Mass Spectrometry Study of Intermediates in Thermal Decomposition of Perchloric Acid and Chlorine Dioxide

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The thermal decomposition of 72 % perchloric acid produced mainly CIO and ClO₂. A much smaller yield of ClO radicals was obtained from the thermal decomposition of chlorine dioxide. It is suggested that the ClO radicals in the acid decomposition were derived mainly from the decomposition of ClO₃ radicals

$$ClO_3 \rightarrow ClO + O_2,$$
 (4)

and production of ClO_2 to arise by the alternative reaction

$$ClO_3 \rightarrow ClO_2 + O,$$
 (3)

although reaction (3) is thermodynamically less favourable than reaction (4). Electron impact studies on chlorine dioxide and ClO radicals gave a value for D(O-ClO) of 55 ± 2 kcal mole⁻¹. The ionization potentials of ClO₂ and ClO were measured directly as 10.7 ± 0.1 and 11.1 ± 0.1 eV respectively.

The precise mechanism of perchloric acid + fuel flames has not been proposed but chlorine oxides such as ClO_3 , ClO_2 and ClO may be participants in the chain propagation reactions.^{1, 2} The overall decomposition of anhydrous perchloric acid in the gas phase was accounted for by the reaction ³

HOClO₃
$$\rightarrow \frac{1}{2}$$
H₂O + $\frac{1}{2}$ Cl₂ + $\frac{7}{4}$ O₂.

No intermediates were identified and the reaction was heterogeneous in the temperature range 200-220°C. Levy 4, 5 also found that a heterogeneous reaction occurred below 310° C and he suggested the homogeneous initiation reaction step,

$$HOClO_3 \rightarrow OH + ClO_3$$

The experimental and calculated activation energies for this reaction were 45 and $47.9 \text{ kcal mole}^{-1}$. Levy proposed for the homogeneous process the subsequent fast reactions,

$$OH + HOCIO_3 \rightarrow H_2O + CIO_4$$
$$CIO_4 \rightarrow Cl + 2O_2$$
$$CIO_3 \rightarrow Cl + \frac{3}{2}O_2$$

This scheme, however, does account for the products, chlorine, oxygen and water. No HCl was detected and water had only a slight inhibiting effect on the reaction rate. Sibbett and Geller ⁶ showed that for the heterogeneous reaction the amount of Cl_2 formed was directly proportional to the amount of acid decomposed.

Heath and Majer 7 have studied the decomposition of perchloric acid (72% acid) in a mass spectrometer. At about 1000°C, the reaction was mainly heterogeneous and the dominant mode of decomposition was

$$HOClO_3 \rightarrow HCl + 2O_2$$
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The presence of HCl was explained in terms of the equilibrium $2HCl + \frac{1}{2}O_2 \rightleftharpoons Cl_2 + H_2O.$

$$O + ClO_2 \xrightarrow{k_1} O_2 + ClO$$
$$O + ClO \xrightarrow{k_2} O_2 + Cl$$

competed and k_1/k_2 was approximately 4.

The object of the present research was to identify and to examine the intermediates formed in the decomposition of 72 % perchloric acid. It was to be expected that bimolecular reactions would only play a secondary part because of the low pressures ($\sim 10^{-2}$ torr) prevailing in the reactor and lower pressures ($\sim 10^{-5}$ torr) in the ion source.

EXPERIMENTAL

The thermal decompositions were studied by means of a modified A.E.I. Ltd. M.S.2 mass spectrometer. The sampling system and reactor unit were essentially the same as those described by Lossing.^{9, 10} Details concerning the modifications and testing of the system have been reported.¹¹ The recording of ionization efficiency curves was possible and tests ¹¹ on methyl and ethyl radicals gave ionization potentials in good agreement with literature values. The usual experimental procedure for recording ionization efficiency curves was adopted.⁹ In all cases an internal standard of ⁸⁴Kr was used to calibrate the electron energy scale.

MATERIALS AND SAMPLING

The perchloric acid was a constant boiling mixture of A.R. material and contained water corresponding to 72 % by weight of percloric acid.

A sample of perchloric acid was vacuum distilled into a glass phial which incorporated a break seal. This phial was glass-blown directly on to the all-glass inlet system to the mass spectrometer which included the low pressure furnace. After breaking the seal the perchloric acid was sampled directly from its reservoir which was maintained at 18°C. Using inlet systems of metal leak valves, Viton valves and greased stopcocks, the results were the same, viz., large ion peaks at 44, 38, 36 and 32 a.m.u. These data suggested that such materials tended to decompose the acid heterogeneously before the gas reached the ion source and so gave rise to CO_2 , HCl and O_2 .

