1 + K_B B)} \quad (1.8)$$

where k'_1 and k'_2 are true rate constants and K_A and K_B are equilibrium constants for the adsorption of perchloric acid and water, respectively. The equation assumes that adsorbed and gaseous species are in equilibrium. If the perchloric acid coverage is always low, i.e. $K_A A \ll 1$, then this rate equation agrees with the rate equation used, where $k_1 = k'_1 K_A^2$ and $k_2 = k'_2 K_A K_B$.

The alternative mechanism, considered that water and perchloric acid adsorbed on the same sites, but that the second reaction is between adsorbed water molecules and gaseous perchloric acid molecules. The following equation results

$$-\frac{dA}{dt} = \frac{2k'_1 K_A^2 A^2}{(1 + K_A A + K_B B)^2} + \frac{k'_2 K_B A B}{1 + K_A A + K_B B} \quad (1.9)$$

This also assumes equilibrium between gaseous and adsorbed species is always maintained. However this equation cannot be reduced to the one used for this would require $K_B \ll 1$ in the first expression and not in the second expression.

It therefore appears that only the former mechanism proposed by Sibbett and Geller leads to the rate equation, which they used.

For a surface/volume ratio of 4.7, they obtained for k_1' a preexponential factor of $9.7 \times 10^7 \text{ min}^{-1}$ and an activation energy of $12.3 \text{ kcal mole}^{-1}$; for k_2' a preexponential factor of $1.95 \times 10^5 \text{ min}^{-1}$ and an activation energy of $20.5 \text{ kcal mole}^{-1}$; and for K_B a preexponential factor of 9.8×10^3 and a heat of adsorption of $13.3 \text{ kcal mole}^{-1}$. The value of $13.3 \text{ kcal mole}^{-1}$ for the heat of adsorption of water on pyrex agrees with other literature values. Both preexponential factors and activation energies varied slightly with surface area.

The mechanism which involves adsorption on different sites gave $k_1 = k_1' K_A^2$ and $k_2 = k_2' K_A K_B$ and hence the observed activation energies, E_1 and E_2 can be related to the true activation energies, E_1' and E_2' by the equations:

$$E_1 = E_1' - 2\lambda_A$$

$$E_2 = E_2' - \lambda_A - \lambda_B$$

λ_A represents the heat of adsorption of perchloric acid on pyrex and λ_B represents the heat of adsorption of water on pyrex. Using the observed values for E_1 and E_2 , gives the two expressions:

$$E_1' = 12.3 + 2\lambda_A \quad (\text{kcal mole}^{-1})$$

$$E_2' = 33.8 + \lambda_A \quad (\text{kcal mole}^{-1})$$

Neither activation energy can be calculated. Sibbett and Lobato attempted to use the activation energy for the liquid phase decomposition and Pearson⁵ used the value for the homogeneous gas phase decomposition, to obtain the heat of adsorption of perchloric acid and also to compare the two proposed mechanisms (one of which is invalid). Neither approach is strictly valid for the true activation energies refer to the heterogeneous reaction on pyrex.

However, E_1 must be less than the homogeneous gas phase activation energy of about 45 kcal mole⁻¹. This gives an upper limit of 16.4 kcal mole⁻¹ for the heat of adsorption of perchloric acid on pyrex and an upper limit of 50.2 kcal mole⁻¹ for the activation energy of the heterogeneous reaction of perchloric acid and water.

The thermal decomposition of perchloric acid has also been investigated by Levy¹⁰ between 200°C and 439°C. Between 200°C and 350°C, anhydrous perchloric acid was used and the kinetics were determined by spectrophotometrically

following the rate of chlorine production. From 350°C to 439°C , 72% acid was used and the kinetics were determined by a flow technique.

In order to check the stoichiometry of the decomposition samples of the anhydrous acid were decomposed at 210°C and 400°C and the products reacted with standard sodium hydroxide. Titrations for hypochlorite ion and chloride ion indicated that no hydrogen chloride was formed and that the stoichiometric equation in fact corresponded to equation 1.1.

Levy studied the low temperature region thoroughly. The rate of chlorine production was found to obey first order kinetics initially. At 250°C the decomposition fitted first order kinetics for the first 50% of the decomposition and at 350°C for the first 90%. Reproducibility of the rate could not be achieved from run to run. At 300°C increasing the initial acid concentration by a factor of ten appeared to increase the first order rate constant by only about 50%, demonstrating the predominantly first order nature of the decomposition. Increasing the surface to volume ratio by about three and a half times did not seem to increase the rate between 248°C and 350°C . However the general lack of reproducibility of results suggested that the reaction was heterogeneous and sensitive to the nature of the surface.

The high temperature region was not studied so

thoroughly. Levy used a flow system and absorbed some of the products in standard sodium hydroxide. First order rate constants were calculated from each flow run. About 12 runs were carried out. At 367°C the calculated first order rate constant varied only slightly when a three-fold increase in acid concentration was used and the amount of decomposition increased from 6% to 18%. The ratio of chlorine produced as calculated from the hypochlorite concentration, to chlorine produced as calculated from the chloride concentration, in the standard sodium hydroxide trap, varied by about 20%. However this was not considered significant. It should also be pointed out that using Levy's data for the percentage decomposition for given residence times, a normal calculation of rate constants give values slightly different to Levy's values.

While the rate constants for the low temperature region are very scattered they correspond roughly to an activation energy of $10 \text{ kcal mole}^{-1}$. Levy suggested that this was the heterogeneous decomposition although the absence of effects due to increasing the surface area were not explained. No mechanism was proposed.

For the high temperature region Levy obtained an activation energy of $45.1 \text{ kcal mole}^{-1}$ and a preexponential factor of $5.8 \times 10^{13} \text{ sec}^{-1}$. However there was a fair amount of scatter in the data. By selecting the points Levy considered to be most reliable an activation energy of

43.6 kcal mole⁻¹ and a preexponential factor of 1.6×10^{13} sec⁻¹ can be obtained.

Levy proposed the following mechanism for the high temperature decomposition,

followed by the fast steps

The preexponential factor obtained lies within the acceptable limits for a unimolecular reaction and the activation energy is also about 3 kcal mole⁻¹ less than the calculated HO-ClO₃ bond dissociation energy. The last two reaction steps are clearly overall steps, the intermediate steps being much more complicated.

Solymosi²⁰, in his study of the catalytic decomposition of perchloric acid observed the uncatalysed decomposition in the range 390 to 440°C. Using apparatus similar to Levy's he measured the extent of decomposition at different temperatures for a constant flow rate and a constant initial acid concentration. A value of 44 kcal mole⁻¹ was obtained for the activation energy.

Gritsan and Panfilov²¹ have very recently reported

a study of the kinetics of chlorine dioxide formation and consumption during the thermal decomposition of perchloric acid, in the range 230 to 440°C. Unfortunately at the time of completion of this thesis, it had not been possible to obtain a copy of this paper.

1.4 Thermal Decomposition in the Mass Spectrometer

The mass spectrum of 72% perchloric acid has been recorded by several authors^{12,22-26}. The spectrum is in part due to electron impact and in part due to thermal cracking. The effects of thermal decomposition are probably least in the spectrum obtained by Cordes and Smith²⁴. The three principal peaks correspond to ClO_3^+ , HClO_4^+ and ClO_2^+ . The ClO_3^+ ion is produced by electron impact on perchloric acid itself. In his attempts to observe the mass spectrum of chlorine hexoxide, Fisher¹⁴ also obtained the mass spectrum of anhydrous perchloric acid. It was the same as for the 72% acid but without the water peak.

Heath and Majer¹² investigated the heterogeneous decomposition of perchloric acid vapour on a hot platinum wire, placed adjacent to the ionization chamber of the mass spectrometer. The mass spectra showed that the hot platinum wire caused the reaction;

Pearson¹⁵ has suggested that at the temperatures and pressures used in these studies, the Deacon process

would account for the large quantities of hydrogen chloride.

Fisher²² has studied the intermediates formed in the thermal decomposition of perchloric acid. He leaked perchloric acid into the mass spectrometer through a heated pyrex reactor. The residence times in this region were of the order of milliseconds and the pressures were between 10^{-2} and 10^{-3} torr. He observed the change in the mass spectrum as the temperature of the reaction zone was increased. The acid decomposition exhibited three zones. The first at 800°C was associated with the decomposition of perchloric acid; the second at 950°C was associated with the decomposition of chlorine dioxide and the third at 1100°C was associated with the decomposition of the ClO radical. Chlorine and hydrogen chloride did not increase until the higher temperature regions were obtained.

It was suggested that chlorine trioxide should be a stable radical and at least as resistant to heterogeneous decomposition on the walls as the lower oxides. Fisher therefore considered the alternative primary step for the decomposition of perchloric acid,

to be more probable than equation 1.3. The enthalpy change is $+31.1 \text{ kcal mole}^{-1}$ as compared to $+48.3 \text{ kcal mole}^{-1}$

for equation 1.10. However, as a large reorganisation of the molecule is involved, the activation energy may be expected to be excessive. This may be greatly lowered if the reaction is heterogeneous.

In his mass spectrometric studies of the thermal decomposition of chlorine heptoxide and chlorine hexoxide, chlorine trioxide and chlorine tetroxide were also not observed. It therefore appears that neither radical can survive the few wall collisions which must take place in the inlet system.

As, at the pressures used, bimolecular reactions may be ignored, the following mechanism for the decomposition was proposed

The ClO radical was the main intermediate and it was postulated that this arose mainly from the chlorine trioxide radical which has only transitory existence. Chlorine dioxide was apparently a poor source of ClO radicals. Fisher suggested that ClO radicals are responsible for the enhanced reactivity of perchloric acid flames.

Pellet and Saunders²⁵ in their study of the heterogeneous decomposition of AP-Catalyst mixtures using pulsed laser mass spectrometry, observed that the perchloric acid which is a primary product, underwent a rapid heterogeneous decomposition on the substrate. Hydrogen chloride and chlorine dioxide were major products. Guillory and King²⁶ have observed similar behaviour. They both suggest that the heterogeneous primary step is in fact equation 1.16.

1.5 Catalytic Decomposition of Perchloric Acid

Sibbett and Geller¹⁸, in their investigation of the decomposition of anhydrous perchloric acid also observed the effect at 200°C, of adding a pellet of alumina. They observed an increase in the decomposition rate. The initial second order rate constant was increased but their pseudo-first order rate constant was unchanged. Clearly alumina can catalyse the reaction.

Solymosi, Börösök and Lázár²⁰ have reported a preliminary investigation of the effect of a number of oxide catalysts on the decomposition of perchloric acid. They used all the catalysts, they had used in studies of AP

catalysis, namely chromium oxide, cupric oxide, ferric oxide, zinc oxide, titanium dioxide and alumina. Neither alumina nor titanium oxide catalyse the decomposition of AP.

A flow technique was used, similar to that used by Levy in his study of the homogeneous decomposition of perchloric acid. A constant flow of nitrogen, saturated with perchloric acid was passed over a small pellet of the catalyst. The chlorine produced was absorbed in standard sodium hydroxide or potassium iodide and the resulting solution was analysed to obtain the kinetics.

All the catalysts were effective in lowering the temperature at which decomposition occurred. Although the effect of changing the initial acid concentration or the flow rate was not investigated, the kinetics were apparently considered to be first order.

Chromium oxide was a good catalyst. It apparently reacted with the acid to give chromyl chloride and higher oxides of chromium. This resulted in a gradual decrease in activity. At lower temperatures the reaction was less and an activation energy of $20.5 \text{ kcal mole}^{-1}$ was obtained. Chromium oxide is a p-type semiconductor. Solymosi studied the effects of doping the chromium oxide with zinc oxide, which should increase the conductivity and titanium dioxide which should decrease the conductivity. The incorporation of zinc oxide increased the activity at 170°C but

did not affect the activation energy, while the incorporation of titanium oxide, initially decreased the activity but it gradually increased to the undoped value. The activation energy was not obtained.

Cupric oxide was found to be less effective than chromium oxide and decomposition was not observed below 200°C. The activity did not vary and an activation energy of 28.8 kcal mole⁻¹ was obtained. Both ferric oxide and zinc oxide were less effective and activation energies of 42.4 and 46 kcal mole⁻¹ were obtained, respectively. Titanium oxide and alumina also lowered the decomposition temperature. No data were given for alumina, but the activation energy on titanium dioxide was given as 24.5 kcal mole⁻¹ although the specific activity was low. Doping of titanium oxide with chromium oxide increased its activity but a constant value could not be obtained.

Solymosi suggested that the activity of catalysts for the decomposition of perchloric acid is linked to the electrical properties of the catalysts, p-type semiconductors being better than n-type semiconductors. However these preliminary results were not conclusive.

Recently Solymosi and Börcsök²⁷ have investigated the catalytic decomposition of perchloric acid on chromium oxide more thoroughly. They found that the decomposition was zero order and had an activation energy of 31 kcal mole⁻¹. Attempts to analyze the catalyst after treatment with per-

chloric acid, using d.t.a. and t.g.a. were not successful but clearly a mixture of higher oxides was formed. The specific activities of the oxides at 160°C were found to be in the order, $\text{Cr}_2\text{O}_3 > \text{CrO}_2 \gg \text{CrO}_3$ and thus the decrease in activity due to the production of higher oxides was explained.

Solymosi suggested that the activity of a catalyst is related to the stability of its perchlorate. The oxide may be converted to the perchlorate which then decomposes to give the final products. Chromium oxide is a good catalyst and chromium perchlorate is thermally unstable and so this fits the hypothesis.

1.6 Perchloric Acid Flames

The earliest reference to perchloric acid flames in the literature is in a brief note by Dietz²⁸ in 1939. He observed the spontaneous ignition of perchloric acid vapour at 400 to 405°C and the subsequent decomposition flame. Hydrogen passed into the vapour also spontaneously ignited at 400 to 450°C but in the presence of steel turnings, the ignition temperature was reduced to 215°C .

Cummings and Pearson²⁹ have stabilised the decomposition flame at one atmosphere using the vapour from 72% acid. Analysis of the products showed a ratio of chlorine to hydrogen chloride of 0.7 which is much greater than the equilibrium ratio of 0.057 expected for a theoretical flame temperature of 1076 K. Correction of the flame temperature

for the observed chlorine distribution gave a value of 1160 K, since the heat release is greater for chlorine formation. This was in good agreement with the observed uncorrected value of 1080 K. The observed burning velocity of 19 cm sec^{-1} was in good agreement with a value of 20 cm sec^{-1} obtained using the theoretical equation of Zeldovitch and Frank-Kamenetsky and the kinetic parameters obtained by Levy¹⁰. The Zeldovitch and Frank-Kamenetsky equation³⁰ is based on a purely thermal model of a flame and is obtained essentially from considerations of energy and mass conservation.

More recently Hall and Pearson³¹ have obtained a value of 12 cm sec^{-1} for the burning velocity, and using the van Tiggelen equation have obtained an activation energy of $25 \text{ kcal mole}^{-1}$. The van Tiggelen equation³⁰ is based on a radical diffusion model of a flame involving branching reactions.

