Journal of Fluorine Chemistry, 11 (1978) 225–241

Received: July 1, 1977

SOLUBILITY AND REACTIONS OF PERCHLORYL FLUORIDE IN WATER

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SUMMARY

Perchloryl fluoride ($C\ell O_3F$) when dissolved in water reacts very slowly with the solvent. The solubility in water at one atmosphere pressure and temperatures up to 40°C is given by the equation, solubility (mol/ℓ) = 6.387×10^{-8} exp 6852/RT. The following reactions have been studied to learn their rate laws and rate constants:

$$C\ell O_3F + 2I^- = I_2 + F^- + C\ell O_3^-$$
$$C\ell O_3F + 2OH^- = C\ell O_4^- + F^- + H_2O$$
$$C\ell O_3F + 3NH_3(aq) = 2NH_4^+ + HNC\ell O_3^- + F^-$$
$$C\ell O_3F + H_2O = C\ell O_4^- + F^- + 2H^+$$

At temperatures near 0°C, perchloryl fluoride and water readily form a solid clathrate hydrate of highly variable composition. The observed minimum ratio of H_2O to $C\ell O_3F$ in the solid is about 7.75.

INTRODUCTION

Perchloryl fluoride, $C\ell O_3F$, was first identified by Engelbrecht and Atzwanger [1] [2]. A good review of its properties has been given by Gall [3]. The work now to be described adds to the knowledge of aqueous solutions of the substance.

The gas is reported to react slowly with sodium hydroxide solution and scarcely at all with water. Anhydrous ammonia reacts rather rapidly with $C\ell O_3F$ forming ammonium fluoride and $NH_4HNC\ell O_3$ [2]. With aqueous ammonia in excess the products are NH_4^+, F^- and $NC\ell O_3^{--}$ ions. As hydrochloric acid is subsequently added to the solution, the $NC\ell O_3^{--}$ ion is first converted to $HNC\ell O_3^-$ and then to $H_2NC\ell O_3$. The dissociation constants for $NH_2C\ell O_3$ as an acid are: $K_1 = 2.0 \times 10^{-6}$; $K_2 = 1.1 \times 10^{-12}$ [4]. Perchloryl fluoride is said [2] to react slowly with a solution of potassium iodide according to the equation $C\ell O_3F + 8I^- + 6H^+ = C\ell^- + F^- + 4I_2 + 3H_2O$ (1) and with increasing rate as the acidity is increased. This equation should hold for solutions which are sufficiently acidic to allow chlorate ion to convert I^- to I_2. It is incorrect, however, for solutions of low acidity.

The present work was started after the author had completed a study of the basic hydrolysis of sulfuryl fluoride [5]. It soon became apparent that the two gases, SO_2F_2 and $C\ell O_3F$, were similar in many ways and that perchloryl fluoride could be detected and measured more readily than sulfuryl fluoride, because of its ability to liberate iodine from a solution containing I^-.

EXPERIMENTAL AND RESULTS

The perchloryl fluoride used in this work was taken directly from a cylinder obtained in 1967 from Pennsalt Chemicals Corp. It was found by numerous tests to be a product of high purity. A trace of "air" may have been present. No other impurities were detected.

Solubility in water

Perchloryl fluoride dissolves readily in water and may be removed rapidly from the solution by stirring the liquid while subjected to the dynamic vacuum of an aspirator or by passage of a stream of air over the stirred liquid.

Saturated solutions were produced by gently shaking a vessel containing air-free water in the presence of gaseous perchloryl fluoride. The pressure of the gas phase was equal to that of the atmosphere and the temperature was that of a controlled water-bath. The concentration of the solute was established in some cases by measuring the decrease in volume of the system as the gas dissolved and in some cases by withdrawing a sample of the liquid into a syringe containing KI solution to permit determination of the $C\ell O_3F$ by titration of the liberated iodine. Results obtained by the two methods agreed well. The rather numerous raw data were then used to calculate the solubilities shown in Table 1. To do this, it was assumed that the gas was ideal and that Henry's Law was valid.