Chlorine dioxide was prepared according to the method described by the Pennsalt Chemical Corporation.¹² ClO₂ was admitted to the mass spectrometer via a cone and socket (lubricated with fluorolube tap grease) and a teflon needle valve. To maintain the vapour pressure of ClO₂ at a sufficiently low value ($\sim 10^{-2}$ torr) for sampling the solid oxide was kept at -78° C. The ion current of ClO₂ for the parent (67 a.m.u.) ion was about 4×10^{-11} ion A.

RESULTS

MASS SPECTRA

The mass spectrum of HOClO₃ was different to that measured previously.⁷ On admitting the acid to the mass spectrometer (ion gauge reading 2×10^{-7} torr) there was an initial conditioning period of several hours during which the predominant peaks were those of HCl and O₂. These peaks gradually decreased to be replaced finally by the reproducible mass spectrum shown in table 1. Table 1 also shows the mass spectrum of ClO₂ which has not been previously reported. In contrast to

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 $HOClO_3$, this spectrum did not require any conditioning period prior to its becoming reproducible. This gas did, however, react slowly with the tap grease and after 2-3 days peaks at higher mass units than parent were observed. With both compounds contamination of the ion source and filament occurred and after continuous sampling for about a week, the filament had to be changed and the ion source plates cleaned.

peak		% of most abundant peak		
a.m.u.	species	HOCIO3	ClO ₂	
28	N_{2}^{+}, CO^{+}	4.5	4 ∙1	
32	O_2^{\mp}	9.0	2.1	
35	35 Č [+	9.0	1.9	
36	H35Cl+	10.0	1.5	
37	37C1+	2.9	0.6	
38	H37Cl+	3.8	0.5	
44	CO_2^+	8.3	10.4	
51	35CĨO+	28.1	31.3	
52	H35ClO+	2.4		
53	37ClO+	9.7	10.1	
54	H37ClO+	0.7		
67	35ClO ⁺	69.1	100	
68	H ³⁵ ClÕ ⁺	2.4		
69	37ClO ⁺	23.6	32.0	
70	H ³⁷ ClÕ ⁺	1.4		
83	35ClO ⁺	100		
85	37ClO ⁺	34		
100	H ³⁵ ClO₄ ⁺	64•6		
102	H ³⁷ ClO ⁷	21.5		

TABLE 1.—MASS SPECTRA OF PERCHLORIC ACID AND CHLORINE DIOXIDE

PYROLYSIS OF PERCHLORIC ACID AND CHLORINE DIOXIDE

The qualitative analysis of these compounds, their decomposition products and any free radical intermediates was carried out by observing the change in ion current for the important peaks as the temperature of the reactor furnace was raised. Fig. 1 shows the change in ion current with temperature for different ions in the mass spectrum of perchloric acid. The curves were obtained by selecting a given peak in the acid spectrum and following the change in peak height at low electron energy. The results were obtained at 1.0 eV above the threshold for each ion. In this manner radical or molecular ions were distinguished from fragment ions.

The acid decomposition exhibits three zones. The first, at about 800°C, may be associated with the decomposition of HOClO₃, and decrease of HOClO₃⁺ and ClO₃⁺. The second, at about 950°C, can be associated with the decomposition of ClO₂, with ClO₂⁺ decreasing, and the third, at about 1100°C, with the decomposition of ClO radicals with ClO⁺ decreasing. The results were not quantitative because sensitivities for the products ClO₂, ClO, HOCl were unknown. Chlorine and HCl did not increase until the higher temperature regions were obtained. No peaks corresponding to Cl_xO_y x > 1 species nor ClO₃ radicals were observed.

The pyrolysis of chlorine dioxide was followed in a similar manner to perchloric acid. The parent ClO_2^+ peak did not (unlike perchloric acid) exhibit a well-defined decomposition temperature. This could have been due either to the maximum attainable reactor temperature being too low or to the presence of some stable impurity which had a fragment ion at this mass number. Both the 67 and 69 peaks



FIG. 1.—HOClO₃ decomposition: variation of ion current with temperature. \bigcirc , HClO[‡]; + ClO⁺₃; \bigcirc , O⁺₂; \triangle Cl[‡]₂; \bigcirc , HCl⁺; \times , ClO⁺; \blacksquare , ClO[±]₂; \bigcirc , HOCl⁺. For clarity the curves for ClO[±]₂ and HOCl⁺, have been raised 2 units.

showed this behaviour. The ionization potential curve for the prepared ClO_2 supports the latter postulate. ClO radicals, ClOH and Cl_2 all increased markedly at about 950°C and molecular O_2 increased at 1000°C.