Powling³² has studied the flat diffusion flames of 72% perchloric acid with ammonia and propane. It appears that HClO_4 decomposes in the flame zone, emitting a reddish glow before reacting with the fuel. A thermocouple trace shows an exothermic bump on the acid side. As no spectral difference was observed between perchloric acid/ammonia and ammonia/chlorine/oxygen flames, it was concluded that HClO_4 probably decomposed before it reacted with the fuel.

Premixed flames have been stabilized for such model fuels as methane^{31,33-39,44-46}, ethane^{34,35,42-44,46}, ethylene^{40,41,44,46}, hydrogen²⁹, methanol³⁵, carbon monoxide³⁵ and formaldehyde⁵. The spectra of these flames^{34,35} show the same band systems as the corresponding oxygen flames, but in addition methane/perchloric acid flame shows strong "cool flame" bands and the ethane/perchloric acid flame "hydrocarbon flame" bands. The fuel/acid flames have much higher burning velocity than the corresponding fuel/oxygen flames at the same temperature. They also achieve their maximum burning velocity well on the fuel-rich side of stoichiometric and are less inhibited by halogenated hydrocarbons than oxygen flames at the same flame temperature. If both oxygen and perchloric acid are premixed with the methane fuel⁴⁵, two flame fronts are formed, one corresponding to the acid flame and downstream of this, one corresponding to the normal oxygen flame. Thus the perchloric acid premixed flame is quite different to the oxygen premixed flame.

Perchloric acid flames have very large flammability limits. In very fuel-rich flames³⁶⁻⁴³, the excess fuel acts simply as a diluent. Pearson⁴⁴ sampled the burnt gas products of binary fuel mixtures and was able to show that selective consumption occurred. The order of increasing ease of attack was methane, ethylene, ethane.

An activation energy of $15 \text{ kcal mole}^{-1}$ was obtained.

for the hydrogen flame²⁹ using the Zeldovitch and Frank-Kamenetsky equation for a second order reaction. Using the same model, activation energies of 30, 37 and 35.6 kcal mole⁻¹ were obtained for the methane³⁷, ethylene⁴⁰ and ethane⁴² flames, respectively. A different process to that involved in the decomposition flame is involved. An activation energy of 23 kcal mole⁻¹ was obtained for the methane flame³¹ using the van Tiggelen equation. This is much less than for the methane/oxygen flame.

Pearson³¹ has proposed a mechanism for the methane/perchloric acid flame in which the methane is rapidly attacked by ClO radicals from the decomposition of the acid.

Successive radical attacks on the formaldehyde produced the carbon monoxide used in the last step. Similar

mechanisms were obtained for both ethane and ethylene flames.

Gombourieu and his group studied the decomposition flame of chlorine dioxide^{47,48} and also the premixed methane/chlorine dioxide flame⁴⁹⁻⁵¹. Pearson³¹ has pointed out that perchloric acid flames and chlorine dioxide flames have a great deal in common but both differ quite considerably from oxygen flames. He suggests that this reflects the similarity in the mechanisms involved. Perchloric acid provides ClO radicals by,

and chlorine dioxide by

The subsequent reaction steps are then the same. However as the flame propagates, it is thought that in the perchloric acid flame further ClO radicals are produced by

and in chlorine oxide by,

Pearson has pointed out that the OH radicals, which are important in fuel/oxygen flames are probably much better hydrogen abstracting agents than are ClO radicals. However, as ClO radicals are readily produced in high concentrations in the early low temperature region of the fuel/perchloric acid flame, these flames are faster than the corresponding oxygen flames.

1.7 Reaction of Perchloric Acid with Ammonia

Sibbett and Lobato¹⁷ studied the reaction between anhydrous perchloric acid and ammonia at 25, 48 and 60°C, using 15:1, 10.6:1 and 3.4:1 mole ratios of ammonia to perchloric acid. The reaction was initiated by rupturing a break-seal between two pyrex vessels. The pressure of ammonia was also at least a factor of ten greater than the pressure of perchloric acid and thus a jet of ammonia passed rapidly into the section of the vessel containing perchloric acid vapour to start the reaction. The reaction was faster than could be followed on the pressure measuring device. Equilibrium pressures were consistently found to exceed calculated values based on 100% ammonium perchlorate formation, despite the formation of a layer of white solid throughout the reaction vessel. The solid

product contained substantial amounts of Cl^- , the Cl^- : ClO_4^- mole ratios varying from 0.93 at 25°C to 12 at 60°C . A satisfactory analysis of the gases was difficult to obtain. When the unreacted ammonia was removed from the sample, mass spectrometric analysis gave 68% O_2 , 15.5% H_2 , 14.9% N_2 and 1.1% NO .

Thus the simultaneous oxidation of ammonia by perchloric acid along with the direct combination to give ammonium perchlorate occurred.

Friedman and Levy^{52,53} have also performed a preliminary investigation of the reaction at 367°C . Separate streams of nitrogen-ammonia and nitrogen-perchloric acid were mixed and passed through a reaction vessel. The products leaving the reaction vessel were then absorbed in a series of traps. Analyses were performed for Cl^- and ClO_4^- . No OCl^- was found. The principal difficulty, they found, was that of mixing the reactants completely in a time short compared to the reaction time. In all four runs, the amount of perchloric acid consumed was greater than would result from just the decomposition of the acid. Assuming that the rate equation was

$$-\frac{d(\text{HClO}_4)}{dt} = k(\text{HClO}_4) + k_2(\text{HClO}_4)(\text{NH}_3) \quad (1.40)$$

Levy and Friedman obtained values for k_2 of 0.29, 1.38, 1.82 and $2.20 \times 10^6 \text{ cm}^3 \text{ moles}^{-1} \text{ sec}^{-1}$.

As only Cl^- was found in these experiments it was assumed that ammonia reacted with perchloric acid to produce chlorine which immediately reacted with further ammonia to give ammonium chloride. It was thought that the last two values of k_2 were more reliable as they refer to experiments in which a more efficient mixer was used.

1.8 Reactions of Chlorine Oxides

A number of chlorine oxides have been postulated as reaction intermediates in the decomposition of perchloric acid. Chlorine dioxide and chlorine monoxide have been observed mass spectrometrically²². Chlorine trioxide and chlorine tetroxide have not been directly observed but their presence has been suggested by Levy¹⁰.

Chlorine tetroxide appears too unstable to have an independent existence. However it is formed as a primary intermediate in the decomposition of chlorine heptoxide^{54,55}.

The reverse reaction⁵⁶,

is also apparently possible, for chlorine heptoxide is formed in substantial yields in the decomposition of chlorine hexoxide in the presence of fluorine. At higher temperatures, chlorine tetroxide decomposes unimolecularly

to give chlorine dioxide and oxygen⁵⁴.

Fisher¹⁴ in his mass spectrometric study of the decomposition of chlorine heptoxide could not observe chlorine tetroxide, presumably due to its rapid unimolecular decomposition. This may have been a wall reaction.

Chlorine trioxide at low temperatures forms an orange solid which melts at 3.5°C. to form a red oil which boils at 20.3°C. In the liquid or solid state, it exists as a dimer, chlorine hexoxide, but in the gaseous state this dissociates completely into chlorine trioxide⁵⁷⁻⁵⁹. It is reported to decompose bimolecularly in three possible ways^{56,60}

the activation energy for each of the reactions being about 12 kcal mole⁻¹. Under the high vacuum conditions existing in a mass spectrometer, the unimolecular decomposition of chlorine trioxide to chlorine dioxide and to chlorine monoxide has been suggested^{14,22}

Chlorine dioxide melts at -59.5°C and boils at 11°C to give a yellowish gas. It is thermally unstable and explodes above 45°C ^{61,62}. The explosive decomposition⁶² has recently been studied and was found to involve degenerate chain-branching with the formation of the stable intermediate, Cl_2O_3 . The initial step is probably the heterogeneous reaction

ClO radicals are the principal chain carriers and react first with chlorine dioxide to form Cl_2O_3

and then with Cl_2O_3

The chlorine atoms produced then undergo chain branching

and chain termination reactions

Arrhenius parameters have been obtained for the reaction of chlorine dioxide with nitrogen dioxide⁶³

and fluorine⁶⁴

Rate constants at room temperature have also been obtained for the fast reactions of chlorine dioxide with oxygen atoms⁶⁵, chlorine atoms^{65,66} and bromine atoms⁶⁷. The reaction with oxygen atoms

has a rate constant of $2 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ and is four times greater than the corresponding ClO radical reaction.

In the mass spectrometer²², the unimolecular decomposition of chlorine dioxide to ClO and to Cl have been postulated

The second of these appears to dominate.

The ClO radical is quite stable with a bond dissociation energy of 63 kcal mole⁻¹ ⁶⁸; consequently the bimolecular decomposition

is favoured^{65,66,69}. The probable mechanism⁶⁶ is

The primary step is rate controlling and has an activation energy of 2.5 ± 0.3 kcal mole⁻¹.

An activation energy of 17 kcal mole⁻¹ has been obtained for the reaction of ClO with NO₃Cl⁷⁰.

At room temperature, the reaction with oxygen atoms⁶⁵, has a rate constant greater than 6×10^{12} cm³mole⁻¹sec⁻¹ and the reaction with nitric oxide⁶⁵ is very fast.

Although the presence of hydrogen⁶⁶ increases the rate of decomposition of ClO, the rate constant at room temperature for their direct bimolecular reaction is less

than $3 \times 10^8 \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$. The enhanced rate is apparently due to

CHAPTER 2

EXPERIMENTAL

As mentioned in Chapter 1, the work described in this thesis was conducted in an attempt to understand more fully the thermal decomposition and reactions of perchloric acid both in the gas phase and on solid surfaces.

A preliminary study of the thermal decomposition suggested that a thorough examination of the decomposition above 280°C might reveal a more complex mechanism than that suggested by Levy¹⁰. This examination of the decomposition of perchloric acid in pyrex reaction vessels constituted the first part of the work.

In the second part of the work, the catalytic decomposition of perchloric acid on a number of commercial catalysts was studied. At the time of the inception of this study, there was no literature available on the catalytic decomposition apart from the report by Sibbett and Lobato¹⁷ of an isolated experiment with alumina. However, it had been suggested that additives could catalyse the acid decomposition and that this was possibly important in the thermal decomposition of AP-catalyst mixtures⁷¹.

The final part of the work consisted of a preliminary investigation of the reaction of perchloric acid with

the model fuels, hydrogen, methane, ethane and ethylene. While a detailed investigation of the reaction with these and other fuels present many technical difficulties a number of suggestions are given at the end of Chapter 4.

2.1 Outline

The same basic experimental system was used for the different studies. As reaction half lives of the order of seconds were encountered, it was necessary to use a flow system. This is represented schematically in Fig. 1.

Carrier gas from a cylinder, fitted with a reducing valve was passed through a rotameter flow meter, the flow rate being controlled by an attached needle valve. During a run, the carrier gas was diverted by means of two three-way taps through hot 72.4% perchloric acid solution, where it became saturated with the acid vapour. The saturated carrier gas passed into a reaction vessel, where reaction took place. In the study of the catalytic decomposition, the catalyst was placed in this reaction vessel and in the study of the reaction with fuels a similarly controlled flow of fuel was introduced into the reaction vessel through a second inlet.

The effluent gas was passed through a trap containing standard sodium hydroxide solution which absorbed the unreacted acid and some of the products. The resulting solution was analysed using volumetric techniques. The flow rate was measured using a soap-bubble flow meter and

the length of the run timed. In some runs, samples of the effluent gas which had passed through the trap were analysed using gas chromatography.

2.2 Materials

Carrier Gas

Nitrogen, helium and oxygen were used. Nitrogen was supplied by Union Carbide, helium by Liquid Carbonic Corp. Ltd. and oxygen by Canadian Liquid Air Ltd. They were all high purity grade and were used direct from the cylinder.

Perchloric Acid

In all these studies the azeotropic mixture of perchloric acid and water was used. This corresponds to a composition of 72.4% by weight of the acid and a molecular formula of $\text{HClO}_4 \cdot 2.17\text{H}_2\text{O}$. Most of the acid used was supplied by Allied Chemicals Canada Ltd., although samples were also used from J.T. Baker Chemicals Ltd., Shawnigan and Anachemia Chemicals Ltd. The solution supplied corresponded to 65-70% acid. Before use, it was therefore concentrated by passing nitrogen through the acid at 110°C . Anhydrous acid was not used, as a fresh sample would have had to be prepared for each run and this would have been excessively time consuming.

Catalysts

The catalysts used were supplied by Harshaw Chemical Co. and are known by their catalogue numbers. They were in the form of small pellets, $1/8$ inch long and $1/8$ inch

in diameter. A brief description of the catalysts is given in Table 1.

Fuels

Hydrogen, methane, ethane and ethylene were used. Hydrogen was supplied by Canadian Liquid Air Ltd. Methane (V.H.P.) and ethylene (C.P.) were supplied by Matheson of Canada Ltd. Ethane (Pure Grade) was supplied by Phillips Petroleum Co. All fuels were used directly from the cylinder.

Analytical Chemicals

All chemicals used in the product analysis were of A.R. grade.

2.3 Apparatus

Flow Rate Control

For the carrier gas stream, two rotameters were used. Either could be selected by manipulating two three-way taps. Their ranges were 30-300 and 300-3000 ml min⁻¹ air at S.T.P. These nominal readings were found useful in pre-selecting the required flow rate and checking constancy of the flow rate. The needle valve incorporated in the rotameter, in conjunction with the cylinder pressure regulator, enabled a constant flow rate to be maintained over many hours. Rather than calibrate these rotameters for different carrier gases, it was found to be more accurate to measure the exit flow rate for each run using a soap-bubble flow meter. The concentration of perchloric acid in the

carrier gas stream was small enough for the residence time of the acid in the reaction vessel to be calculated from the flow rate of the carrier gas alone.

In the reaction with fuels, the fuel stream also passed through a rotameter. The flow rate was measured for fuel alone and then for fuel and perchloric acid carrier gas.

Perchloric Acid Saturator

This is shown in Fig. 2. Both the saturator and its associated preheat coil were made of pyrex. It was immersed in a stirred oil bath of silicone 200 oil which was heated by a 200 watt coiled heater. The temperature of the bath was controlled to better than $\pm 0.5^{\circ}\text{C}$ using a Fisher Temperature Controller. The temperature was measured by a mercury thermometer and was usually kept at about 115°C .

Thus at the beginning of a run, the carrier gas could be diverted, by manipulating two three-way taps, through the preheat coil and bubbled through the hot 72.4% perchloric acid. To prevent the perchloric acid which saturated the carrier gas, from condensing elsewhere in the system all the tubing was heated to about 125°C with Flexicoil heating tape. The bore of the three-way tap, through which the acid passed was heated with nichrome wire wrapped in Refrasil silica sleeving. All taps were lubricated with Kel-F grease which was quite resistant to chemical attack

by the hot acid.

The concentration of perchloric acid in the carrier gas could be altered by adjusting the temperature of the oil bath.