TABLE 1

Solubility of $C\ell O_3F$ (1 atmosphere pressure) in water

Temp., °C	5	10	15	20	25	40
$C\ell O_3F$, mol/ℓ	.0154	.0124	.0100	.00819	.00673	.00386

These values lie on a line represented by equation (2).

$$\text{Solubility (mol/liter)} = 6.387 \times 10^{-8} \exp 6852/RT \qquad (2)$$

In this work the volumes of liquid samples were measured at approximately 21°C. One may compare the value given above for 25° with a solubility of 0.0059 moles per liter reported by Gall [3].

Reaction with iodide ion

When a 9.16 ml (STP) sample of $C\ell O_3F$ gas was shaken in a syringe with 3.6 ml of a deaerated solution of potassium iodide (containing an excess of I^-) iodine was liberated rather rapidly. Only a tiny bubble of gas (.03 ml) remained. Titration of the iodine consumed 8.15 ml of 0.1002 N-$Na_2S_2O_3$. A second 9.16 ml sample of $C\ell O_3F$ was also allowed to react with an excess of potassium iodide solution. The fluoride ion in the product was titrated and found to consume 4.20 ml of 0.09710 N-$La(NO_3)_3$. These data say that 4.090 mmol of $C\ell O_3F$ yielded 4.083 mmol I_2 and 4.078 mmol of F^-. As the reaction occurred, there was very little change in pH, the observed value being about 6.5. The observed stoichiometry corresponds to equation (3).

$$C\ell O_3F + 2I^- = I_2 + F^- + C\ell O_3^- \qquad (3)$$

If the solution had been rather strongly acidic, a subsequent slow reaction of $C\ell O_3^-$ could have produced $C\ell^-$ and additional I_2 as called for by equation (1).

The rate of liberation of iodine was determined at temperatures ranging from 0° to 34.7°C and at various concentrations of potassium iodide. The iodide was present in such large excess that less than 1% of the I^- was consumed by reaction with perchloryl fluoride. During a run, the concentration of iodine was measured using a Bausch and Lomb Spectronic 20 spectrophotometer set at either 400 or 340 nanometers wave length. The absorbance was shown to be proportional to the concentration of iodine. To make a run, a 4.9 ml sample of potassium iodide solution in a tube for the spectrophotometer was brought to the desired constant temperature in a water bath. At time zero, a 0.1 ml portion of approximately 0.002 M-$C\ell O_3F$ solution in water was mixed rapidly with the solution of potassium iodide. The tube was usually allowed to remain in the water bath without additional stirring long enough for about 50 to 75% of the $C\ell O_3F$ to react. For most of the runs this period was less than a minute. The tube was then wiped dry on the outside and placed, without stirring, in the spectrophotometer. Absorbance was then measured at frequent intervals until it became constant, indicating complete consumption of $C\ell O_3F$. During a run, the temperature was constant until the tube was placed in the spectrophotometer. After that, the temperature did not change much within the short period while significant absorbance readings were taken. Several of the runs were made at 22°. For these the temperature remained nearly constant for the whole run. Absorbance measurements were started 20 seconds after mixing and were continued for several minutes.

At any time, t, during a run, the concentration of $C\ell O_3F$ was proportional to the quantity (Final absorbance-absorbance at time, t). A graph of ln of this quantity vs t was a straight line. For runs at 22° there were several points on the line. This showed the rate, at constant concentration of I^- to be proportional to the molarity of $C\ell O_3F$. For a run at a temperature other than 22°, the graph had a point for t=0 and this was followed by a few other points starting after about one or two half-life periods of the $C\ell O_3F$. The slope of the line through the initial point and the subsequent first few experimental points was used as a basis for calculating the rate constant, k(for I^-).