ELECTRON IMPACT



FIG. 2.—Ionization efficiency curves for the CIO radical and ⁸⁴Kr. O, ⁸⁴Kr⁺; ×, CIO⁺.

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radical. The method of determination was the semi-logarithmic plot as used by Lossing.⁹ The value of I(ClO) so obtained was $11\cdot1\pm0\cdot1$ eV. Attempts were made to determine appearance potentials for the oxychlorine fragments from perchloric acid but the resulting curves exhibited tailing over 6 eV and were unsuitable for deriving threshold energies. The ionization potential of ClO formed in the pyrolysis of ClO₂ was also $11\cdot1\pm0\cdot1$ eV.

A determination of $I(ClO_2)$ from the prepared chlorine dioxide was made to ascertain that the ClO₂ formed in the pyrolysis of perchloric acid was the same as the prepared sample. Fig. 3 shows the ionization efficiency curves for ClO₂⁺ and also the curve for $A(ClO^+)$ from ClO₂.



The hump in curve 2 at about 2 eV above the threshold indicated a change in ionization cross-section attributable to an impurity or some excited state of ClO₂. No such change was observed for the dioxide derived from the perchloric acid pyrolysis. By treating curve 2 in fig. 3 as a two component curve, the amount of each component being ~ 50 % of the total, the corrected curve 4 was obtained where $I(\text{ClO}_2)$ was 10.7 ± 0.1 eV. This value compares with 10.7 ± 0.1 eV in the perchloric acid system.

The appearance potential curve of ClO⁺ from ClO₂ exhibited some tailing (see curve 3, fig. 3). Such curves are to be used with caution when deriving threshold energies but, providing the tailing is not too severe, the method of extrapolated differences ¹³ can be used to give accurate results. The use of this method gave $A(ClO^+)$ from ClO₂ as 13.5 ± 0.1 eV. This value must be an upper limit to the appearance potential of ClO⁺ from ClO₂. A small yield of mass 52, corresponding to ClOH, was observed in the ClO₂ pyrolysis. A value of $I(ClOH) = 11.7\pm0.2$ eV was obtained.

Table 2 summarizes the results obtained in the pyrolysis of perchloric acid and chlorine dioxide.

TABLE 2

pyrolysis system	intermediates studied	ionization potential eV	maximum ion A	1 current
perchloric acid $I(\text{HOCIO}_3) = 13.05 \pm 0.1 \text{ eV}$ initial ion current = $5 \times 10^{-11} \text{ A}$	ClO2 ClO ClOH	$\begin{array}{c} 10.7 \pm 0.1 \\ 11.1 \pm 0.1 \\ 11.7 \pm 0.1 \end{array}$	$\begin{array}{c} 2 \cdot 2 \times 10^{-11}, \\ 2 \cdot 5 \times 10^{-11}, \\ 6 \times 10^{-12}, \end{array}$	875°C 1050°C 950°C
chlorine dioxide $I(CIO_2) = 10.7 \pm 0.1 \text{ eV}$ initial ion current = $3.75 \times 10^{-11} \text{ A}$	ClO ClOH	11·1 ±0·1 11·7 ±0·2	$7.5 \times 10^{-12},$ ~ $10^{-12},$	1000°C 900°C

DISCUSSION

PYROLYSIS OF PERCHLORIC ACID

Fig. 1 showed that at about 800°C the parent HOClO₃⁺ ion and the fragment ClO_3^+ ion both decreased to zero. Simultaneous increases in ClO_2^+ and ClO_2^+ ions were observed. The ClO_3^+ ion results from the dissociative ionization reaction

$e + HOClO_3 \rightarrow ClO_3^+ + O, H + 2e$

and a decrease in the concentration of perchloric acid, brought about by pyrolysis, will give a decrease not only in the parent $HOClO_3^+$ ion but also in the fragment ClO_3^+ ion. To account for the initial increases in ClO_2 and ClO the reaction proposed by Levy ⁴

$$HOClO_3 \rightarrow OH + ClO_3$$
 (1)

is considered. He equated the activation energy of decomposition of reaction (1) with the bond dissociation energy $D(HO-ClO_3)$, but in the present system, no ClO_3 radicals were observed. Now $D(O-ClO_2)$ is given by

$$D(O-ClO_2) = \Delta H_f(ClO_2) + \Delta H_f(O) - \Delta H_f(ClO_3) = 47 \text{ kcal mole}^{-1}.$$

