A REDETERMINATION OF THE HEAT OF FORMATION OF PERCHLORYL FLUORIDE

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SUMMARY

A standard enthalpy of formation for perchloryl fluoride of -22.6 ± 1.0 kJ mol^{-1} was determined from its heat of alkaline hydrolysis which compared with a previously obtained value of -26.5 ± 2.9 kJ mol^{-1} from the heat of hydrogenation. A convenient calorimeter for gas-liquid reactions is described. The thermo-chemistry of hydrolysis and bond fission of perchloryl fluoride is discussed in relation to known reactions of the fluoride.

INTRODUCTION

According to early work on perchloryl fluoride its quantitative hydrolysis required heating with concentrated aqueous alkali at 250 - 300°C for some hours [1]. However Cady has shown recently that these conditions are excessive [2]. Indeed perchloryl fluoride can be hydrolysed rapidly at room temperatures according to ClO_3F + $2NaOH$ = NaF + $NaClO_4$ + H_2O. The rate law followed is $d[ClO_3F]/dt$ = $k[OH^-][ClO_3F]$ where $k = 1.98$ mol^{-1} dm^3 sec^{-1} at 25°C.

It therefore appeared feasible to determine the heat of
formation of perchloryl fluoride from its heat of alkaline
hydrolysis in a similar manner to our determination of the enthalpy
of sulphuryl fluoride [3]. Presumably the supposed hydrolytic
stability of perchloryl fluoride caused Neugebauer and Margrave [4]
to measure the heat of hydrogenation of the fluoride as a method
for determining its enthalpy. In this method the small formation
enthalpy of ClO_3F carries all the error inherent in measuring a
large heat of hydrogenation. Hence a re-determination by an
independent method was thought desirable.

EXPERIMENTAL

Two cylinders of perchloryl fluoride from Ozark-Mahoning
Company were used. One was nearly full and contained about 2 moles
of liquid; the other contained a residue of 0.02 moles. The gas
purity was indicated by the agreement between heats of reaction
obtained with samples from both cylinders. (Impurities would have
been fractionated to different extents in the two cylinders).
Chemical analyses indicated purities of $\not< 99.5\%$ [Ratio $[H^+]/[F^-]$ on
hydrolysis 1.998 ± 0.012; ratio $[I_2]/[F^-]$ on reaction with aq.KI
1.008; mol.wt. by gas density 102.5].

The essential parts of the calorimeter system are illustrated.
The calorimeter head was made of polymethylmethacrylate sheet and
carried standard glass taper sockets cemented in with an epoxy resin.
The ground rim of the glass Dewar vessel, when lightly greased, made
a liquid-tight seal with the plastic head. Alternative types of
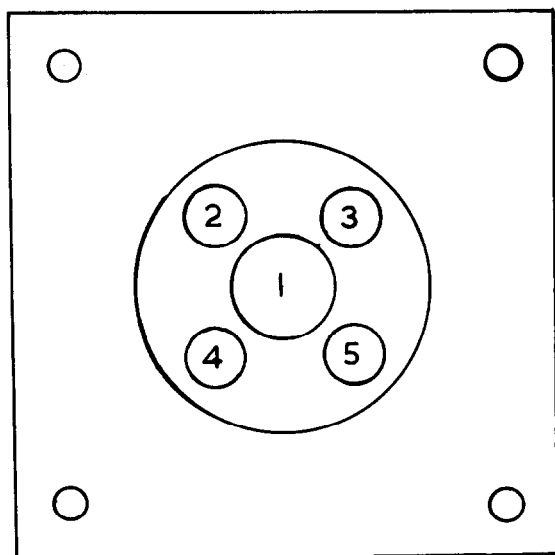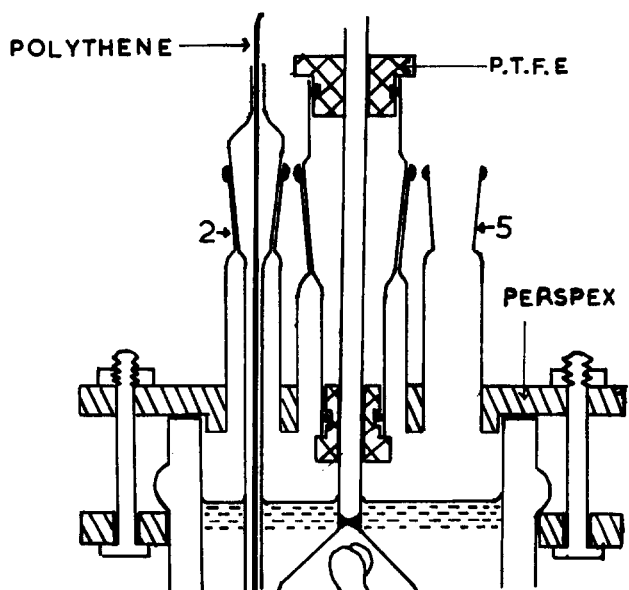bell shaped containers for the gas were tried. The first