Furnace

The reaction vessel was heated by an aluminium block furnace. This consisted of a horizontal cylinder of aluminium, 8 inches in diameter and 16 inches long, with a 2½ inch diameter hole drilled through it in which the reaction vessel fitted. The block was wound noninductively with 64 feet of Chromel A 1/8 inch tape ($0.235 \text{ ohm ft}^{-1}$). The windings were insulated from the block by several layers of asbestos paper and the windings were covered by Alundum refractory cement and several more layers of asbestos paper. The block sat in a transite pipe fitted with end plates and packed with vermiculite insulation. When in use the two ends of the furnace were packed with asbestos wool.

There were two further holes drilled in the block from one end to the middle. One of these carried a thermocouple, the other carried a temperature probe. The probe, in conjunction with a Hallakainen 2505 Thermotrol temperature controller maintained the temperature to better than $\pm 0.5^\circ\text{C}$ over the entire working range. By probing with a second thermocouple the furnace was found to have a region of constant temperature greater than 20 cm in length, even

in the high temperature region. When this second thermocouple was calibrated against the first, this constant temperature was found to be within 0.5°C of the block temperature. All temperatures quoted in Chapter 3 are block temperatures.

Reaction Vessels

Four pyrex reaction vessels of different body volumes were used during this work. Reaction Vessel I is shown in Fig. 3 and Reaction Vessel III is shown in Fig. 4. Reaction Vessel II was similar to Reaction Vessel I but had a smaller body volume and Reaction Vessel IV consisted simply of a U-tube. The general dimensions of all four vessels are shown in Table 2.

The decomposition of perchloric in the absence of any added catalyst was investigated in all four reaction vessels. Reaction Vessel II was also used in the study of the catalytic decomposition and Reaction Vessel III, which had two inlets was also used in the investigation of the reaction of perchloric acid with fuels.

It was found that the condition of the pyrex surface was important and that this could change spontaneously after remaining constant for many weeks. Apart from this ageing effect, the surface condition also depended upon its pretreatment. This is discussed more fully later. The three standard pretreatments which were used were annealing, washing and coating. Annealing was achieved by

leaving the reaction vessel in a glass blower's annealing oven overnight. Washing was with a mixture of concentrated sulphuric acid and potassium permanganate. After rinsing thoroughly with distilled water, any manganese dioxide deposited was removed with a mixture of nitric acid and hydrogen peroxide. The reaction vessel after further rinsing was then dried in a current of dry air. Only one coating was used. This was boric acid. It was applied in a 5% solution in ethanol. The evaporation of the solvent left a dull coating of the boric acid.

2.4 Analysis

In order to study the kinetics of perchloric acid decomposition and its reaction with fuels, an analysis of the product gas stream from the reaction vessel must be made.

For the decomposition of perchloric acid alone, the catalysed decomposition and the reaction with hydrogen, the product gas stream can only contain unchanged perchloric acid, water, oxygen, chlorine and hydrogen chloride. For this case, a sufficient analysis can be achieved by passing the product gas stream through a trap containing standard sodium hydroxide and analysing the resulting solution using volumetric techniques. A full analysis is not achieved, but by considering the chlorine balance it is possible to obtain kinetic results.

For a study of the reaction of perchloric acid with

other fuels, in which other products are formed this analysis is not sufficient and an analysis involving gas chromatography is required.

Volumetric Analysis

In the former studies, the product stream was bubbled through a trap of standard sodium hydroxide (usually 50 ml N/10 NaOH). This efficiently absorbed all the unchanged perchloric acid, the chlorine and the hydrogen chloride. When very fast flow rates were used a second trap was sometimes necessary.

After a run, the solution was carefully transferred to a volumetric flask. It was necessary to wash into the flask any perchloric acid or hydrogen chloride which had condensed inside the inlet sinter tube. This was best achieved by putting a trap of water in place and applying a small positive pressure to the outlet using a rubber bulb. Three aliquots of this solution were taken and analysis was made for chloride ion, hypochlorite ion and hydroxide ion.

Unchanged perchloric acid consumes sodium hydroxide according to the equation,

Chlorine consumes sodium hydroxide according to the equation,

Hydrogen chloride consumes sodium hydroxide according to the equation,

Therefore for every atom of chlorine in the original perchloric acid (i.e. before decomposition), one molecule of sodium hydroxide is consumed. Also every molecule of chlorine gives one chloride ion and one hypochlorite ion and every molecule of hydrogen chloride gives one chloride ion.

Therefore the analysis, together with a value for the flow rate and for the length of the run, allows the initial perchloric acid concentration, final perchloric acid concentration, final chlorine concentration and final hydrogen chloride concentration to be calculated.

The analysis for hypochlorite was by the iodometric⁷² method. Chloride was determined by Volhard's method⁷³ and hydroxide by an acid base titration with bromothymol blue as indicator. In the last two titrations it was necessary to reduce the hypochlorite to chloride to prevent its interference. In the acid base titration this was achieved by excess sodium nitrite and in the Volhard titration by the stoichiometric amount of arsenious oxide solution.

This analysis was found to be reliable. Tests were made using pure chlorine and also the chloride analysis

was checked using a gravimetric method. While agreement was good it was clear that in the normal analysis of many of the runs only slight errors in titration could lead to a significant difference in the calculated ratios of chlorine and hydrogen chloride produced. Kinetic data were therefore always calculated in terms of amount of perchloric acid decomposed.

Gas Chromatographic Analysis

While a gas chromatographic analysis of the product gas stream would be much less time consuming than the volumetric techniques, it does present a number of technical difficulties. Before attempting to analyse the product gas from the reaction of perchloric acid with fuels, the simpler problem of analysing the product gas from the decomposition was tried. A Hewlett-Packard 5750 Research Chromatograph fitted with a thermal conductivity detector was used. Helium was used as the carrier gas both for the flow system and the chromatograph. Therefore sampling of the product gas into the chromatograph should reveal only products of decomposition with no large carrier gas peak. While there is no reference to the separation of similar mixtures in the literature, it was thought that a 4 m column, packed with 30% Halocarbon oil on silica-gel⁷⁴ or a 10 foot column packed with Kel-F Wax on Haloport F support⁷⁵ would be a suitable starting point as both have been used

in the separation of chlorine compounds. However a number of problems were encountered in sampling the gas stream and so their suitability was never really tested.

Initially a Carle micro-volume sampling valve with a capacity of 5 ml was used. This and all the other parts of the system through which the perchloric acid passed were heated with flexicoil heating tape to prevent condensation of the acid. However the valve offered a large resistance to the effluent gas flow resulting in a dangerous back pressure in the saturator. As the possibility of catalytic decomposition of the perchloric acid on the hot metal also seemed likely, a pyrex sampling system was constructed using two four-way taps. This is shown in Fig. 5. The bores of these taps were also heated with nichrome wire, wrapped in Refrasil silica sleeving, to prevent condensation of the acid. The sampling system functioned well at room temperature and even at elevated temperatures. However, the presence of hot perchloric acid in the effluent gas attacked the Kel-F grease sufficiently to allow the chromatograph carrier gas, which was at a high pressure, to leak. Spring loading the taps and also pumping on the key did not alleviate this problem.

Attempts were then made to remove the perchloric acid from the gas stream before sampling the gas stream and hence to detect only the other components. Passing the gas stream through a trap at room temperature was not effective

due to the hygroscopic nature of perchloric acid. The perchloric acid removed the water which then dissolved the chlorine and hydrogen chloride leaving only oxygen in the gas stream. There was no suitable chemical means of removing only the perchloric acid.

A number of runs were therefore carried out in which both the volumetric and chromatographic techniques were used simultaneously. The product gas was passed through a trap containing standard sodium hydroxide and then through a cold trap to remove any water vapour. The gas stream was then sampled into the gas chromatograph. A 6 foot column packed with Molecular Sieve 5A and maintained at 70°C was used in the chromatograph. This technique allowed the amount of oxygen as well as the amounts of chlorine, hydrogen chloride and unchanged perchloric acid in the effluent gas stream to be obtained.

The same technique was used to study the reaction of perchloric acid with fuels. In this case the results obtained can only be semi-quantitative as unknown amounts of chlorinated organic compounds were produced which invalidate the use of the chlorine balance to interpret the volumetric titrations. This is discussed further in Chapter 3.

2.5 Computing

All computing mentioned in Chapter 3 and 4 was carried out in the U.W.O. Computing Centre, using an I.B.M. 7040 Computer.

Three basic programmes, KASE, NLIN and FUNMIN were used. KASE is a weighted least squares programme with plotting, written at the University of Missouri. KASE was used to obtain the Arrhenius parameters from all the simple Arrhenius plots. FUNMIN is a simpler and more versatile least squares programme, supplied by Dr. I.H. Hillier. This was used for all the early work on investigating simple kinetic models. NLIN, a non-linear least squares programme was used for the later work. This is a more sophisticated programme and is available as I.B.M. Share Program No. 1428.

CHAPTER 3

RESULTS

As the work described in this thesis was in three parts, this chapter is subdivided into three sections: the decomposition of perchloric acid in pyrex reaction vessels; the decomposition of perchloric acid in the presence of added catalysts and the reaction of perchloric acid with fuels.

3.1 Decomposition of Perchloric Acid in Pyrex Reaction Vessels

The kinetics of the decomposition of perchloric acid were investigated between 279 and 471°C with initial acid concentrations of 1×10^{-4} to 1.5×10^{-3} moles litre⁻¹. Four different reaction vessels were used and a range of residence times from 0.9 sec to 2.8 min was employed. The effect of packing, ageing, washing and coating reaction vessels was investigated.

Reaction Vessel I

Reaction Vessel I is shown in Fig. 3. It had a body volume of 110 ml. Other dimensions are given in Table 2. Before it was used it had been fully annealed.

The decomposition was initially investigated at nine temperatures between 286 and 386°C, with an initial acid

concentration of 2.5×10^{-4} mole litre⁻¹.

The results, obtained from volumetric analysis, suggested that 85-95% of the perchloric acid decomposed to give chlorine while 5-15% decomposed to give hydrogen chloride. However the precise determination of the Cl₂/HCl ratio is very difficult and it was clear from the very nature of these calculations that only small differences in the titration values would produce significant changes in these percentages. Therefore a number of runs were carried out at 370°C, in which the experimental conditions were adjusted to give optimum accuracy in the titrations. These were supplemented by gravimetric analyses of the chloride produced in the sodium hydroxide trap. These results suggested that $95 \pm 5\%$ of the decomposition was to chlorine. At a later date, the oxygen yield was measured for a number of runs using gas chromatography. The results were not however entirely conclusive and it was impossible to improve on the accuracy which had already been attained.

First order rate plots for the decomposition at the nine temperatures are included in Fig. 6. All the kinetic data were treated in terms of perchloric acid decomposed rather than in terms of products formed. All are good straight lines but the reaction at 364 and 355°C, which was studied to high conversions, shows a falling off in rate as compared to a simple first order reaction.

The first order rate constants, from these plots are included in Table 3 and also in the Arrhenius plot in Fig. 7. The Arrhenius plot is essentially linear above 340°C but below this temperature it forms a gentle curve. The linear portion would correspond to an activation energy of $35.2 \text{ kcal mole}^{-1}$ and a preexponential factor of $3 \times 10^{10} \text{ sec}^{-1}$.

The deviations from the first order rate plots at high conversions and the non-linearity of the Arrhenius plot over the whole temperature range, suggested that the decomposition was not entirely first order under these experimental conditions. The good reproducibility, even at low temperatures (in contrast to Levy's experience¹⁰), suggested, however, that a single overall mechanism might explain all the data.

In order to see if modifications of first order kinetics could explain the data, two other simple models were considered:

- 1) Parallel first and zero order reactions i.e.

for which,

$$a = (k_0/k_1 + a_0)e^{-k_1 t} - k_0/k_1$$

2) Parallel first and second order reactions i.e.

for which,

$$a = \frac{a_0 k_1}{(k_1 + 2k_2 a_0) e^{k_1 t} - 2k_2 a_0}$$

Attempts were made to fit the data at each temperature to both models using mainly the least squares minimisation programme FUNMIN. It was not generally possible to fit the data to model 1 unless the zero order rate constant was negative which could have no physical meaning. A good fit could be obtained at all temperatures for model 2 ; however, the function was in fact quite insensitive to the values of the second order rate constant k_2 . The first order and second order rate constants which were initially obtained obeyed the Arrhenius equation. For the first order reaction, the activation energy was 22 kcal mole⁻¹ and the preexponential factor was $4.4 \times 10^5 \text{ sec}^{-1}$. For the second order reaction, the activation energy was 42 kcal mole⁻¹ and the preexponential factor was $3.6 \times 10^{15} \text{ sec}^{-1}$. The values of these Arrhenius parameters would require that both the first and

second order reactions represent complex reactions. This analysis of the data predicted that at low temperatures the first order reaction should predominate and at high temperatures the second order reaction should predominate.

Before this was tested by extending the study to higher temperatures, the effect of varying the initial acid concentration at 364°C was observed. A flow technique is not really suitable for measuring initial rates at different initial concentrations, which is one method of determining the order of a reaction. It becomes essentially a one point method. Therefore a number of runs at different residence times were carried out for each initial acid concentration. The first order rate plots for these are shown in Fig. 8. All the data fit the same straight line except at high conversions where deviations occur. The deviation increases with increasing initial acid concentration. However, the decomposition at 364°C is clearly predominantly first order.

The decomposition was then investigated at three more temperatures, extending the temperature range up to 406°C . The first order rate plots for the decomposition at these temperatures are given in Fig. 6. The calculated first order rate constants are included in Table 3 and in the Arrhenius plot in Fig. 7. The effect of varying the initial acid concentration on the calculated first order rate constant was observed at 374°C . The results are shown in

Table 4. Both these sets of results show that the decomposition is essentially first order in this temperature region. The model, involving parallel first and second order reactions was therefore not valid. Both the deviation observed in the first order plots at high conversions and the non-linearity of the Arrhenius plot could not be explained by a simple deviation from a single first order reaction.

The shape of the Arrhenius plot for the first order rate constants suggested that the decomposition occurred by two parallel first order reactions. At the low temperatures, the reaction with the lower activation energy would predominate and at the high temperatures, the reaction with the higher activation energy would predominate. The Arrhenius plot would therefore consist of a curve asymptotic to the straight lines which corresponded to these individual reactions. Using the programme NLIN, it was possible to obtain the Arrhenius parameters for the two reactions. The reaction predominating at high temperatures had an activation energy of $43.3 \text{ kcal mole}^{-1}$ and a preexponential factor of $6.7 \times 10^{12} \text{ sec}^{-1}$ and the reaction predominating at low temperatures had an activation energy of $16 \text{ kcal mole}^{-1}$ and a preexponential factor of $2.0 \times 10^3 \text{ sec}^{-1}$. This analysis into two parallel first order reactions could not explain the observed deviations from first order kinetics.

An attempt to obtain more data in the low temperature region revealed an ageing effect. The first order rate constants obtained at the three temperatures 280, 312 and 349°C, are shown in Table 5. They are considerably less than expected. The decomposition was, however, still first order as varying the initial acid concentration at 312°C did not affect the calculated first order rate constant. This is shown in Table 6. It therefore appeared that before this low temperature investigation began, there had been a change in the nature of the surface. However the reproducibility of the previous work suggested that the surface could remain unchanged for a period of weeks.