Table 2 gives concentrations and temperatures for experimental runs and reports the rate constants calculated from these and the slopes of the lines in the graphs. The slope was d ln (Final absorbance-absorbance at time, t)/dt with t measured in seconds. At constant temperature (observed for 22.0°) the slope was proportional to the molarity of I^- and independent of the concentration of H^+. It follows that the rate law is

$$\frac{d[C\ell O_3F]}{dt} = -k\ (\text{for } I^-)[C\ell O_3F][I^-] \qquad (4)$$

and that k(for I^-) may be calculated from equation (5).

$$k(\text{for } I^-) = \frac{d\ \ln\ (\text{Final absorbance-absorbance at time,t})}{dt} \times \frac{1}{[I^-]} \qquad (5)$$

The rate constants found in this way can be summarized by equation (6).

$$k(\text{for } I^-) = 6.209 \times 10^{11} \times \exp. -15{,}659/RT \qquad (6)$$

Observed rate constants shown in Table 2 are close to those calculated from equation (6).

The rate controlling step for the reaction involves collision between a $C\ell O_3F$ molecule and an I^- ion but is not dependent upon H^+.

TABLE 2

Rate constants for reaction of $C\ell O_3F$ with I^-.

Temp. °C	[KI] mol/1	[HCℓ] mol/1	k(for I^-) for t in sec.	Temp. °C	[KI] mol/1	[HCℓ] mol/1	k(for I^-) t in sec.
0.0	.010	.01	.179	22.0	.010	.02	1.55
0.0	.010	.01	.185	22.0	.010a	0	1.50
4.5	.098	0	.276	26.0	.006	0	2.16
5.3	.098	0	.325	26.0	.010	0	2.08
6.6	.060	0	.353	26.0	.020	0	2.05
11.6	.040	0	.564	26.0	.040	0	2.10
19.2	.020	0	1.12	27.3	.010	0	2.31
22.0	.005	.01	1.63	28.2	.010	.01	2.77
22.0	.010	.01	1.53	34.0	.010	0	4.26
22.0	.020	.01	1.52	34.1	.010	.01	4.56
22.0	.040a	.01	1.51	34.7	.010	.01	4.88

[a] HCℓ also present at 0.01 molar concentration.

Reaction with hydroxide ion

The reaction of perchloryl fluoride with a strong base is known to give F^- and $C\ell O_4^-$ ions [2]. This has been confirmed and the stoichiometry found to be that shown in equation (7).

$$C\ell O_3F + 2OH^- = F^- + C\ell O_4^- + H_2O \qquad (7)$$

Perchloryl fluoride, 0.0865 g (0.000844 mol), was absorbed in 20.00 ml of 0.1036 N-NaOH and found by titrations of the product to react with .00171 mol of OH^- and to produce .000843 mol of F^-. While the reaction was not fast, it was much more rapid than one would expect from the literature [2]. At room termperature the rate is convenient for study when the concentration of OH^- ion is about 0.01 mol per ℓ.