Figure 1 Elevation and Plan of Calorimeter
1 = stirrer , 2 = gas introduction , 3 = heater
4 = thermistor , 5 = sampling port

(Figure 2b) was held stationary in the calorimeter and the liquid and gas trapped under the bell stirred in the annular space by a U-shaped stirrer. The second type of bell had paddles attached to its walls (Figure 2a) and the whole unit was rotated at up to 2,000 r.p.m. This type, which gave a stream-line flow with the gas-liquid interface a paraboloid of revolution, was less efficient than the first which produced turbulence and continuous disruption of the interface. Hydrolysis times of 14 min were required for 50 ml quantities of ClO_3F in 330-350 g of 0.1M NaOH with the stationary bell unit (1,200 r.p.m.) in contrast with 30-35 min with the rotating unit (2,000 r.p.m).
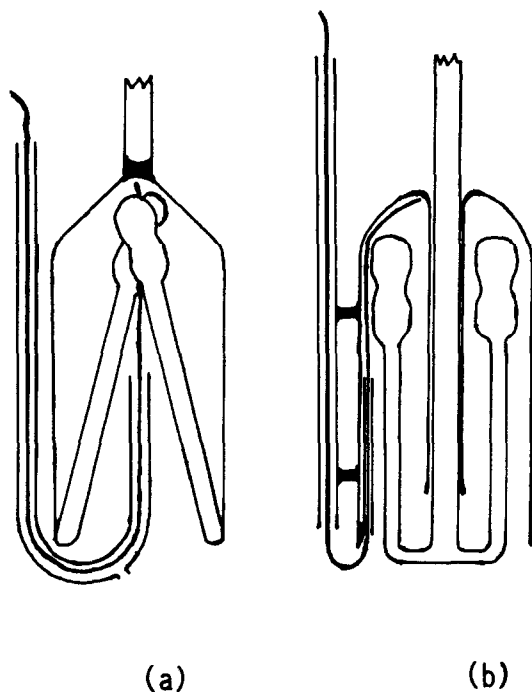

(a)   (b)

Figure 2   Gas holding devices
    (a) Combined Holder/Stirrer (b) Fixed Holder

Gas samples, taken in a plastic syringe fitted with a miniature three-way tap and Luer taper joints, were injected under the bell via a syringe needle attached to narrow bore (0.5 mm) polythene tubing. (The stopper in the sampling port had to be removed to release pressure as the liquid levels were displaced). The heat changes were followed with a thermistor probe in a Wheatstone bridge network as described previously [3]. Electrical calibrations were run before and after each hydrolysis. The calorimetric fluid was titrated for excess alkali in situ with standard hydrochloric acid (0.5 M) to a pH of 7.00 using a glass electrode and then for fluoride, after readjusting to a pH of 6.30, with cerium(III) chloride. (Full details of this acidimetric titrating of fluoride are given in a later paper). The fluoride titration is less accurate than the acid titration because (a) twice as much H^+ is released as F^- in the hydrolysis and (b) the presence of a salt concentration spreads out the inflection in the fluoride titration and makes the end-point less precise. The titres are therefore weighted towards the acid titration according to the mean deviations actually obtained. The results are collected in Table 1.