As it was now clear that at least in the low temperature region, surface effects were important, the reaction vessel was packed with glass wool. This had a surface area of about $6 \times 10^3 \text{ cm}^2$ and it was thought that this large increase in surface should emphasise the surface effects. The decomposition was investigated at 286 and 358°C. The first order rate constants are shown in Table 7. At 286°C, the rate constant was even lower than for the aged vessel and at 358°C, it was the same as for the annealed reaction vessel. There was no obvious simple explanation of this. Two possibilities presented themselves. It was possible that the surface of the glass wool was practically inert in catalysing the decomposition and that these

effects were due to the nature of the reaction vessel surface changing. An alternative explanation was that the decomposition was in fact a complex chain reaction, in which both initiation and termination were, in part at least, heterogeneous. The effect of a surface may be to increase or decrease the rate depending on the relative importance of the two steps.

At a later stage in the investigation, the decomposition was studied in Reaction Vessel I after it had been thoroughly washed. By using a series of two product absorption traps, faster flow rates could be used. The kinetics were studied at six temperatures up to 435°C . At the three highest temperatures, 400, 416 and 435°C , the decomposition was first order and the calculated rate constants are shown in Table 8. At the three lowest temperatures, 386, 374 and 361°C , the decomposition did not appear to be first order. The reaction was faster than the previous results suggested and there was also an induction period. Plots of the percentage decomposition of the acid against residence time for the six temperatures are shown in Fig. 9. A true induction period can result only from catalysis by products or a degenerate chain branching mechanism involving an intermediate with a half-life of the order of seconds. An apparent induction period can result from self-heating. This is discussed later. These results showed that surface effects could

be important at temperatures at least up to 380°C and that washing the surface altered its activity.

This washed reaction vessel was again packed with glass wool and the decomposition investigated at five temperatures between 290 and 417°C . The surface area of the glass wool was roughly $6 \times 10^3 \text{ cm}^2$. The first order rate plots are shown in Fig. 10 and are linear. The calculated rate constants are shown in Table 9 and in the Arrhenius plot in Fig. 11. The rate of the decomposition appears to be faster than in the annealed vessel but lower than in the washed vessel, particularly at the lower temperatures. The Arrhenius plot was curved. An analysis into two components as was done for the decomposition in the annealed vessel was not attempted, because there were only five points.

Reaction Vessel II

In order to extend the study to higher temperatures, it was necessary to use shorter residence times. Reaction Vessel II was therefore used. This had a body volume of 80 ml . Other dimensions are given in Table 2. Before being used it was thoroughly washed.

The decomposition was studied at eight temperatures between 362 and 470°C . The first order rate plots are shown in Fig. 12. The calculated first order rate constant at 362°C was not affected by varying the acid concentration. This is shown in Table 10 and confirms the

essential first order~~nature~~ of the decomposition. The first order rate constants for the eight temperatures are shown in Table 11 and in the Arrhenius plot in Fig. 13. The Arrhenius plot was linear and corresponds to an activation energy of 41 ± 0.4 kcal mole⁻¹ and a preexponential factor of 1.3×10^{12} sec⁻¹. There was no apparent surface reaction.

The effect of changing the carrier gas from nitrogen to helium and oxygen was negligible. This is shown in Table 12.

Reaction Vessel III

Reaction Vessel III is shown in Fig. 4. It had a body volume of 80 ml. Other dimensions are given in Table 2. It was used mainly in the study of the reaction between perchloric acid and fuels. Initially it was used in an annealed state and the decomposition observed at 365°C. The surface of the reaction vessel was then coated with boric acid and the decomposition observed at 365 and 417°C. The first order rate plots are shown in Fig. 14. The calculated first order rate constants are shown in Table 13. Coating with boric acid increased the rate.

Reaction Vessel IV

Reaction Vessel IV had a body volume of 25 ml. Other dimensions are given in Table 2. It was initially used without annealing. The original intention was to

extend the study of the decomposition to even higher temperatures, however the rate was found to be very fast even at 403°C. The kinetics were studied at four temperatures from 403 to 298°C. At all temperatures there was an apparent induction period. Plots of percentage decomposition against residence time are shown in Fig. 15.

After this initial study, the reaction vessel was removed and after a few weeks re-used. The decomposition was reinvestigated at 364 and 416°C. The rate had decreased by a factor of about two but the reaction still showed an induction period. The reaction vessel was removed and annealed. A further reexamination of the decomposition at 365, 416 and 454°C, showed that the rate had decreased still further and now followed first order kinetics. The first order plots are shown in Fig. 16 and the rate constants in Table 14. The results obtained in Reaction Vessel IV clearly illustrate the strong surface effects which can be important even at high temperatures.

Summary

i) In the range 280 to 470°C, perchloric acid decomposes according to the equation,

although small amounts of hydrogen chloride may be formed.

ii) The decomposition is basically first order at all temperatures and in all reaction vessels. However,

deviations were observed at high conversions. Also, in the washed Reaction Vessel I below 380°C , and in the nonannealed Reaction Vessel IV, apparent induction periods were observed.

iii) An ageing effect can occur, in which the rate of the decomposition may change without there being an active external change in the experimental conditions. In Reaction Vessel I, the rate decreased suddenly after many weeks.

iv) The rate of the decomposition may be changed by washing the reaction vessel. In the case of Reaction Vessel I, the rate increased.

v) The rate of the decomposition may be changed by coating the reaction vessel. The rate in Reaction Vessel IV was increased by coating with boric acid.

vi) Packing the reaction vessel with glass wool may alter the rate but not dramatically. In the aged Reaction Vessel I, the rate was decreased at low temperatures but was unchanged at intermediate temperatures. In the washed Reaction Vessel I, the rate was decreased.

vii) The Arrhenius plot for first order rate constants in an apparently non-ageing reaction vessel may be curved, as for the annealed Reaction Vessel I, or linear as for the washed Reaction Vessel II. The curved Arrhenius plot may be analysed in terms of the sum of two first order rate constants.

3.2 Decomposition of Perchloric Acid in the Presence of Added Catalysts

The catalytic effect of five different Harshaw catalysts was studied. The catalysts are known by their catalogue numbers and Table 1 contains a brief description of their properties. Reaction Vessel II was used and the catalysts were packed in this, between plugs of glass wool. The effluent gas stream was analysed using only volumetric techniques. In the temperature range used, there was no measurable decomposition in the absence of catalyst. Very little, if any hydrogen chloride was produced, the decomposition occurring according to the equation,

Harshaw Catalyst - Cu-0203

Two samples, each weighing 30 g and having surface areas of $3.45 \times 10^2 \text{ m}^2$ were used. Both samples were studied at 261°C and the second sample was studied at five other temperatures before non-reproducible results were obtained. The initial perchloric acid concentration was varied from 3.5 to 9.9×10^{-4} mole litre⁻¹. A range of residence times from 0.05 to 0.26 minutes were employed.

Preliminary work on the first sample showed that initially all the perchloric acid which was passed over the catalyst was consumed. After a few runs, the catalytic effect could be observed. The activity of the

catalyst then increased to more than ten times the original value.

The second sample showed the same effect. After this initial conditioning period fairly reproducible results could be obtained for about 15 runs. After this the results were not very reproducible but the activity generally decreased.

The first order rate plots for the decomposition on the conditioned catalyst are given in Fig. 17 and the rate constants in Table 15. The Arrhenius plot for the specific rate constants is shown in Fig. 18. The decomposition is first order under these conditions with a preexponential factor of $2.5 \times 10^{22} \text{ min}^{-1} \text{ m}^{-2}$ and an apparent activation energy of $54 \text{ kcal mole}^{-1}$.

Both catalyst samples were visibly attacked by the perchloric acid producing a ginger coloured product.

Harshaw Catalyst Fe-0301

A 30 g sample of the catalyst, having a surface area of $1.23 \times 10^3 \text{ m}^2$ was studied at five temperatures from 177 to 238°C . The initial perchloric acid concentration was varied from 2×10^{-4} to $1 \times 10^{-3} \text{ mole litre}^{-1}$ and residence times from 0.05 to 0.7 min were used.

After an initial conditioning period in which the activity increased, reproducible results were obtained. The first order rate plots are shown in Fig. 19 and the rate constants in Table 16. The Arrhenius plot of the

specific rate constants is shown in Fig. 20. Under these conditions, the decomposition is first order with a pre-exponential factor of $2.5 \times 10^{10} \text{ min}^{-1} \text{ m}^{-2}$ and an apparent activation energy of $28.6 \text{ kcal mole}^{-1}$.

The catalyst did not show any visible signs of attack by the perchloric acid.

Harshaw Catalyst - Al-0104

A 30 g sample having a surface area of $2.36 \times 10^3 \text{ m}^2$ was studied at five temperatures between 176 and 251°C . The initial acid concentration was varied from 3.2×10^{-4} to $4.0 \times 10^{-4} \text{ mole litre}^{-1}$ and residence times from 0.06 to 1.0 min were used.

No conditioning period was required and the activity of the catalyst remained constant. The first order rate plots are shown in Fig. 21 and the rate constants in Table 17. The Arrhenius plot of the specific rate constants is shown in Fig. 22. Under these conditions, the decomposition is first order with a preexponential factor of $1.3 \times 10^{10} \text{ min}^{-1} \text{ m}^{-2}$ and an apparent activation energy of $28.8 \text{ kcal mole}^{-1}$.

There was no visible change in the catalyst after it had been used as a substrate for the perchloric acid decomposition.

Harshaw Catalyst - Cu-0803

A 10 g sample, having a surface area of $1.37 \times 10^3 \text{ m}^2$ was studied at six temperatures between 196 and 250°C .

The initial acid concentration was varied from 2×10^{-4} to 1.5×10^{-3} mole litre $^{-1}$ and residence times from 0.05 min to 0.2 min were used.

The activity initially decreased to a relatively constant value. The first order rate plots are shown in Fig. 23 and the rate constants in Table 18. The Arrhenius plot of the specific rate constants is shown in Fig. 24. The decomposition is first order under these conditions with a preexponential of 8×10^{14} min $^{-1}$ m $^{-2}$ and an apparent activation energy of 39.0 kcal mole $^{-1}$.

The perchloric acid reacted with the catalyst changing its colour from dark green to light green.

Harshaw Catalyst - Mn-0201

A 30 g sample, having a surface area of 2.06×10^3 m ^{2} was studied at five temperatures between 142 and 207°C. In the initial work an initial acid concentration of about 3×10^{-4} moles litre $^{-1}$ was used and residence times from 0.02 to 0.5 min were used. Reproducibility was very good but the kinetics were not first order. Plots of percentage decomposition against residence time are shown in Fig. 25. There is an apparent induction period. Attempts were made to fit the data to a number of Langmuir-Hinshelwood type models using the programme FUNMIN but without success.

At 177°C, the decomposition was observed for a number of different initial acid concentrations at the same

residence time. The percentage decomposition decreased slightly with increasing acid concentration suggesting an apparent order less than one.

Further analysis was not possible but Mn-0201 appeared to be very good catalyst. At a later date, self-heating was considered as an explanation of the observed kinetics. This is discussed in Chapter 4. There was no visible change in the catalyst after it had been used as the substrate for the perchloric acid decomposition.

Summary

i) All the catalysts tried catalyze the decomposition positively.

ii) The decomposition follows the equation,

iii) The decomposition on the catalysts, Cu-0203, Fe-0301, Al-0104 and Cu-0803, follows first order kinetics under the experimental conditions used. The decomposition on Mn-0201, showed an apparent induction period.

iv) Arrhenius parameters were obtained for the first four catalysts. These are shown in Table 19.

v) The perchloric acid produced a visible change in the catalysts Cu-0203 and Cu-0803.

3.3 Reaction of Perchloric Acid with Fuels

Preliminary studies have been carried out on the reaction of perchloric acid with hydrogen, methane, ethane and ethylene; Reaction Vessel III was used. This had two inlets and is shown in Fig. 4. For the reaction with hydrogen, volumetric methods of analysis were used almost exclusively and the results are quantitative. For the reaction of perchloric acid with the other fuels a combination of volumetric and chromatographic techniques were used. These results can only be semi-quantitative. Owing to the experimental system used, the fuel stream was always in large excess and so it is convenient to represent the reaction in terms of the amount of perchloric acid consumed.

Reaction with Hydrogen

The reaction vessel had been annealed before use. The reaction of perchloric acid with hydrogen was observed at six temperatures between 146 and 417°C. The initial acid concentration was approximately 3×10^{-4} mole litre⁻¹ and the initial hydrogen concentration was varied from 1.4×10^{-3} to 1.2×10^{-2} mole litre⁻¹. A residence time of 0.1 min was used. The general results are shown in Table 20.

At all temperatures the reaction was faster than for the simple decomposition and the only chlorine-containing product was hydrogen chloride. At a later date, the

product gas stream was analysed after passing through the sodium hydroxide trap. No oxygen was observed.

At 349°C and above, essentially all the perchloric acid was consumed in less than 0.1 min. Below this, reproducible results were not obtained. The results obtained at 147°C are shown in Table 21. The amount of perchloric acid which decomposed in 0.1 min did not appear to be related to the hydrogen concentration in the range studied. There appeared to be more of an ageing effect which showed that surface effects were important at least in this temperature region. The rate of reaction increased until after six runs, practically all the perchloric acid had decomposed in 0.1 min. This was however a general trend with some discrepancies.

In an attempt to improve reproducibility, the reaction vessel was coated with boric acid. The reaction was observed at 365 and 147°C and the general results are shown in Table 22. The rates were still fast. At 365°C , all the perchloric acid was consumed in less than 0.1 min. The results obtained at 147°C are shown in Table 23. Reproducibility was not achieved and once more an apparent ageing effect was observed. The initial runs showed a lower rate of reaction than for the reaction in the uncoated vessel and the ageing appeared to be slower.

Reaction with Methane

The reaction of perchloric acid with methane was investigated at 143, 350 and 417°C. Reaction Vessel III was used after it had been rinsed with distilled water. For most runs, the initial acid concentration was in the region 4.7×10^{-4} to 7.6×10^{-4} mole litre⁻¹ and the initial methane concentration was varied from 4.5×10^{-3} to 3.4×10^{-2} mole litre⁻¹.

No reaction was observed at 143°C, although residence times up to 0.6 min were used. At 350°C, no reaction was observed for a residence time of 0.1 min; however, when the residence time was increased to 0.8 min reaction occurred. Only a small initial acid concentration had been used but hydrogen chloride and carbon monoxide were observed as products. Hydrogen chloride was observed in the volumetric analysis and carbon monoxide in the chromatographic analysis.

Investigations at 417°C, confirmed that hydrogen chloride and carbon monoxide were principal products. No chlorine was observed in the volumetric analysis and the oxygen yield was either very low or non-existent. No carbon dioxide was liberated when a sample of the trap contents were acidified, which suggested that carbon dioxide was not a major product. It was not possible to detect any organic products either visually or by their odour.

For a residence time of 0.11 min, using the normal method of calculation, 50% of the perchloric acid was consumed and the carbon monoxide to hydrogen chloride ratio was approximately two. For a residence time of 0.40 min, 80% of the perchloric acid was consumed and the ratio was nearer three.