(a) Procedure

A 19 ml sample of sodium hydroxide solution of known concentration was drawn into a 20 ml glass syringe equipped with a needle about 10 cm long. A short magnetic stirring bar was present in the syringe. It was possible to use the stirrer and hold the solution at substantially constant temperature during a run. Before starting a run, six small test tubes were lined up in readiness. Each contained 1.00 ml of a solution of KI mixed with an excess of $HC\ell$ over that required to neutralize the base present in a 2 ml portion of the solution in the syringe. Each test tube had a mark at the 3.00 ml level. With the NaOH solution at constant temperature, approximately 1 ml of $C\ell O_3F$ gas was drawn into the syringe. The syringe was shaken vigorously for about 5 to 10 seconds. All of the gas phase was then ejected leaving only liquid solution. After using the stirring bar for mixing the solution, a 2 ml portion was added at the bottom of the KI solution in one test tube. This occurred at time=0 for the reaction. During the run the temperature was kept constant, the solution was mixed at times, and at known intervals 2.00 ml samples were taken. Each was injected at the bottom of a 1 ml portion of acidic KI solution in one of the six test tubes. Acid stopped the reaction of $C\ell O_3F$ with OH^- and the perchloryl fluoride remaining at the time of sampling liberated an equivalent amount of iodine. After the run was over, the iodine in each test tube was determined by titration with 0.01 N-$Na_2S_2O_3$. For titrating, the sodium thiosulfate was held in a 1 ml plastic hypodermic syringe which could be weighed (When shielded in aluminum foil because of electrical charge on the plastic). Typical titrations required from about .01 to about 0.4 g of sodium thiosulfate solution. This procedure gave the molar concentration of $C\ell O_3F$ at known times during a run. The solution remaining in the glass syringe was finally used for determination of the concentration of OH^- ion. To a measured weight of the solution, enough solid barium chloride was added to precipitate the carbonate. The solution was then titrated with 0.1 N-$HC\ell$ until the pink color of phenolphthalein indicator disappeared. This gave the final concentration of OH^- ion. The initial concentration of OH^- was considered to equal the final concentration plus two times the molarity of $C\ell O_3F$ at time zero for the reaction. Column 4 of Table 3 gives the average of the initial and final concentrations of base.

(b) Results and Discussion

For a run, a graph of $\ln[C\ell O_3F]$ vs t, in seconds, was a straight line, showing the rate, at constant temperature and fixed OH^- concentration to

TABLE 3

Rate constants for reaction of OH^- with $C\ell O_3F(aq)$

Base	Temp. °C	$\frac{d\ \ln(C\ell O_3F)}{dt}$ time=sec.	Normality of base, average	k(for OH^-) $\frac{\text{Column 3}}{\text{Column 4}}$	k(for OH^-) from equation (9)
NaOH	0.0	.00102	.00744	.137	.133
NaOH	0.0	.00342	.00257	.133	
NaOH	0.0	.00697	.00524	.133	
NaOH	0.0	.0105	.0892	.118	
KOH	0.0	.00812	.0606	.134	
$Ba(OH)_2$	0.0	.00207	.0166	.125	
$Ba(OH)_2$	0.0	.00373	.0363	.103	
NaOH	9.3	.00857	.0224	.383	.384
NaOH	19.45	.0109	.00957	1.139	1.133
NaOH	24.3	.0172	.00929	1.852	1.851
.01M-Borax	25.0	$3.26\text{x}10^{-5}$	.000015a	2.13	1.984
Buffer .001M-$NaHCO_3$ .0015M-Na_2CO_3	25.0	.00158	.00020a	7.9	1.984
Buffer .05M-Na_2CO_3 .05M-$NaHCO_3$	21.1	.00139	.00018a	7.8	1.341
Buffer .2M-KCN .1M-$HC\ell$	25.0	.00036	.00002a	18	1.984

[a] Concentration of OH^- ion.

be proportional to the molarity of $C\ell O_3F$. The rate was also proportional to the molarity of OH^- ion as shown by the runs for NaOH at 0.0° reported in Table 3. This gave the rate law

$$\frac{d[C\ell O_3F]}{dt} = -k(\text{for } OH^-)[C\ell O_3][OH^-] \qquad (8)$$

Since the slope of the line in the graph just mentioned was $d\ \ln[C\ell O_3F]/dt$, it follows that k(for OH^-) could be calculated by dividing the number in column 3 by the number in column 4. A graph of ln k(for OH^-) vs. 1/T for the data obtained with NaOH was a straight line described by the equation

$$k(\text{for } OH^-) = 1.3317 \times 10^{13} \exp -17499/RT \tag{9}$$

Although this does not appear at first glance to be much like the equation for k(for I^-), actually the rates of the two reactions are very close to each other. At 28.9°C the rate constants are identical. The activation energy is somewhat larger for the reaction with hydroxide ion.