TABLE 1 Heats of reaction of ClO_3F in 0.1M NaOH in H_2O

| ClO_3F dissolved/m.mole as measured by		Heat evolved/J	Heat per mole ClO_3F/kJ calculated from analysis	
$[H^+]/2$	F^-		H^+	F^-
1.729	1.728	469.28	271.48	271.57
2.372	2.396	639.58	269.69	266.94
1.899	1.884	513.06	270.19	272.32
-	2.389	644.20	-	269.52
-	2.409	654.13	-	271.50

Mean value 270.45 ± 0.35 270.57 ± 1.67

Weighted mean 270.5 ± 0.4

The last two results were obtained with gas from cylinder II

DISCUSSION

The rate of hydrolysis of perchloryl fluoride with excess alkali should follow a pseudo-first order law and 99.9% of the hydrolysis is expected in about ten half-lives. According to Cady's rate constant at 25°C this should occur within a minute under our experimental conditions. Hence the rate determining step in the calorimeter is mass transfer of gas across the liquid-gas interface and not the rate of hydrolysis. This is confirmed by the shorter hydrolysis times achieved with turbulent stirring. Little hydrolysis would occur if the gas were merely bubbled through the alkali and it is essential to hold the gas for some time in contact with the liquid as in the described calorimeter design.

A value of -22.6 kJ mole^{-1} is obtained for the standard enthalpy of formation of perchloryl fluoride using the mean heat of hydrolysis (270.5 kJ mol^{-1}), the heats of formation for NaOH.55OH$_2$O (-469.9 kJ), NaF.10,000OH$_2$O (-575.6 kJ), NaClO$_4$.10,000OH$_2$O (369.0 kJ) and H$_2$O (-285.8 kJ) and allowing for the diminution in gas volume (RT = 2.48 kJ) according to the equation

$$ClO_3F(g) \ + \ 2NaOH(aq) \ = \ NaClO_4(aq) \ + \ NaF(aq) \ + \ H_2O(\ell)$$
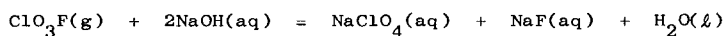
This assumes that the heat of solution of the product mixture is the same in 0.1M NaOH as the sum of the components in water and also that the gas is ideal.

A rough value for the heat of formation of perchloryl fluoride was obtained mass spectrometrically when the appearance potentials of fragments resulting from electron impact were measured [5]. Thus the appearance of Cl$^+$ ions at 23.0 eV was attributed to the process

$$ClO_3F \ \rightarrow \ Cl^+ \ + \ O \ + \ F$$
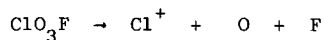
By deducting the product enthalpies from the appearance potential one obtains a $H_f(ClO_3F)$ of -9.2 ± 20 kJ assuming the products carry no excess kinetic, excitational or vibrational energies.

The other available value was derived from the hydrogenation of perchloryl fluoride in a bomb calorimeter [4]

$$ClO_3F(g) + 4H_2(g) = HF(0.6M) + HCl(0.6M) + 3H_2O(\ell)$$
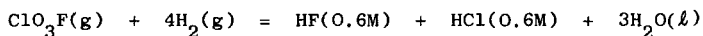
This value when corrected with new figures for the heats of formation of the acids is -26.5 ± 2.9 kJ mol^{-1}. In order to assess the agreement between this and the hydrolysis result we need to follow the same treatment of errors as given by Neugebauer and Margrave (Table 2).

TABLE 2

Assessment of errors

Errors (Δ)	Hydrogenation /kJ mol^{-1} of ClO_3F	Hydrolysis
Calorimeter	0.9	0.7
Precision	1.7	0.5
Accuracy	2.2	0.5
$(\Sigma\Delta^2)^{\frac{1}{2}}$	2.9	1.0

The calorimeter error is derived from the calorimeter calibration. In the bomb calorimeter the energies of combustion of benzoic acid had an average deviation of 0.066% which is 0.9 kJ on the heat of hydrogenation. Our solution calorimeter gave heats of solution reproducible to 1 in 400 and hence on a heat of hydrolysis of 270.5 kJ an error of $\pm$ 0.7 kJ. The precision error measures the reproducibility of results and we downweight our fluoride analytical results in the same way as the chloride values were downweighted in the hydrogenation experiments. (The lower precision of the latter is also seen in the

spread of 7.5 kJ as against 1.8 kJ in the hydrolysis experiments).