These percentage decomposition can only be approximate as a complete product analysis was not achieved. The production of non-ionizable chlorine products would result in a value of the percentage decomposition which was too low, while the production of compounds other than hydrogen chloride which will consume sodium hydroxide, would result in too high a value.

Reaction with Ethane

The reaction of perchloric acid with ethane was investigated at 147 and 417°C. The initial acid concentration was in the range 3.5×10^{-4} mole litre⁻¹ and the initial ethane concentration was varied from 6.8×10^{-3} to 1.4×10^{-2} mole litre⁻¹.

There was no reaction at 147°C. The major products at 417°C were hydrogen chloride and carbon monoxide. No chlorine was observed but appreciable amounts of oxygen were formed. Droplets of organic liquids were produced in the sodium hydroxide trap and there was a persistent odour. For residence time of 0.10 min, the calculated consumption of perchloric acid was 26%. The carbon

monoxide to hydrogen chloride ratio was approximately 0.8 and the oxygen to hydrogen chloride ratio was approximately 0.4. For a residence time of 0.21 min, 51% of the acid was consumed and the ratios were 3 and 0.8, respectively. The run, with a residence time of 0.10 min had an ethane to perchloric acid ratio of 15 which was about a third of the value for the run, with a residence time of 0.21 min.

Reaction with Ethylene

The reaction of perchloric acid with ethylene was investigated at 147 and 417°C. An initial perchloric acid concentration of 7.2×10^{-4} mole litre⁻¹ and an initial ethylene concentration of 6.4×10^{-3} mole litre⁻¹ were used.

There was no reaction at 147°C. Only one run was carried out at 417°C; a residence time of 0.10 min was used. Hydrogen chloride and carbon monoxide were the main products. An appreciable amount of oxygen was formed and there was a large soot formation. Organic oils collected in the sodium hydroxide trap and there were persistent odours. The calculation based on the volumetric analysis suggested that 63% of the perchloric acid had been consumed. The ratio of carbon monoxide to hydrogen chloride was approximately four and the oxygen to hydrogen chloride ratio was 0.3.

CHAPTER 4

DISCUSSION

The results contained in the previous chapter have, with a few exceptions, been presented in chronological order. Particularly in section 3.1, it was necessary at various stages to discuss briefly the results and to draw limited conclusions, in order to reveal the motivations behind the subsequent work. In the first section of this chapter, the decomposition of perchloric acid in pyrex reaction vessels will be discussed and the kinetic models which were mentioned previously, will be fully developed. The ability of each of these models to explain the large body of results, presented in section 3.1, will be considered. The second section will be devoted to the meaning and significance of the results obtained on the catalytic decomposition and in the third section, the preliminary work on the reaction of perchloric acid with the fuels will be discussed and the relevance of these results to the decomposition will be considered. In the final section, the conclusions of the entire work will be summarised and the relevance of these conclusions to the decomposition of AP will be briefly touched upon along with suggestions for further work.

4.1 Decomposition of Perchloric Acid in Pyrex Reaction

Vessels

A large body of results on this reaction were presented in the previous chapter. Before suggesting any reaction mechanisms to explain these results, a number of qualitative features of the decomposition will be discussed.

Perchloric acid decomposes to give mainly chlorine, oxygen and water,

although small amounts of hydrogen chloride are probably produced. The calculated hydrogen chloride yield was always small. The largest yields were observed in the decomposition in Reaction Vessel I and these were consistently higher than the values observed for the decomposition in the other reaction vessels. It is not possible to explain these small amounts of hydrogen chloride in terms of the Deacon equilibrium

for the equilibrium constant is very small at these temperatures.

The hydrogen chloride is probably produced in a side reaction. As this is always small and probably variable it was not possible to observe any clear dependence of

the hydrogen chloride yield on temperature.

In observing the decomposition of perchloric acid in Reaction Vessel I, it was found that washing the reaction vessel not only increased the rate of decomposition but also apparently changed the reaction mechanism. In the annealed reaction vessel the decomposition was basically first order, however in the washed reaction vessel the decomposition below 380°C , was apparently much more complex. Plots of the extent of decomposition against time were sigmoid in shape, exhibiting an induction period. These curves were never mathematically analysed.

A similar observation was made in the decomposition in Reaction Vessel IV. Sigmoid shaped decomposition curves were observed at all temperatures, even after ageing which resulted in a decrease in rate. It was not until the reaction vessel was annealed that the decomposition became first order and this also was accompanied by a decrease in rate.

Such complex kinetics can result from a number of causes. Auto-catalytic reactions in which the rate is catalysed by a product, have sigmoid decomposition time curves. There is no evidence to suggest that the decomposition of perchloric acid, under the experimental conditions used, is autocatalytic. The decomposition is certainly not catalysed by oxygen or water and it would be difficult to propose a mechanism for the autocatalysis

by chlorine. Most autocatalytic reactions in fact occur in condensed phases.

Kinetic schemes involving induction periods are common in combustion studies in which complex chain reactions occur. Sometimes these are a consequence of inhibition by impurities, which break the chains in the early part of the reaction, being themselves consumed in the process. Semenov however postulated the existence of degenerate or delayed branching mechanisms which seem to be more generally applicable. The basic assumption is that chain branching is due to a relatively stable intermediate which has a half-life of the order of seconds. This intermediate is formed in a non-branching process and is then able to react to give either inert products or radicals which can initiate the primary chain leading to the formation of more intermediate. Neither of these explanations seem applicable to the decomposition of perchloric acid. There are no obvious impurities which would consume radicals and no intermediate was found. The analysis of the product gas stream during the induction period was not any different to the normal analysis. In fact, none of the possible intermediates have half-lives as long as a few seconds, at these temperatures.

Sigmoid decomposition curves may also result from self-heating. If a reaction is exothermic, self-heating occurs if the rate of heat production exceeds the rate of

heat loss. As rate constants increase rapidly with increasing temperature, according to the Arrhenius equation, thermal explosion can result. The sigmoid decomposition curves obtained for the decomposition of perchloric acid are a consequence of self-heating. Thermal explosion does not occur because most of the perchloric acid is consumed before the self-heating effect is large. The decomposition is therefore always first order but if the rate is much larger than normal due presumably to strong surface effects, self-heating can mask the first order nature.

The reason self-heating effects are not always important is due to the high dilution of the perchloric acid. Without such dilution, perchloric acid spontaneously ignites at 400°C ²⁸ and in the presence of catalysts at even lower temperatures.

The rate of the perchloric acid decomposition is often irreproducible, especially at the low temperatures. This clearly demonstrates the importance of surface effects, which may even be significant at quite high temperatures. The ageing effect observed in Reaction Vessel I illustrates how the magnitude of this effect may change suddenly. The difficulty of reproducing a surface is illustrated by the effect of washing Reaction Vessels I and II. Washing Reaction Vessel II presumably reduced the surface effect while washing Reaction Vessel I increased it. Any reaction mechanism, which is proposed

must clearly include surface reactions.

Three possible mechanisms will be considered, two of which are chain mechanisms. One difficulty involved in proposing a mechanism is the lack of kinetic information on all but a very few of the possible intermediate reactions.

Simple Model

This is essentially the mechanism suggested by Levy¹⁰. Perchloric acid decomposes both in the gas phase and heterogeneously on the pyrex surface. The gas phase decomposition is unimolecular and the heterogeneous decomposition is first order.

The unimolecular decomposition probably corresponds to the breaking of the HO-ClO₃ bond,

for which the enthalpy change $\Delta H = 48.3 \text{ kcal mole}^{-1}$.

If the chlorine trioxide radical is too unstable to have a separate existence, two other alternatives are possible

These involve enthalpy changes of +35.9 and +96.3 kcal mole⁻¹, respectively. The second reaction, 4.5 would seem very unlikely due to this high positive

enthalpy change.

A third alternative²²,

involves only an enthalpy change of $+31.1 \text{ kcal mole}^{-1}$; however, a high activation energy would be expected due to the large internal rearrangement involved.

As only final products were observed, it is not possible to distinguish between these alternatives. However, equation 4.3 probably represents the initial step although equation 4.4 is possible.

If perchloric acid is not consumed by any other reaction, the rate equation is given by,

$$-\frac{d(\text{HClO}_4)}{dt} = k_1(\text{HClO}_4) \quad (4.7)$$

Levy¹⁰ suggested that the hydroxyl radical produced in equation 4.3, abstracts a hydrogen atom from a second perchloric acid molecule,

The enthalpy change for this reaction is $\Delta H = -8.3 \text{ kcal mole}^{-1}$. If the hydroxyl radical is in its steady state concentration, then the rate of perchloric acid decomposition is given by

$$- \frac{d(\text{HClO}_4)}{dt} = 2k_1(\text{HClO}_4) \quad (4.9)$$

Levy used equation 4.7.

The heterogeneous decomposition corresponds to the first order decomposition of perchloric acid adsorbed on the pyrex surface. On a Langmuir-Hinshelwood model, the perchloric acid is only sparsely adsorbed on the surface. In practice, the perchloric acid is probably adsorbed on many different types of sites some of which may even be saturated; however, those sites on which most of the perchloric acid decomposes are sparsely populated. These sites correspond to a low activation energy for the decomposition. Once more it is not possible to decide which is the initial step. Reaction 4.6 is now also possible because adsorption of the activated complex will lower the activation energy.

The heterogeneous rate equation will correspond to either 4.7 or 4.9 depending on the fate of the hydroxyl radical which is produced. The heterogeneous rate constant, k'_1 contains the equilibrium constant for the adsorption of perchloric acid on pyrex, K , and the surface area of the pyrex, S , as well as the specific rate constant, k_s ,

$$k'_1 = KSk_s \quad (4.10)$$

The overall rate of decomposition is therefore,

$$-\frac{d(\text{HClO}_4)}{dt} = (k_1 + k'_1)(\text{HClO}_4) \quad (4.11)$$

This simple model therefore has a number of consequences:

i) The decomposition should be first order under all conditions.

ii) The Arrhenius plot of the first order rate constants should normally be a smooth curve. The asymptote with the higher slope should correspond to the unimolecular decomposition and the asymptote with the lower slope should correspond to the heterogeneous decomposition.

iii) If there is no surface reaction, the Arrhenius plot should be linear and correspond to the unimolecular decomposition.

iv) If the number but not the type of decomposition sites is changed, then the position of the lower asymptote in the Arrhenius plot should change but the slope should remain the same.

v) If either the number or type of the sites is constantly changing irreproducible rate constants should be obtained.

The observed results agree quite well with the above general features. This model cannot, however, explain the deviations from first order kinetics obtained at high conversions.

The linear Arrhenius plot for the decomposition in

Reaction Vessel II suggests that washing the reaction vessel has poisoned all the sites. The activation energy for the unimolecular decomposition is $41.2 \text{ kcal mole}^{-1}$ and the preexponential factor is $1.3 \times 10^{12} \text{ sec}^{-1}$. If the hydroxyl radical does react with a further perchloric acid molecule the preexponential factor is then $6.5 \times 10^{11} \text{ sec}^{-1}$.

A curved Arrhenius plot was obtained for the decomposition in the annealed Reaction Vessel I. This could be analysed to obtain the Arrhenius parameters for the two separate reactions as was mentioned in section 3.1; however, the errors in these values could be significant. Owing to a technical problem in the computer analysis it was not possible to calculate these errors. If the Arrhenius parameters obtained for the unimolecular decomposition in Reaction Vessel II were used an activation energy of $15.1 \text{ kcal mole}^{-1}$ and a preexponential factor of $5.6 \times 10^4 \text{ sec}^{-1}$ were obtained for the heterogeneous reaction.

Only three rate constants were obtained for the aged reaction vessel and so it is difficult to decide whether both the Arrhenius parameters for the heterogeneous decomposition had changed or just one. It is also possible that the parameters were not constant for the three rate constants. If the activation energy had remained constant at about $15 \text{ kcal mole}^{-1}$, this would

correspond to a preexponential factor of $2.0 \times 10^4 \text{ sec}^{-1}$ which would suggest that about 65% of the sites had become poisoned.

The results obtained when this reaction vessel was then packed, suggest that the glass wool packing was essentially inert and possessed few if any suitable decomposition sites. The variations in the rate constant are presumably due to a further ageing of the pyrex surface which initially decreased the heterogeneous reaction at 286°C but then increased it at 366°C .

Washing Reaction Vessel I increased the heterogeneous reaction. Due to the effect of self-heating it is not possible to make any quantitative conclusions; however, at the higher temperatures the rate constants agree quite closely with those obtained in Reaction Vessel II demonstrating that the unimolecular decomposition predominates at high temperatures.

When this Reaction Vessel was then packed with glass wool, a curved Arrhenius plot was obtained. Again it seems probable that the glass wool is inert and that the decrease in rate is due to an ageing of the washed surface. This can be analysed in a similar way to the annealed vessel and an activation energy of $15.4 \text{ kcal mole}^{-1}$ and a pre-exponential factor of $1.4 \times 10^5 \text{ sec}^{-1}$ were obtained. The washed reaction vessel therefore had two and a half times as many sites as the annealed vessel. As the sur-

face area was the same, this means that the concentration of surface sites had increased by a factor of two and a half.

Three rate constants were obtained using Reaction Vessel III, but only one of these was in the annealed reaction vessel. The rate constant obtained at 366°C for the decomposition in the annealed vessel was the same as that obtained in the annealed Reaction Vessel I. The surface area of Reaction Vessel III is about 90% of the area of Reaction Vessel I, and so provided the activation energy is still the same this corresponds to approximately the same concentration of sites.

Coating the reaction vessel at 366°C increased the rate by a factor of two. This suggests that the decomposition on boric acid has a lower activation energy than on pyrex and that the concentration of sites is probably increased. At 416°C , the rate constant agrees with the value obtained in Reaction Vessel II and so the heterogeneous contribution to the decomposition is small, as expected.

It is not possible to draw any quantitative conclusions on the decomposition of perchloric acid in Reaction Vessel IV, where sigmoid shaped decomposition curves were observed. It is clear that the heterogeneous reaction was very important in these cases. This is presumably associated with the contamination of the surface.

Three rate constants were obtained for the decomposition in the annealed vessel. The two values obtained in the high temperature region demonstrate that at these temperatures only the unimolecular decomposition is important. The rate constant obtained at 366°C is only a little higher than the value obtained in the annealed Reaction Vessel I. The surface area is about 70% of the surface area of Reaction Vessel I. This means that provided the activation is unchanged, the concentration of sites is only slightly higher than on the annealed Reaction Vessel I.

Simple Chain Model

In practice, it is often very difficult to distinguish between a unimolecular decomposition and a chain reaction. Chain reactions are involved in perchloric acid flames and there is a strong possibility that the normal decomposition involves a chain mechanism. This may explain the deviations from first order kinetics observed at high conversions, which cannot be explained on the first model. The simple model also required a number of rather special and perhaps arbitrary assumptions to explain the surface effects; however, a chain model may offer a more realistic explanation.