The lifetime of the ClO₃ radical at about 800°C is about the same as that of perchloric acid itself as Clyne and Coxon ⁸ showed that reaction (2)

$$O + ClO_2 \rightarrow ClO + O_2 \tag{2}$$

was temperature independent. At 800°C, nearly all the perchloric acid was decomposed and ClO_3 radicals were not observed. A comparison of the reactions (3) and (4),

$$ClO_3 \rightarrow ClO_2 + O$$
 (3)

$$ClO_3 \rightarrow ClO + O_2$$
 (4)

show that $\Delta H_3 = 47$ kcal mole⁻¹, whilst $\Delta H_4 = -13$ kcal mole⁻¹. One would expect reaction (4) to be the primary source of ClO radicals. In this research, bimolecular reactions have, of necessity, been reduced to a minimum and it was thought that such a large yield of ClO₂ could not be accounted for by such reactions.

The second zone of fig. 1 at about 950°C is associated with the decrease of the ClO_2^+ ion and the further increase of the ClO^+ ion, and is probably due to breaking of the O—ClO bond :

$$ClO_2 \rightarrow ClO + O,$$
 (5)

since ClO radicals were observed in the decomposition of ClO₂. The maximum yield of ClO radicals from HOClO₃ was about 2.5×10^{-11} ion A, whereas the maximum yield from ClO₂ was only 7.5×10^{-12} ion A (table 2). The amount of ClO₂ of ionization potential = 10.7 eV in the prepared oxide was 3.7×10^{-11} ion A. This ClO₂ ion current was greater than the maximum yield of ClO₂ (2.2×10^{-11} ion A) from the

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perchloric acid decomposition yet the ClO radical ion current in the latter system was about 2.5×10^{-11} ion A. Hence, ClO₂ is only a minor source of ClO radicals in the perchloric acid decomposition, the major source being through reaction (4).

The occurrence of ClOH in both the decomposition of the acid and oxide suggests a wall reaction,

$$ClO + wall \rightarrow ClOH.$$
 (6)

Reaction (7) must predominate particularly in the oxide decomposition where the alternative source of ClOH,

Cl+OH→ClOH

does not occur. The main mode of decomposition of ClO_2 in both systems must be $ClO_2 \rightarrow Cl + O_2$.

In this way such products as Cl_2 and HCl, which increase before the ClO radical peak decreases, can be explained. The final reaction zone at about 1100°C can be associated with the decomposition of the ClO radical to atomic products.

There was no indication of the heterogeneous reaction noticed by Levy ⁴ at 300° C with anhydrous HOClO₃, nor evidence for the reaction scheme of Majer and Heath,⁷ viz.,

$HOClO_3 \rightarrow HCl + 2O_2$,

nor of the isomer of ClO₂, Cl—O—O, proposed by Porter *et al.*¹⁴ Benson ¹⁵ calculated that such a radical would have a negligible lifetime at temperatures above ambient. Also such species as Cl_xO_y (x>1), which have been proposed in the decomposition of the anhydrous acid,⁶ were absent.

A scheme for the decomposition of perchloric acid vapour in the present system might be:

HOClO₃
$$\rightarrow$$
ClO₃+OH
ClO₃ \rightarrow ClO₂+O
ClO₃ \rightarrow ClO+O₂
ClO₂ \rightarrow Cl+O₂
ClO₂ \rightarrow Cl+O
ClO \rightarrow Cl+O

Cl, ClO, OH \rightarrow HCl, ClOH, H₂O

C

The results show that the main intermediate is the ClO radical which, it has been postulated, arises mainly from the ClO_3 radical which has but a transitory existence; ClO_2 is a relatively poor source of ClO radicals and probably ClO radicals are responsible for the enhanced reactivity of perchloric acid-fuel flames.