The rate for KOH appears to be the same as for NaOH while the rate for $Ba(OH)_2$ may be somewhat less. For a borax buffer the rate is substantially that expected from the concentration of OH^- ion. The other two buffer systems shown in Table 3 react more rapidly than would be expected from the OH^- concentration. It appears that CN^- and CO_3^{--} (known to be nucleophiles) react with perchloryl fluoride.

Since the rate of basic hydrolysis of $C\ell O_3F$ is proportional to the molarities of $C\ell O_3F$ and OH^-, it is probable that the rate controlling step is a nucleophilic displacement

$$C\ell O_3F + OH^- \rightarrow [HOC\ell O_3F]^- \rightarrow F^- + C\ell O_4^- + H^+ \tag{10}$$

followed by neutralization of H^+ or $HC\ell O_4$. The reaction is similar to, but much slower than, the basic hydrolysis of SO_2F_2, which is considered to be a nucleophilic displacement [5]. Nucleophiles other than OH^- ion also react with dissolved $C\ell O_3F$. These include CO_3^{--}, CN^-, NH_3 (see below), amines and phenoxide ion. The author doubts whether the reaction of $C\ell O_3F$ with I^- should be regarded as a nucleophilic displacement. Neither $C\ell^-$ nor Br^- reacts appreciably with $C\ell O_3F$ in water at room temperature. Additional evidence regarding this question is furnished by sulfuryl fluoride which behaves much like $C\ell O_3F$ toward nucleophiles. The rate of reaction of SO_2F_2 to give F^- ion is nearly as great in water as in 0.05 M-$KC\ell$ or 0.05 M-KI. Neither $C\ell^-$ nor I^- behaves as a strong nucleophile toward SO_2F_2.

Reaction of perchloryl fluoride with ammonia in water.

Solutions used in this study contained both ammonia and ammonium chloride, the latter being added to reduce the concentration of hydroxide ion. At the pH values of these solutions, the reaction of $C\ell O_3F$ with ammonia gave $HNC\ell O_3^-$ ion [4].

$$C\ell O_3F + 3NH_3(aq) = HNC\ell O_3^- + F^- + 2NH_4^+ \tag{11}$$

The author has found no reaction of aqueous $C\ell O_3F$ with dissolved ammonium chloride at room temperature. He has confirmed the observation that the product of reaction of $C\ell O_3F$ with NH_3(aq) is a rather good oxidizing agent [4]. It liberates iodine from an acidic solution of potassium iodide and, unlike $C\ell O_3F$, is not removed from solution by dynamic vacuum. It is stable in solution even at 70°C.

The procedure for studying this reaction involved the assumption that $C\ell O_3F$ was consumed by two substances: (1) NH_3(aq), (2) OH^-. During a run, the concentrations of these species were held substantially constant while the total rate of consumption of $C\ell O_3F$ was measured. To obtain the rate due to NH_3(aq) the calculated rate for OH^- was subtracted from the total rate.

(a) Procedure

Aqueous ammonia of very low carbonate content was prepared by absorbing gaseous ammonia from a cylinder, in deaerated water. The solution was held in a stoppered vessel which was opened only for brief periods when samples were removed. For preparing the solutions, deaerated water was used.