Unfortunately there is little information on the possible reactions involved and this makes it difficult to be sure about a mechanism. Chain reactions in general consist of an initiation reaction, propagation reaction and a

termination reaction. The most likely chain carrier would appear to be the ClO radical since it has the necessary stability (in contrast to chlorine dioxide, chlorine trioxide and chlorine tetroxide) and might be expected to be an efficient hydrogen abstraction agent. It has been suggested³¹ as the probable chain carrier in perchloric acid flames. The following mechanism was therefore proposed,

The significance of two very recent reports^{76,77} on the reactivities of both perchloric acid and the ClO radical will be considered later.

The above reactions are not necessarily simple reaction steps, and if they are not then the rate constant may contain the rate constants for the several steps which are involved. As surface effects are obviously important, a gas phase and a heterogeneous initiation

reaction, 4.12 and 4.13, are included. The enthalpy change for these reactions is $\Delta H = +48.3 \text{ kcal mole}^{-1}$. As the ClO radical is the proposed chain carrier, equations 4.14 and 4.15 represent the propagation reactions. The enthalpy changes for these reactions are $\Delta H = -18.9 \text{ kcal mole}^{-1}$ and $\Delta H = +12.9 \text{ kcal mole}^{-1}$, respectively. The termination reaction, 4.16, is the recombination of the ClO radicals and involves an enthalpy change of $\Delta H = -48.4 \text{ kcal mole}^{-1}$. The mode in which any of the other intermediates are removed will not affect the kinetics unless they consume perchloric acid.

On this model the rate of perchloric acid decomposition is given by

$$-\frac{d(\text{HClO}_4)}{dt} = k'(\text{HClO}_4) - k_2(\text{ClO})(\text{HClO}_4) + 2k_3(\text{HOCl})(\text{HClO}_4) \quad (4.18)$$

where $k' = k_1 + k'_1$. If the ClO radicals and the hypochlorous acid molecules are in their steady state concentrations, the rate becomes

$$-\frac{d(\text{HClO}_4)}{dt} = k'(\text{HClO}_4) + \frac{k_2^2}{2k_4} (\text{HClO}_4)^2 \left[1 + \left(1 + \frac{8k_1k_4}{k_2^2(\text{HClO}_4)} \right)^{1/2} \right] \quad (4.19)$$

If the hydroxyl radical attacks a second perchloric acid

molecule by reaction 4.8, then k' must be replaced by $2k'$ in the above equation.

If the first term in equation 4.19 is dominant, then the overall rate of decomposition will be basically first order but modified by the second term. This might explain the deviations observed at high conversions.

The Arrhenius parameters for reaction 4.14 have not been determined; however it is useful to see the effect of using estimated values. In the annealed Reaction Vessel I at 350°C , k' is approximately 10^{-2} sec^{-1} ; the value of k_4 has been given by Clyne⁷⁷ as $10^{11.89} \exp(-2,300/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ so that at 350°C , k_4 is approximately $10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$. The initial perchloric acid concentration was $2 \times 10^{-4} \text{ mole litre}^{-1}$. Bimolecular reactions usually have preexponential factors of about $10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ and so if reaction 4.14 does not require an activation energy then k_2 will be approximately $10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$.

For these values, the rate equation reduces to

$$-\frac{d(\text{HClO}_4)}{dt} = k'(\text{HClO}_4) + \frac{k_2^2}{k_4} (\text{HClO}_4)^2 \quad (4.20)$$

and the second term is much larger than the first. This means that the decomposition would be basically second order which is not the case.

If reaction 4.14 has an activation energy of approx-

imately $15 \text{ kcal mole}^{-1}$ or more, the rate equation becomes

$$-\frac{d(\text{HClO}_4)}{dt} = k'(\text{HClO}_4) + \left(\frac{2k'}{k_4}\right)^{1/2} k_2(\text{HClO}_4)^{3/2} \quad (4.21)$$

where the second term is less than 1% of the first term at $t = 0$ for the above choice of the activation energy. As the concentration of perchloric acid decreases, the approximation to first order kinetics improves so that departures from first order behaviour cannot be explained if the above condition on k_2 is satisfied.

Also as the only heterogeneous rate constant in equation 4.19 is k'_1 , which is contained in k' , this simple chain model offers no alternative explanation for the variation of the observed first order rate constants under different surface conditions. It thus suffers from the same disadvantages as the first model at the cost of added complexity.

Complex Chain Model

The simple chain mechanism which was considered, could not provide an alternative explanation of the surface effects because only one heterogeneous reaction was involved. In this complex chain model, as well as the steps proposed in the simple chain model, that is reactions 4.12 to 4.17, the following heterogeneous termination reaction will be considered,

The overall enthalpy change for this reaction is $\Delta H = -24.2 \text{ kcal mole}^{-1}$.

The rate of perchloric acid decomposition is given by equation 4.18 but the expressions for the steady state concentrations of the intermediates are changed.

If reaction 4.22 was the only termination reaction, the rate equation is

$$-\frac{d(\text{HClO}_4)}{dt} = k'(\text{HClO}_4) + \frac{2k'k_2(\text{HClO}_4)^2}{k_5 - k_2(\text{HClO}_4)} \quad (4.23)$$

For probable values of the unknown rate constants, this becomes,

$$-\frac{d(\text{HClO}_4)}{dt} = k'(\text{HClO}_4) + \frac{2k'k_2}{k_5} (\text{HClO}_4)^2 \quad (4.24)$$

This model cannot therefore explain the deviations from first order kinetics at high conversions nor provide an alternative explanation of the surface effects.

If both termination reactions are considered, the following rate equation results,

$$-\frac{d(\text{HClO}_4)}{dt} = k'(\text{HClO}_4) + \frac{k_2(\text{HClO}_4) [k_2(\text{HClO}_4) - k_5]}{2k_4} \left[1 + \left(1 + \frac{8k'k_4(\text{HClO}_4)}{(k_2(\text{HClO}_4) - k_5)^2} \right)^{\frac{1}{2}} \right] \quad (4.25)$$

This rate equation is complex and as the Arrhenius parameters for both k_2 and k_5 are unknown, it is difficult to apply. However, using the values for the known rate constants at 350°C in the annealed Reaction Vessel I and roughly estimating the unknown values, the rate equation reduces to,

$$-\frac{d(\text{HClO}_4)}{dt} = \left(k' - \frac{k_2 k_5}{k_4} \right) (\text{HClO}_4) + \frac{k_2^2}{k_4} (\text{HClO}_4)^2 \quad (4.26)$$

This rate equation also cannot explain the deviations observed at high conversions and the second order term must be negligible. However, an alternative explanation of the surface effects is suggested. The observed first order rate constant now contains two heterogeneous rate constants, k_5 and k'_1 , which is included in k' . Increasing the surface, increases not only k'_1 but k_5 . It is therefore the difference in these effects which controls the change in rate. The rate may either increase or decrease depending on the relative magnitudes of these two effects. As nearly all experiments on packing reaction vessels resulted in a decrease in rate it would suggest that the heterogeneous termination is the most sensitive to area. However it is clear that ageing effects do occur and so perhaps both effects are involved.

No attempt was made to analyse the Arrhenius plots in terms of this model in view of the large number of unknown parameters involved. If k_5 and k'_1 were zero at all temperatures, then the Arrhenius plot for the first order rate constants would be linear and if k_5 was zero at all temperatures the Arrhenius plot would be gently curved as in the simple model. If k_5 was finite this would result in a decrease in the rate constant but it is difficult to estimate whether this would be clearly observable in the Arrhenius plot.

The analysis into two first order reactions which was possible for the decomposition in the annealed Reaction Vessel I might suggest that

$$E'_1 = E_5 + E_2 - E_4 = 15 \text{ kcal mole}^{-1}$$

$$A'_1 - (A_5 A_2)/A_4 = 5.6 \times 10^4 \text{ min}^{-1}.$$

However as both A'_1 and A_5 should be proportional to the surface area, it would mean that the overall preexponential factor should be proportional to the surface area. This was not observed experimentally. This may mean that the two exponentials are not the same and that the analysis into two first order reactions is only an approximation to the true analysis into the equivalent of three first order reactions. Unfortunately it was not possible to extend the temperature range to even lower temperatures which might have revealed this effect. An alternative

explanation may be that the surface ageing effects mask this effect.

The possibility therefore exists that the decomposition of perchloric acid involves a chain mechanism, which has both heterogeneous and homogeneous initiation and termination reactions. However, the absence of Arrhenius parameters for reactions 4.14 and 4.22 makes it difficult to draw more definite conclusions regarding the mechanism.

4.2 Decomposition of Perchloric Acid in the Presence of Added Catalysts

The five Harshaw catalysts, which were used, all catalysed the decomposition of perchloric acid. These included Cu-0203, whose effectiveness as an AP catalyst is utilised in certain rocket propellants, and Al-0104 which is known to have no effect on the decomposition of AP. While there has been no previous investigation of the catalytic effect of Cu-0803, Fe-0301 and Mn-0201 on the decomposition of AP, a number of preliminary experiments using a Perkin-Elmer Differential Scanning Calorimeter DSC-1B demonstrated that all three were positive catalysts. The transition metal oxides which are contained in these catalysts, namely cupric oxide, ferric oxide and manganese dioxide are also known to be AP catalysts¹.

The stoichiometry of the decomposition corresponded to equation 4.1. The calculated hydrogen chloride yields

were significantly less than in the uncatalysed decomposition and were generally either very small or zero.

Under the experimental conditions used, the decomposition of perchloric acid was clearly first order on all the catalysts, except Mn-0201. It is probable that the sigmoid shaped decomposition curves, obtained on Mn-0201 do not reflect a complex mechanism, but are a consequence of self-heating. Mn-0201 was a very effective catalyst and as such the heat evolution could exceed the heat loss. The decomposition of perchloric acid on Mn-0201 may also therefore be first order. At the temperatures used, the homogeneous decomposition and the heterogeneous decomposition on pyrex were negligible in comparison to the observed decomposition. The simplest explanation of the first order kinetics is in terms of a Langmuir-Hinshelwood model, in which the perchloric acid is decomposing on active sites, which are sparsely populated. If it had been technically possible to increase the perchloric acid concentration sufficiently, the decomposition would presumably have become zero order.

The apparent activation energy obtained from the first order rate constants in a Langmuir-Hinshelwood system, is the sum of the activation energy for the surface reaction and the heat of adsorption of the reactant on the surface. Therefore, the apparent activation energies which are given in Table 19, represent the smallest

values possible for the true surface reaction. The heats of adsorption may be expected to be at least 10 to 15 kcal mole⁻¹.

At 170°C, Fe-0301 is the most effective catalyst in the decomposition of perchloric acid; the order of decreasing specific rate being Fe-0301 > Al-0104 > Cu-0803 ~ Cu-0203. At 250°C, the order is practically reversed with Cu-0203 » Cu-0803 > Fe-0301 > Al-0104.

While it is clear that there is no simple correlation between the activity of a catalyst for the decomposition of perchloric acid and its activity for the decomposition of AP, it is worth noting that Cu-0203 has very little effect on the low temperature AP decomposition but considerably accelerates the high temperature decomposition¹.

The reversal in the order of activity between 170 and 250°C is caused by the different activation energies which are observed on the different catalysts. These range from 28 to 54 kcal mole⁻¹ and in order of decreasing activation energy correspond to Cu-0203 > Cu-0803 > Al-0104 ~ Fe-0301. Such a wide range of activation energies would normally lead to very large differences in the specific rates observed on different catalysts, however this is compensated for by a similar variation in the values of the preexponential factors. A plot of apparent activation energy against logarithm of the specific preexponential factor is shown in Fig. 26. This is a straight line and

the apparent activation energy in kcal mole⁻¹ and the specific preexponential factor in min⁻¹ m⁻² are related by the equation,

$$E = 2.1 \log_{10} A + 7.7$$

Compensation effects have been observed in many investigations of heterogeneous catalysis, however as yet there does not appear to be a universally applicable explanation of its occurrence. As the specific preexponential factor contains terms involving the entropy of activation and also the concentration of active sites, it would appear that one or both of these terms is related to the activation energy.

In view of the large activation energy observed for the decomposition of perchloric acid on Cu-O2O3, it is probable that this contains an energy of formation of the active sites. This would occur if the concentration of sites increased exponentially with temperature. This may also be the case with the other catalysts.

Chemical reaction between the perchloric acid and catalyst was observed for Cu-O2O3 and Cu-O8O3, and this may in part be responsible for the observed conditioning periods before a constant activity was observed. The colour change observed in Cu-O2O3 corresponds to the oxidation of Cr^{III} to Cr^{VI} and Cr^{VII} while the colour change in Cu-O8O3 is probably due to the formation of the

chloride, although only a weak positive chloride test was observed. There was no visible change in the case of Mn-0201, Fe-0301 and Al-0104 although a conditioning period was observed for Fe-0301.

4.3 Reaction of Perchloric Acid with Fuels

While it was possible to make only a preliminary study of the reaction of perchloric acid with various fuels, a number of interesting observations were made. Perchloric acid appears to react in a similar manner with the different hydrocarbon fuels, but the reaction with hydrogen appears to be quite different.

The stoichiometry of the reaction of perchloric acid with hydrogen is,

and the enthalpy change is $\Delta H = -250.9 \text{ kcal mole}^{-1}$. The reaction was observed at temperatures well below the decomposition temperature of the perchloric acid alone and it is clear therefore, that direct reaction between hydrogen and perchloric acid occurs. The ageing effect observed at 146°C illustrates that, at least at low temperatures, this direct reaction is heterogeneous. The subsequent fast reactions of the primary products may also be heterogeneous but in view of their reactive nature they probably react mainly in the gas phase. The following mechanism is suggested,

All the above equations refer to reactions which are thermodynamically feasible.

By analogy with the reaction of hydrogen and oxygen, an alternative mechanism may be proposed,

where S represents the surface. However, this mechanism seems unlikely as oxygen was not observed as a major product. Also, Clyne⁷⁶ has very recently reported that in a discharge-flow system, no reaction between hydrogen atoms and perchloric acid could be observed at 500 K. It would appear that in this study the walls of the reaction vessel were covered by recombining hydrogen atoms, preventing the adsorption of perchloric acid, necessary for reaction 4.28.

The reaction of perchloric acid with the hydrocarbon fuels was only observed under conditions in which the

perchloric acid decomposes alone. It therefore appears that no direct reaction between the perchloric acid and the fuel occurs, but that the fuel reacts with the decomposition intermediates of perchloric acid. At 417°C , the decomposition of perchloric is basically unimolecular and about 50 to 55% decomposition would be expected after 0.1 min. In the presence of methane, the percentage decomposition calculated in the normal way from the volumetric analysis results, was 50%. The values, when ethane and ethylene were used, were 26 and 63%, respectively. It might appear that ethane reduces the amount of decomposition and that ethylene increases it, but it is more likely that the discrepancy reflects the failure of the volumetric analysis to give the true extent of decomposition. A low value of the calculated percentage decomposition would result from the formation of chlorine compounds in which the chlorine was not ionizable and high values would result from the formation of other products, besides hydrogen chloride, which consume sodium hydroxide. While the experimental errors in this series of experiments were larger than in the other work, owing to the difficulty of maintaining a constant residence time, it is clear that chlorinated organic compounds are formed when perchloric acid decomposes in the presence of ethane. This would explain the formation of oil droplets in the sodium hydroxide trap. The oils formed in the presence of ethylene

probably include addition compounds, rather than chlorine compounds. If it is assumed that the hydrocarbon fuel does not affect the extent of decomposition, it would appear that at 417°C , approximately 1.5 moles of carbon monoxide are produced for every mole of perchloric acid decomposed, for residence times of 0.11 and 0.4 min. For ethane, the amount of carbon monoxide is 0.3 moles at 0.1 min and 1.3 moles at 0.2 min and for ethylene, it is 5 moles at 0.1 min. The number of moles of oxygen which is apparently produced for every mole of acid decomposed is probably an artifact, in view of the fuel-rich systems studied. The apparent oxygen yields probably arose from an incomplete flushing of the flow system with helium, after the sodium hydroxide trap was replaced.