ELECTRON IMPACT RESULTS

Indirect estimates of the ionization potentials of ClO₂ and ClO have been made from electron impact studies on the ionization and dissociation of perchloryl fluoride.¹⁶ Dibeler *et al.*¹⁶ estimated $I(ClO_2)$ to be 11·1 eV from the appearance potential of ClO₂⁺ from FClO₃. Dibeler's value of $A(ClO_2^+) = 15.7 \pm 0.5$ eV gave an upper limit to $\Delta H_f(ClO_2^+)$ of 281±10 kcal mole⁻¹, the error quoted being in the appearance potential measurement. Using the relationship

 $\Delta H_f(ClO_2^+) - \Delta H_f(ClO_2) \ll I(ClO_2)$

he obtained $I(\text{ClO}_2) = 11 \cdot 1 \pm 0.5 \text{ eV}$. Thus, our value of $I(\text{ClO}_2) = 10 \cdot 7 \pm 0.1 \text{ eV}$ by direct ionization of ClO_2 falls within the errors quoted by Dibler. The value of $I(\text{ClO}_2) = 10 \cdot 7 \text{ eV}$, again, is an upper limit and the amount by which the measured value exceeds the true or adiabatic value is difficult to assess. Using $I(\text{ClO}_2) = 10 \cdot 7 \text{ eV}$ the value of $\Delta H_f(\text{ClO}_2^+)$ can be recalculated as $\ll 272 \pm 2 \text{ kcal mole}^{-1}$.

With similar arguments, Dibeler calculated $I(ClO) \le 10.4 \pm 0.5 \text{ eV}$, using an incorrect value for $\Delta H_f(ClO)$. With $\Delta H_f(ClO) = 24$, and not 33 kcal mole⁻¹, Dibeler's value becomes $10.85 \pm 0.5 \text{ eV}$. This value compares favourably with $I(ClO) \le 11.1 \pm 0.1 \text{ eV}$ found in this work by direct ionization of the radical. $\Delta H_f(ClO^+)$ is calculated to be $\le 280.2 \pm 2 \text{ kcal mole}^{-1}$.

The electron impact work on chlorine dioxide enabled a direct estimate of D(O-ClO) to be made. For the ClO₂ molecule, the relationship

$$D(O - ClO) \ge A(ClO^+) - I(ClO)$$

is valid. I(CIO) has been determined directly both in the acid and oxide pyrolysis to be $\ll 11.1 \pm 0.1$ eV and $A(CIO^+)$ from CIO_2 is 13.5 ± 0.1 eV. D(O-CIO) is therefore 55 ± 2 kcal mole⁻¹.

If some impurity exists in the prepared ClO₂, then there would probably be a fragment ClO⁺ ion in its spectrum. The pyrolysis of the prepared ClO₂ showed that the impurity was more stable than ClO₂ itself. Such strong bonds in the impurity would therefore imply a high appearance potential for fragmentation to ClO⁺. The impurity was thought not to be a source of ClO radicals as the maximum yield of ClO radicals fell over a period of 2-3 days as the impurity concentration increased. Thus, the value of $A(\text{ClO}^+) = 13.5 \pm 0.1$ eV can be used with confidence.

The bond energy is given by

$$D(O-ClO) = \Delta H_f(O) + \Delta H_f(ClO) - \Delta H_f(ClO_2)$$

providing that the activation energy for the reaction,

 $O + ClO \rightarrow ClO_2,$ (-5)

is zero. Thus, D(O-ClO) was calculated to be 58.5 kcal mole⁻¹. Clyne and Coxon⁸ have shown reaction (-5) to be practically temperature independent but only a small value of E_{act} for reaction (-5) would correlate the electron impact and thermodynamic values for D(O-ClO).

The ionic bond dissociation energies can also be computed thus :

 $D(O-CIO^+) = A(CIO^+) - I(CIO_2) = 64.5 \text{ kcal mole}^{-1}$

and

$$D(O^+-Cl) = I(O) + D(O-Cl) - I(OCl).$$

A spectroscopic value for D(O-Cl) is available ¹⁷ (63·3 kcal mole⁻¹) so $D(O^+-Cl) =$ 120 kcal mole⁻¹. For the minimum energy process giving Cl⁺ ions, $D(O-Cl^+) =$ 110 kcal mole⁻¹. Apparently, as with the neutral molecule ClO₂, the second bond in the ion is greater than the first though the difference in strengths is considerably greater. This is in contrast to D(O-F) and $D(O^+-F)$ where these bonds are comparatively weak.¹⁸

All thermochemical values were taken from JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Michigan up to Quarterly Supplement No. 17, March, 1965. Ionization potentials were taken from N.A.S.A. Document TN D 1791, 1963, Washington.

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