A solution containing ammonia and ammonium chloride was placed in a 20 ml glass syringe which did not have the usual metal needle. (The common metal needles react with ammonia (aq) plus oxidizing agent.) A Teflon and glass closure was used. The solution was brought to the desired temperature and held at that temperature during a run. A short stirring bar was present in the syringe and was used at times to stir the solution while a run was in progress. To start a run, about 1 ml of gaseous $C\ell O_3F$ was injected into the syringe. The vessel was shaken vigorously for a few seconds to cause $C\ell O_3F$ to dissolve; then all of the gas phase was removed. This whole operation required only a few seconds and the time at which shaking took place was taken as time, t=0 seconds. A run usually required a matter of hours to go to completion. Samples were taken at times which gave a good distribution of experimental points and each run was allowed to continue for at least seven half-life periods of the dissolved $C\ell O_3F$. The reaction proceeded substantially to completion. For some runs 1.00 ml samples were forced from the syringe into a pipet. For other runs, weighed samples of about 1 g were taken. When a sample was taken, it was immediately subjected to sweeping by a stream of air while the liquid was vigorously agitated by shaking. This removed the unreacted $C\ell O_3F$ from the sample very quickly. The sample was later made acidic with acetic acid, and some potassium iodide was added. After waiting at least 15 min. to allow complete reaction, the free iodine was titrated with .004 N-$Na_2S_2O_3$. Working in this way the concentration of non-volatile oxidizing agent was found for several different time stations during the run. A graph of the quantity ln (Final concentration of oxidant-conc. of oxidant at time, t) vs t (in seconds) gave a straight line having the slope given in column 5, Table 4. Column 6 gives the correction to be made because of the concentration of OH^- ion shown in column 4. By subtracting the number in column 6 from that in column 5 the slope, reported in column 7, for the reaction of $C\ell O_3F$ with NH_3(aq) was obtained.

TABLE 4.

Rate constants for the reaction of NH_3(aq) with $C\ell O_3F$(aq).

Temp. °C	Concentrations, mol/l			d ln ($C\ell O_3F$)/dt			k(for NH_3)	k from
	NH_3	$NH_4C\ell$	OH^- x10^5	Total observed	Due to OH^-, calc.,x10^5	Due to NH_3	time in sec.	eq.13
11.00	.101	0.100	1.6	.000133	0.78	.000125	.00124	.00125
20.03	.0840	0.170	0.84	.000293	1.1	.000282	.00336	.00324
20.05	.0512	0.050	1.7	.000184	2.2	.000162	.00316	.00325
20.00	.102	0.100	1.7	.000360	2.2	.000338	.00331	.00324
20.00	.104	0.100a	2.3	.000608	2.3	.000585	.00563	.00324
20.02	.104	1.00	0.18	.000480	0.2	.000478	.00457	.00324
20.03	.201	1.00	0.34	.000930	0.44	.000926	.00461	.00324
30.02	.0965	0.100	1.8	.000889	6.2	.000827	.00857	.00871

[a] $KC\ell$ also present; conc. = 0.9 molar

(b) Results and Discussion

The data for runs at 20° show that the rate of reaction is proportional to the molarity of ammonia. This gives the rate law

$$\frac{d(C\ell O_3F)}{dt} = -k(\text{for } NH_3)[C\ell O_3F][NH_3] \qquad (12)$$

Values of the rate constant, for time expressed in seconds, are given in column 8, Table 4. The runs involved solutions having ionic strengths from that of 0.05 M-$NH_4C\ell$ to that of 1 M-$NH_4C\ell$. The data show some increase in k(for NH_3) with ionic strength, but suggest that rate constants for zero ionic strength should not be much less than those shown for 0.1 M-

NH_4Cl. For solutions having the ionic strength of 0.1 M-NH_4Cl, the rate constants agree closely with the equation

$$k(\text{for } NH_3) = 3.35 \times 10^{10} \exp -17{,}458/1.9872\ T \qquad (13)$$

While the activation energy is about the same as the k(for OH^-), the rate at a given temperature is much less for ammonia than for OH^-. The smaller rate is consistent with the classification of ammonia as a weaker nucleophile than hydroxide ion. A nucleophilic displacement mechanism seems probable.

$$ClO_3F + NH_3(aq) \rightarrow [H_3NClO_3F] \xrightarrow{2NH_3} NHClO_3^- + F^- + 2NH_4^+ \qquad (14)$$