4.4 Conclusions

Three reaction mechanisms were considered for the decomposition of perchloric acid in pyrex reaction vessels. It was seen that the results could be explained in terms of a parallel unimolecular gas phase reaction and a first order heterogeneous reaction, and also in terms of a chain reaction involving both heterogeneous and homogeneous initiation and termination reactions. The first model required rather special assumptions about the activities of the different surfaces while the chain mechanism offered a more realistic explanation of the surface effects. However, the chain mechanism contained too many unknown

parameters, which make a quantitative treatment impossible.

Clyne^{76,77} has very recently reported that the ClO radical is apparently quite unreactive. No reaction could be observed with nitrous oxide or carbon monoxide and only a very slow reaction with hydrogen and methane was observed even at 587 K. He also found that perchloric acid had a low kinetic reactivity at temperatures near 500 K in respect to its reaction with free atoms. It would therefore appear that reaction 4.14 would be very slow. The simple model, not involving a chain reaction therefore appears to be the most probable.

However, it is clear that, whether chain steps are important or not, above approximately 400°C the decomposition is essentially unimolecular. The activation energy for this is $41.2 \text{ kcal mole}^{-1}$ and the preexponential factor is $1.3 \times 10^{12} \text{ sec}^{-1}$. The preexponential factor lies within the accepted range for a unimolecular reaction. The activation energy is $7.1 \text{ kcal mole}^{-1}$ below the calculated HO-ClO_3 bond energy of $48.3 \text{ kcal mole}^{-1}$ ¹⁰. In view of the preliminary nature of the previous studies^{10,20}, this value is to be preferred, however it is not clear why it is 7 kcal mole^{-1} below the bond energy.

If the unimolecular decomposition was occurring at its low pressure limit, then the activation energy should be $48.3 - sRT \text{ kcal mole}^{-1}$ where s is the effective number of degrees of freedom. On Slater's theory this is half

the total number of degrees of freedom and this theory would thus predict a value for the activation energy of approximately $4\frac{1}{2}$ kcal mole⁻¹ at a mean temperature of 600 K. However, while the perchloric acid pressure is only a few torr, the total pressure of the system is atmospheric and the high pressure limit should be the one concerned. In that case it is difficult to understand an activation energy substantially less than the bond energy.

In the decomposition of perchloric acid in the presence of methane and ethylene, there did not appear to be dramatic change in rate. This suggests that either the reaction

is very fast and so the hydroxyl radical concentration is not affected by reactions with organic radicals or that this reaction does not occur in the normal decomposition. The hydroxyl radical may react with chlorine oxide intermediates.

If the low temperature reaction represents simply a heterogeneous reaction of the Langmuir-Hinshelwood type, then the reaction on pyrex has an activation energy of 15 kcal mole⁻¹ and probably a value even less on boric acid. The concentration of the active sites is very sensitive to pre-treating and ageing the surface.

The decomposition of perchloric acid can be cata-

lysed by a number of Harshaw catalysts, however it is clear that there is no simple relationship between the activities of a catalyst in the perchloric acid decomposition and the AP decomposition, as alumina is a positive catalyst for the decomposition of perchloric acid but has no effect on the decomposition of AP. However, the strong catalytic effect of Cu-0203 on the high temperature decomposition of AP is probably due to the enhanced decomposition of the primary product perchloric acid on the catalyst surface. Both decompositions, have high activation energies in the region of $50 \text{ kcal mole}^{-1}$. It would be interesting to extend this study, by concentrating on the two catalysts Cu-0203 and Al-0104. The former, while of more technical interest, has the inconvenience of non-constant activity; the latter appears to remain constant indefinitely. By selecting a smaller sample it may be possible to observe the change in kinetics from first order to zero order, and this would enable the heat of adsorption and the activation energy of the true surface reaction to be found. In practice, this may prove difficult, for a smaller sample size requires a higher temperature to give observable decomposition and the gas phase decomposition may become significant.

Perchloric acid reacts with hydrogen heterogeneously on pyrex and an inability to produce reproducible surfaces may make a systematic study of this reaction difficult.

The reaction of perchloric acid with hydrocarbon fuels appears to involve only the reaction of decomposition intermediates with the fuel. Probably a systematic study of these reactions would throw more light on the decomposition. Provided a constant surface could be used, a study of the reaction at low temperatures may prove whether a chain mechanism is involved in the decomposition. Such a study presents many analytical problems, however by using smaller concentrations of fuel, it should be possible to measure the amount of fuel consumed which would be a useful parameter. This also allows the fuel concentration to be varied without affecting the perchloric acid concentration. As there is no direct reaction between the fuel and perchloric acid, the problem of ensuring complete mixing in the reaction vessel can be overcome by pre-mixing at temperatures below the reaction temperature.

Until such a systematic study has been made, it would appear difficult to rule out the possibility of a chain mechanism being important in the thermal decomposition of perchloric acid.

TABLE 1
CATALYST PARAMETERS

HARSHAW NUMBER	NOMINAL COMPOSITION (BY WEIGHT)	COLOUR	SURFACE AREA $\text{m}^2 \text{g}^{-1}$
Cu-0203	78% CuO 20% Cr_2O_3	dark brown	10 - 13
Fe-0301	20% Fe_2O_3 on Al_2O_3	rust brown	41
Cu-0803	10% CuO on Al_2O_3	light green	137
Al-0104	99% Al_2O_3	white	80
Mn-0201	19% MnO_2 on Al_2O_3	black	69

TABLE 2
REACTION VESSEL PARAMETERS

REACTION VESSEL	BODY VOLUME ml	PREHEAT VOLUME ml	BODY SURFACE cm ²	PREHEAT SURFACE cm ²
I	110	25	160	167
II	56	14.5	115	97
III	80	13	140	87
IV	25	-	110	-

TABLE 3
FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION
ANNEALED REACTION VESSEL I

RUN	TEMP. °C	$10^3/T$ K ⁻¹	k min ⁻¹	LOG ₁₀ k
1	335.8	1.642	0.334	1.524
2	354.9	1.592	0.633	1.802
3	369.9	1.555	1.21	0.0835
4	386.1	1.517	2.42	0.384
5	331.3	1.654	0.276	1.462
6	311.6	1.710	0.155	1.192
7	286.0	1.788	0.0749	2.874
8	346.2	1.614	0.472	1.674
9	364.4	1.568	0.942	1.974
10	406.0	1.472	5.53	0.743
11	394.6	1.497	3.32	0.521
12	378.6	1.534	1.75	0.243

TABLE 4
EFFECT OF INITIAL ACID CONCENTRATION
ON THE FIRST ORDER RATE CONSTANT
AT 374.4°C ANNEALED REACTION VESSEL I

$10^4 a_0$ mole litre ⁻¹	t_r min	% DECOMP	k min ⁻¹
4.8	0.185	25.8	1.6
3.8	0.183	25.1	1.6
8.6	0.173	22.0	1.4
14.8	0.181	24.9	1.6

TABLE 5
FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION
AGED REACTION VESSEL I

RUN	TEMP. °C	$10^3/T$ K ⁻¹	k min ⁻¹	LOG ₁₀ k
1	311.9	1.709	0.064	2.81
2	279.3	1.810	0.037	2.57
3	348.8	1.607	0.34	1.53

TABLE 6
EFFECT OF INITIAL ACID CONCENTRATION
ON THE FIRST ORDER RATE CONSTANT
AT 311.9°C AGED REACTION VESSEL I

$10^4 a_0$ mole litre ⁻¹	t_r min	% DECOMP	k min ⁻¹
4.6	1.62	9.5	0.062
6.4	1.74	9.9	0.060
9.5	1.72	11.7	0.072
10.2	1.73	10.5	0.064
4.7	1.67	10.0	0.063

TABLE 7
 FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION
 AGED REACTION VESSEL I
 PACKED WITH GLASS WOOL

RUN	TEMP. °C	$10^3/T$ K ⁻¹	k min ⁻¹	LOG ₁₀ k
1	285.7	1.789	0.025	2.40
2	358.5	1.583	0.76	1.88

TABLE 8
FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION
WASHED REACTION VESSEL I

RUN	TEMP. °C	$10^3/T$ K ⁻¹	k min ⁻¹	LOG ₁₀ k
1	434.6	1.413	16.1	1.21
2	416.3	1.450	8.41	0.93
3	400.1	1.485	4.95	0.70

TABLE 9

FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION
WASHED REACTION VESSEL I PACKED WITH GLASS WOOL

RUN	TEMP. °C	$10^3/T$ K ⁻¹	k min ⁻¹	LOG ₁₀ k
1	364.2	1.569	1.36	0.13
2	416.8	1.449	9.8	0.99
3	291.1	1.772	0.17	1.24
4	322.5	1.679	0.31	1.49
5	388.1	1.512	3.1	0.49

TABLE 10
EFFECT OF INITIAL ACID CONCENTRATION
ON THE FIRST ORDER RATE CONSTANT
AT 362°C WASHED REACTION VESSEL II

$10^4 a_0$ mole litre ⁻¹	t_r min	% DECOMP	k min ⁻¹
3.7	0.440	20.1	0.51
6.5	1.15	45.3	0.53
8.9	1.45	53.8	0.54

TABLE 11
FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION
REACTION VESSEL II

RUN	TEMP °C	$10^3/T$ K ⁻¹	k min ⁻¹	LOG ₁₀ k
1	450.2	1.382	27.6	1.44
2	470.9	1.344	64.5	1.81
3	434.1	1.414	13.4	1.13
4	416.0	1.451	7.25	0.861
5	399.5	1.487	3.13	0.496
6	443.9	1.395	20.7	1.32
7	362.0	1.574	0.53	1.72
8	376.2	1.540	1.06	0.025

TABLE 12
EFFECT OF CARRIER GAS ON THE FIRST ORDER RATE CONSTANT
AT THREE TEMPERATURES WASHED REACTION VESSEL II

RUN	TEMP °C	k (N ₂) min ⁻¹	k (He) min ⁻¹	k (O ₂) min ⁻¹
5	399.5	3.13	3.04	-
6	443.9	20.7	23.1	-
7	362.0	0.53	0.45	0.43

TABLE 13
FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION
REACTION VESSEL III

RUN	TEMP. °C	$10^3/T$ K ⁻¹	k min ⁻¹	LOG ₁₀ k
UNCOATED 1	365.2	1.566	0.90	1.95
BORIC ACID COATED 2	365.2	1.566	1.89	0.28
3	416.9	1.449	7.90	0.90

TABLE 14
FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION
ANNEALED REACTION VESSEL IV

RUN	TEMP. °C	$10^3/T$ K ⁻¹	k min ⁻¹	LOG ₁₀ k
1	364.7	1.568	1.06	0.025
2	416.2	1.451	8.75	0.94
3	453.6	1.376	37.5	1.57

TABLE 15
FIRST ORDER RATE CONSTANTS
CATALYTIC DECOMPOSITION ON Cu-O2O3

RUN	TEMP °C	$10^3/T$ K ⁻¹	k_s min ⁻¹ m ⁻²	LOG ₁₀ k_s
1	206.4	2.085	1.01×10^{-3}	3.06
2	186.2	2.177	3.34×10^{-4}	4.52
3	227.9	1.996	5.9×10^{-2}	2.77
4	238.5	1.954	2.06×10^{-1}	1.32
5	250.3	1.910	3.34×10^{-1}	1.52

TABLE 16
FIRST ORDER RATE CONSTANTS
CATALYTIC DECOMPOSITION ON Fe-0301

RUN	TEMP °C	$10^3/T$ K ⁻¹	k_s min ⁻¹ m ⁻²	LOG ₁₀ k_s
1	196.1	2.131	1.12×10^{-3}	3.05
2	216.7	2.041	4.46×10^{-3}	3.65
3	238.5	1.954	1.68×10^{-2}	2.23
4	176.7	2.223	3.56×10^{-4}	4.55
5	206.5	2.085	2.17×10^{-3}	3.34

TABLE 17
FIRST ORDER RATE CONSTANTS
CATALYTIC DECOMPOSITION ON Al-0104

RUN	TEMP °C	$10^3/T$ K ⁻¹	k_s min ⁻¹ m ⁻²	LOG ₁₀ k_s
1	202.0	2.104	6.99×10^{-4}	4.845
2	222.4	2.018	2.54×10^{-3}	3.405
3	234.1	1.971	6.06×10^{-3}	3.783
4	251.3	1.907	1.20×10^{-2}	2.079
5	176.2	2.225	1.32×10^{-4}	4.121

TABLE 18
FIRST ORDER RATE CONSTANTS
CATALYTIC DECOMPOSITION ON Cu-0803

RUN	TEMP °C	$10^3/T$ K ⁻¹	k_s min ⁻¹ m ⁻²	LOG ₁₀ k_s
1	216.7	2.041	3.04×10^{-3}	3.481
2	238.5	1.954	2.35×10^{-2}	2.372
3	250.0	1.911	3.70×10^{-2}	2.568
4	227.6	1.997	7.74×10^{-3}	3.888
5	206.3	2.086	1.34×10^{-3}	3.129
6	196.0	2.131	5.88×10^{-4}	4.770

TABLE 19
ARRHENIUS PARAMETERS
CATALYTIC DECOMPOSITION

HARSHAW NUMBER	APPARENT ACTIVATION ENERGY kcal mole ⁻¹	SPECIFIC PREEXPONENTIAL min ⁻¹ m ⁻²
Cu-0203	54.0	2.5 x 10 ²²
Fe-0301	28.6	2.5 x 10 ¹⁰
Al-0104	28.8	1.3 x 10 ¹⁰
Cu-0803	39.0	8.0 x 10 ¹⁴

TABLE 20
GENERAL RESULTS FOR HYDROGEN REACTION
IN UNCOATED REACTION VESSEL III

TEMP °C	INITIAL H ₂ CONC RANGE 10 ⁻³ M	% DECOMP RANGE WITH H ₂	% DECOMP WITHOUT H ₂
250.6	1.8 - 11.2	60 - 90	0
349.1	4.5 - 11.2	87 - 90	3.7
416.9	2.2 - 4.5	94 - 97	4.3
453.8	4.9	99	76
146.5	1.4 - 11.6	30 - 90	0
361.9	4.5	90	7.7

TABLE 21
 PERCENTAGE DECOMPOSITION FOR A RESIDENCE TIME
 OF 0.10 MIN AT 146.5°C
 IN UNCOATED REACTION VESSEL III

INITIAL HClO_4 CONCENTRATION 10^{-4} M	INITIAL H_2 CONCENTRATION 10^{-3} M	% DECOMP
3.4	4.5	33.6
3.3	0	0
2.8	11.6	30.4
3.6	3.4	87.9
3.7	1.4	62.6
3.5	4.4	92.6