The accuracy error is the most difficult to estimate. It is meant

to allow for sample impurity, extraneous heats etc. In the

hydrogenations two samples were used one of which contained 12% N_2

and 3-4% CO_2, and the other 3% N_2. However the important impurity

would be oxygen which could not be assessed mass spectrographically

because perchloryl fluoride itself gives O_2^+ and O^+ ions. If only 0.1%

of O_2 had been present then the measured heat would have included a

contribution from the reaction $2H_2 + O_2 = 2H_2O(\ell)$ which is much less

than the heat of the perchloryl fluoride hydrogenation and hence an

underestimation of 0.75 kJ mol^{-1}. There was also some heat generated

by corrosion of metal in the calorimeter vessel and valve which was

estimated as up to 0.5% of the total acidity. Assuming formation of

iron(II) salts it can be calculated to contribute an extra heat of

0.4 kJ. The non-ideality correction carried an uncertainty of 0.4 kJ.

In the hydrolysis experiments impurities in the form of non-

acidic gases such as O_2 will not react. Neither are there any

corrosion problems. The non-ideality correction is five times

smaller and would be less than 0.1 kJ. Carbon dioxide could give

rise to an error of less than 0.1 kJ if present at the 0.1% level.

Its presence is unlikely in view of the fractionation which would

have given different values between our two samples. Heats of

solution could also be in error by 0.4 kJ. Taking these errors

into account the new value of -22.6 ± 1.0 kJ just overlaps the old

value of -26.5 ± 2.9 kJ. (Both values carry the uncertainty of

± 0.8 kJ from the fluoride ion value which has been ignored in this

treatment). A revised standard free energy of formation of

+ 49.4 kJ mol^{-1} is derived from the entropy value S_{25}^{o} of 278.9 J mol^{-1} K^{-1}.

The heat and free energy changes calculated for possible

hydrolysis reactions are collected in Table 3.

TABLE 3

Enthalpy and free energy of hydrolysis of ClO_3F

Reaction	ΔH kJ mol^{-1} ClO_3F	ΔG
$ClO_3F(g) + H_2O(\ell) = HF(g) + HClO_4(\ell)$	-5.5	-
$ClO_3F(g) + H_2O(\ell) = HF(aq) + HClO_4(aq)$	-156.6	-102.4
$ClO_3F(g) + 2OH^-(aq) = F^-(aq) + ClO_4^-(aq) + H_2O(\ell)$	-270.5	-261.4

The first reaction with a limited supply of water is almost thermo-neutral as expected from the "isoelectronic heats of formation" [8]. The free energy change would also be small because only a small decrease in entropy is expected due to association of hydrogen fluoride vapour. If both products were in the gas phase the free energy change would be positive and hence the stability of perchloryl fluoride to steam is explicable on thermodynamic grounds.

The hydrolyses with excess water are thermodynamically favourable because of the heats of solvation.

Perchloryl fluoride has been used extensively in organic reactions [9,10] and hence it is of interest to examine thermochemical aspects of bond fission.
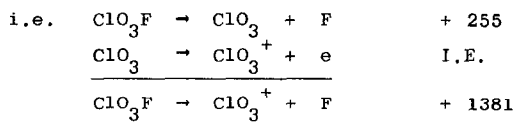
Homolysis of the O_3Cl-F bond is by far the easiest process and has about the same energy as the bond dissociation in ClF or Cl_2. Reactions are not carried out under thermal or photolytic conditions because of explosion dangers from chloric acid and

TABLE 4

Heats of homolytic and heterolytic bond fission of ClO_3F ($kJ \quad mol^{-1}$)