TABLE 22
GENERAL RESULTS FOR HYDROGEN REACTION
IN BORIC ACID COATED
REACTION VESSEL III

TEMP °C	INITIAL H ₂ CONC RANGE 10 ⁻³ M	% DECOMP RANGE WITH H ₂	% DECOMP WITHOUT H ₂
365.2	4.5	94	14
147.2	2.4 - 9.3	4 - 83	0

TABLE 23
 PERCENTAGE DECOMPOSITION FOR A RESIDENCE TIME
 OF 0.10 MIN AT 147.2°C IN BORIC
 ACID COATED REACTION VESSEL III

INITIAL HClO_4 CONCENTRATION 10^{-4} M	INITIAL H_2 CONCENTRATION 10^{-3} M	% DECOMP
3.8	0	0
3.5	4.5	4.6
3.0	9.3	3.8
3.7	2.4	68.3
3.4	5.9	33.9
3.7	4.4	78.2
3.8	2.4	83.2

FIG. 1
SCHEMATIC DIAGRAM OF FLOW SYSTEM

FIG. 2
PERCHLORIC ACID SATURATOR

FIG. 3
REACTION VESSEL I

FIG. 4
REACTION VESSEL III

FIG. 5
SAMPLING SYSTEM

NORMAL POSITION

SAMPLING POSITION

FIG. 6
FIRST ORDER RATE PLOTS
ANNEALED REACTION VESSEL I

FIG. 7

ARRHENIUS PLOT FOR FIRST ORDER RATE CONSTANTS
ANNEALED REACTION VESSEL I

FIG. 8

FIRST ORDER RATE PLOTS AT 364.4°C FOR THREE
INITIAL ACID CONCENTRATIONS - ANNEALED REACTION VESSEL I

FIG. 9
PERCENTAGE DECOMPOSITION PLOTS
WASHED REACTION VESSEL I

FIG. 10
 FIRST ORDER RATE PLOTS
 WASHED REACTION VESSEL I PACKED WITH GLASS WOOL

FIG. 11

ARRHENIUS PLOT FOR FIRST ORDER RATE CONSTANTS
WASHED REACTION VESSEL I PACKED WITH GLASS WOOL

FIG. 12
 FIRST ORDER RATE PLOTS
 WASHED REACTION VESSEL II

FIG. 13:
ARRHENIUS PLOT FOR FIRST ORDER RATE CONSTANTS
WASHED REACTION VESSEL II

FIG. 14
FIRST ORDER PLOTS
COATED AND UNCOATED REACTION VESSEL III

FIG. 15
PERCENTAGE DECOMPOSITION PLOTS
UNTREATED REACTION VESSEL IV

FIG. 16
 FIRST ORDER RATE PLOTS
 ANNEALED REACTION VESSEL IV

FIG. 16
FIRST ORDER RATE PLOTS
ANNEALED REACTION VESSEL IV

FIG. 17
FIRST ORDER RATE PLOTS

Cu-0203

FIG. 18
ARRHENIUS PLOT OF FIRST ORDER RATE CONSTANTS
Cu-0203

FIG. 19
FIRST ORDER RATE PLOTS
Fe-0301

FIG. 20
ARRHENIUS PLOT OF FIRST ORDER RATE CONSTANTS
Fe-0301

FIG. 21
FIRST ORDER RATE PLOTS
Al-0104

FIG. 22
ARRHENIUS PLOT OF FIRST ORDER RATE CONSTANTS
A1-0104

FIG. 24
ARRHENIUS PLOT OF FIRST ORDER RATE CONSTANTS
Cu-0803

FIG. 25
PERCENTAGE DECOMPOSITION PLOTS

Mn-0201

FIG. 26
COMPENSATION EFFECT PLOT
HARSHAW CATALYSTS

REFERENCES

1. P.W.M. Jacobs and H.M. Whitehead, Chem. Rev., 69, 551 (1969).
2. C.U. Pittman, "The Mechanism of Decomposition of Ammonium Perchlorate: A Review," U.S. Army Missile Command, Redstone Arsenal, RK-TR-66-13, August 1966.
3. A.R. Hall and G.S. Pearson, "Ammonium Perchlorate: A Review of its Role in Composite Propellant Combustion," R.P.E. Technical Report 67/1, 1967; Oxidation Combust. Rev., 3, 129 (1968).
4. A.G. Keenan and R.F. Siegmund, Quart. Rev., 23, 430 (1969).
5. G.S. Pearson, "Perchloric Acid: A Review of the Physical and Inorganic Chemistry," RPE Technical Memo 352, March 1965; Advan. Inorg. Radiochem., 8, 177 (1966).
6. C.C. Addison, "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry," Supplement II, Part I, Longmans, Green and Co., London, 1956, Chapter II, p 598.
7. J.C. Schumacher, Ed., "Perchlorates, Their Properties, Manufacture and Uses," Reinhold Publishing Corp., New York, N.Y., 1960, p 11.
8. A.A. Zinov'ev, Usp. Khim., 32, 590 (1963); Russ. Chem. Rev., 32, 268 (1963).
9. V.Ya. Rosolovskii, "The Chemistry of Anhydrous Perchloric Acid," Nauka, Moscow, 1966.
10. J.B. Levy, "The Thermal Decomposition of Perchloric Acid," Atlantic Research Corp., Alexandria, Va.,

AFOSR TN 1555, oct 1961 (AD 265 051); J. Phys. Chem., 66, 1092 (1962).

11. A.H. Clark, B. Beagley and D.W.J. Cruickshank, Chem. Commun., 14 (1968).
12. G.A. Heath and J.R. Majer, "A Preliminary Investigation by Mass Spectrometry of the Thermal Decomposition of Ammonium Perchlorate," RPE Technical Note No.219, April 1963; Trans. Faraday Soc., 60, 1783 (1964).
13. V.H. Dibeler, R.M. Reese and D.E. Mann, J. Chem. Phys., 27, 176 (1957).
14. I.P. Fisher, "Some Intermediates in the Pyrolysis and Electron Impact of Chlorine Monoxide and Chlorine Heptoxide," R.P.E. Technical Report 67/10, Oct 1967; Trans. Faraday Soc., 64, 1852 (1968).
15. G.A. Cummings and G.S. Pearson, "Perchloric Acid: A Review of Its Thermal Decomposition and Thermochemistry," RPE Technical Note No.224, Oct 1963.
16. G.S. Pearson, Oxidation Combust. Rev., 4, 1 (1969).
17. D.J. Sibbett and J.M. Lobato, "Investigation of the Mechanism of Combustion of Composite Solid Propellants," Aerojet-General Corp., Azusa, Calif., Aerojet Report No. 1782, April 1960 (AD 240 274).
18. D.J. Sibbett and I. Geller, "Kinetics of the Decomposition of Anhydrous Perchloric Acid," Aerojet-General Corp., Azusa, Calif., Report 0372-01F, Appendix C.
19. D.J. Sibbett, F.J. Cheselke, I. Geller, J.M. Lobato, F.E. Sutherland and R.F. Chaiken, "Decomposition, Combustion and Detonation of Solids," Aerojet-General Corp., Azusa, Calif., Abstracted in AFOSR 2348, April 1962 (AD 274 132).
20. F. Solymosi, S. Borcsok and M.E. Lazarn, Magy. Kem. Foly., 72, 329 (1967); Combust. Flame, 12, 398 (1968).
21. V.I. Gritsan and V.N. Panfilov, Kinet. Katal., 11, 235 (1970).

22. I.P. Fisher, "A Mass Spectrometric Study of the Thermal Decomposition of Perchloric Acid and Chlorine Dioxide," R.P.E. Technical Report 66/13, Nov 1966; Trans. Faraday Soc., 63, 684 (1967).
23. M.H. Studier, J. American Chem. Soc., 90, 1901 (1968).
24. H.F. Cordes and S.R. Smith, J. Chem. Eng. Data, 15, 158 (1970).
25. G.L. Pellett and A.R. Saunders, "Heterogeneous Decomposition of Ammonium Perchlorate-Catalyst Mixtures Using Pulsed Laser Mass Spectrometry," AIAA Sixth Aerospace Sciences Meeting, New York, N.Y., Jan 1968, AIAA Preprint 68-149.
26. W.A. Guillory and M. King, J. Phys. Chem., 73, 4367 (1969).
27. F. Solymosi and S. Borcsok, J. Chem. Soc., 601 (1970).
28. W. Dietz, Angew. Chem., 52, 616 (1939).
29. G.A.McD. Cummings and G.S. Pearson, "Flames Supported by Perchloric Acid. II. The Decomposition Flame," RPE Technical Note 226, Oct 1963; Combust. Flame, 8, 199 (1964).
30. M.W. Evans, Chem. Rev., 51, 363 (1952).
31. A.R. Hall, G.S. Pearson, J. Combourieu and R. Moreau, "Perchloric Acid and Chlorine Dioxide Flames," R.P.E. Technical Report No.69/4, Feb 1969; Combust. Flame, 13, 596 (1969).
32. J. Powling, unpublished results quoted by G.S. Pearson in reference 5.
33. G.A.McD. Cummings and A.R. Hall, "Flames Supported by Perchloric Acid: Part I. Premixed Flames with Methane," RPE Technical Note No.222, June 1963.
34. G.A.McD. Cummings and A.R. Hall, "Tenth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1965, pp 1365-1372.

35. G.A.McD. Cummings and A.R. Hall, "Perchloric Acid Flames: Part III, Some Flame Temperatures and Burning Velocities," R.P.E. Technical Report No.65/5, Sept 1965.
36. G.S. Pearson, Nature, 208, 283 (1965).
37. G.S. Pearson, "Perchloric Acid Flames: Part IV, Methane-Rich Flames," R.P.E. Technical Report No.65/6, Aug 1965.
38. G.A. Heath and G.S. Pearson, "The Chemical Structure of Methane-Perchloric Acid Flames," RPE Technical Memo 399, April 1966: "The Eleventh Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1967, pp 967-977.
39. G.S. Pearson, Combust. Flame, 11, 89 (1967).
40. G.S. Pearson, "Perchloric Acid Flames: Part V. Ethylene-Rich Flames," R.P.E. Technical Report No.66/1, March 1966.
41. G.S. Pearson, Combust. Flame, 11, 97 (1967).
42. G.S. Pearson, "Perchloric Acid Flames: Part VI. Ethane-Rich Flames," R.P.E. Technical Report No. 66/2, March 1966.
43. G.S. Pearson, Combust. Flame, 11, 103 (1967).
44. G.S. Pearson, "Perchloric Acid Flames: Part VII. Mixed Fuel-Rich Flames," R.P.E. Technical Report No.67/3, March 1967; Combust. Flame, 11, 471 (1967).
45. G.S. Pearson, "Perchloric Acid Flames: Part VIII, Methane-Rich Flames with Oxygen," R.P.E. Technical Report No.67/51 May 1967; Combust. Flame, 12, 54 (1968).
46. A.R. Hall and G.S. Pearson, "Perchloric Acid Flames: Part IX. A Two-Flame Structure with Hydrocarbons," R.P.E. Technical Report No.68/4, March 1968; "Twelfth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1968 pp
47. P. Lafitte, J. Combourieu, I. Hajal, M. Ben Caid and R. Moreau, "Eleventh Symposium (International) on

Combustion," The Combustion Institute, Pittsburgh, Pa., 1967, pp 941-950.

48. M. Ben Caid, Doctorate Thesis, Paris (1966).
49. R. Moreau and J. Combourieu, Compt. Rend., C265, 440 (1967).
50. J. Combourieu and R. Moreau, "Twelfth Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1968, pp
51. R. Moreau, Doctorate Thesis, Paris (1968).
52. R. Friedman and J.B. Levy, "Research on Solid Propellant Combustion," Atlantic Research Corp., Alexandria, Va., Final Technical Report AFOSR 2005, Dec 1961.
53. J.B. Levy, Comment on a paper by G.A.McD. Cummings and A.R. Hall, see reference 34.
54. R.V. Figini, E. Coloccia and H.J. Schumacher, Z. Phys. Chem. (Frankfurt am Main), 14, 32 (1958).
55. E. Coloccia, R.V. Figini and H.J. Schumacher, Angew. Chem., 68, 492 (1956).
56. A.J. Arvia, W.H. Basualdo and H.J. Schumacher, Z. Anorg. Allg. Chem., 286, 58 (1956).
57. C.F. Goodeve and F.D. Richardson, J. Chem. Soc., 294 (1937).
58. J. Farquharson, C.F. Goodeve and F.D. Richardson, Trans. Faraday Soc., 32, 790 (1936).
59. Z.G. Szabo, J. Chem. Soc., 1356 (1950).
60. H.J. Schumacher, Z. Phys. Chem. (Frankfurt am Main), 13, 353 (1957).
61. H.J. Schumacher and G. Stieger, Z. Physik. Chem., B7, 363 (1930).
62. E.T. McHale and G. von Elbe, J. Phys. Chem., 72, 1849 (1968).
63. H. Martin, W. Meise and E. Engelmann, Z. Phys. Chem. (Frankfurt am Main), 24, 285 (1960).

64. P.J. Aymonino, J.E. Sicre and H.J. Schumacher, J. Chem. Phys., 22, 756 (1954); Anales Asoc. Quim. Argentina, 43, 26 (1955).
65. M.A.A. Clyne and J.A. Coxon, Trans. Faraday Soc., 62, 1175 (1966).
66. M.A.A. Clyne and J.A. Coxon, Proc. Roy. Soc. (London), A303, 207 (1968).
67. M.A.A. Clyne and J.A. Coxon, Proc. Roy. Soc. (London), A298, 424 (1967).
68. R.A. Durie and D.A. Ramsay, Can. J. Phys., 36, 35 (1958).
69. G. Porter and F.J. Wright, Discussions Faraday Soc., 14, 23 (1953).
70. L.F.R. Cafferata, J.E. Sicre and H.J. Schumacher, Z. Phys. Chem. (Frankfurt am Main), 29, 188 (1961).
71. P.W.M. Jacobs and A. Russel-Jones, "Eleventh Symposium (International) on Combustion," The Combustion Institute, Pittsburgh, Pa., 1966, pp 457-462.
72. I.M. Kolthoff and E.B. Sandell, "Textbook of Quantitative Analysis," The MacMillan Co., New York, N.Y., 1961, p 559.
73. Ibid., p 545.
74. A. Engelbrecht, E. Nachbauer and E. Meyer, J. Chromatography, 15, 228 (1964).
75. Anon., Anal. Chem., 29, 23A and 26A (1957).
76. M.A.A. Clyne, "Reaction Kinetics Related to Ammonium Perchlorate Decomposition: Part 1," Extramural Research Contract Report No.3, Department of Chemistry, Queen Mary College, London, April 1970.
77. M.A.A. Clyne, "Reaction Kinetics Related to Ammonium Perchlorate Decomposition: Part 2," Extramural Research Contract Report No.3, Department of Chemistry, Queen Mary College, London, May 1970.