Process (with heats of formation)	ΔH
(1) $ClO_3F \rightarrow ClO_3 + F$ $\quad -23 \qquad 155 \qquad 79.5$	257.5
(2) $ClO_3F \rightarrow ClO_3^+ + F^-$ $\quad -23 \quad < 1280 \quad -272$	< 1,031
(3) $ClO_3F \rightarrow ClO_3^- + F^+$ $\quad -23 \qquad -226 \qquad 1,766$	< 1,561

chlorine oxides. However the variety of products formed in some

reactions may be due partly to fluorine atom reactions. The

heterolysis to the perchloryl cation is the next most favourable

process. The ionization energy $ClO_3 \rightarrow ClO_3^+ + e$ is an upper

limit value. It is derived from the appearance potential of

ClO_3^+ [5] less the bond dissociation energy $O_3Cl - F$.

$$\begin{array}{llll} \text{i.e.} & ClO_3F \rightarrow ClO_3 + F & + 255 \\ & ClO_3 \rightarrow ClO_3^+ + e & I.E. \\ \hline & ClO_3F \rightarrow ClO_3^+ + F & + 1381 \end{array}$$

It should be noted that the heat of formation of ClO_3^+ is little

greater than that of the nitronium ion (1159 $kJ \quad mol^{-1}$) and it should

be possible to form stable salts with suitable Lewis acids analogous

to the well established nitronium salts [11,12]. Indeed the adduct $HClO_4.2SO_3$ [14] could be formulated as $ClO_3^+(HS_2O_7)^-$ analogous to the nitronium salt. The perchloryl cation should have a transient existence in the formation of perchloryl aromatics under Friedel-Craft reaction conditions [9] and is even more likely as the intermediate in the preparation of perchloryl fluoride from $KClO_4$ and HSO_3F or HSO_3F/SbF_5 [13].

The heterolysis to a fluorine cation is the least favourable process. The heat of formation of ClO_3^- was derived from the electron affinity figure of ClO_3 radical. This was calculated from Born-Haber cycles on chlorate salts [15]. It seems to be too stable an entity because the heat of formation of ClO_3^- (aq) is only -100 kJ mol^{-1} and hence the heterolysis is likely to have 1561 kJ mol^{-1} as a lower limit.

The mechanism for fluorination by perchloryl fluoride probably involves similar intermediates to that proposed by Cady to explain the alkaline hydrolysis reaction. The partial charge distribution calculated by Sanderson's method of electronegativity equalization [16] is $\begin{matrix} +0.01 & +0.07 & -0.10 \\ O_3 & Cl & F \end{matrix}$ and hence an anion or carbanion will tend to approach the oxygen face of the tetrahedral molecule collinear with the Cl-F axis to produce the trigonal bipyramidal intermediate

Anion —— $\begin{matrix} O \\ O \quad Cl —— F \\ O \end{matrix}$
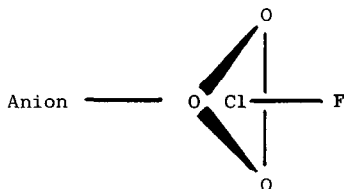
It has been suggested that the carbanion formed from β-carbonyl systems will give cyclic intermediates with the perchloryl fluoride and allow a concerted fluorination and elimination

of chloric acid [10]. However the geometry of the trigonal bipyramidal system is unfavourable for such an intermediate and it is more likely that fluoride ion is released before it fluorinates.

The mechanisms illustrated by electron movements such as

$$\underset{\diagup}{\diagdown}C^- \; + \; F - ClO_3 \; \rightarrow \; \underset{\diagup}{\diagdown}CF \; + \; ClO_3^-$$
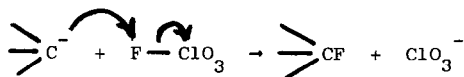
are unlikely because the intermediate is approaching the positive fluorine extreme which is energetically prohibitive.

It seems that the inertness of perchloryl fluoride has been exaggerated. It is best considered as the end member of a reactivity series

$$SiF_4 \; > \; OPF_3 \; > \; O_2SF_2 \; > \; O_3ClF$$
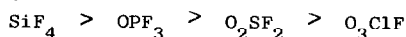
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