Reaction of perchloryl fluoride with water

While the hydrolysis of perchloryl fluoride is known to be very slow [2] [3] no quantitative measurements of the rate have been reported. The reaction is so slow that good rate constants are difficult to determine, because of the tendency of the gas to escape from solution. While the stoichiometry has not been determined exactly, it seems almost certain that the reaction is

$$ClO_3F + H_2O \rightarrow 2H^+ + ClO_4^- + F^- \qquad (15)$$

In work on this reaction, the author has dissolved perchloryl fluroide in water and has held the solution in a closed glass container with no gaseous phase being present. After standing for several days, samples were taken. Perchloryl fluoride was determined iodometrically. Fluoride and H^+ were measured by use of specific ion electrodes, after removal of ClO_3F by dynamic vacuum. In two cases, H^+ was also determined by titration with 0.02 N-NaOH. The most nearly successful experiment on stoichiometry gave the following data: A solution which in the beginning contained 0.001183 mol of ClO_3F in 277.5 ml of water was allowed to stand at room temperature (average = 22.7°C) for 32.75 days. During the run, samples were taken at times by displacing solution by adding water. At the end of the run, analyses showed that if no samples had been removed, the solution would have contained 0.001007 mol of ClO_3F (0.000176 mol consumed). At the same time 0.000385 mol of H^+ and .000174 mol of F^- would have been formed. These data correspond to the relative amounts 1:2.19:.989. An independent determination of the ratio, H^+/F^-, gave the value 2.36. Determinations of H^+ and F^- by potentials of specific ion electrodes were not precise, largely because the readings were on a logarithmic scale.

The rate of hydrolysis was measured at room temperature and at 0°C by the type of experiment described in the preceding paragraph. From a knowledge of the initial concentration of $C\ell O_3F$ and of the concentration of F^- at time, t, and from the rate law

$$\frac{d[C\ell O_3F]}{dt} = -k(\text{for } H_2O)[C\ell O_3F] \qquad (16)$$

the values of k(for H_2O) shown in Table 5 were calculated using equation (17).

$$k(\text{for } H_2O) = \frac{\ln[C\ell O_3F]_i - \ln\{[C\ell O_3F]_i - [F^-]_i\}}{t} \qquad (17)$$

in which $[C\ell O_3F]_i$ is the initial molarity of $C\ell O_3F$ and $[F^-]_i$ is the molarity of F^- at time, t, measured in days. Equation (16) is shown to hold by the fact that the values of k(for H_2O) for hydrolysis of $C\ell O_3F$ at various concentrations at about 22.7° are approximately the same.

TABLE 5

Rate of reaction of $C\ell O_3F$ with water.

Initial concentration of $C\ell O_3F$, molar	Temp. °C	Time, days	k(for H_2O) fraction per day	Final observed pH
.00426	about 22.7	3.7	0.0043	3.65
		19.7	0.0046	3.13
		32.75	0.0048	3.07
.00610	about 22.7	24	0.0044	3.30
.001487	about 22.7	16.9	0.0051	3.65
.000431	about 22.7	16.8	0.0054	3.91
.000246	about 22.7	16.9	0.0064	4.02
.00658	0.0	25.7	0.00025	3.95
		28	0.00023	

The two values of k(for H_2O), 0.00023 at 0° and 0.0048 at about 22.7°, have been used to obtain equation (18).

$$k(\text{for } H_2O) = 3.62 \times 10^{13} \exp -21494/1.9872\ T \qquad (18)$$

It is probable that values of the rate constant calculated from this within the range 0° to 25° would be approximately correct.

As the hydrolysis progressed, the solution increased in concentration of H^+. The rate of hydrolysis was practically constant, however, as shown by the three sets of data for the 0.00426 molar solution of $C\ell O_3F$. This indicates that only a small part of the observed hydrolysis was due to the OH^- ion. The observed rate in pH range about 3 to 4 was as great as the basic hydrolysis at pH=6.5. One might expect the fraction of $C\ell O_3F$ reacting per day at 22.7° at a constant pH of 6.5 to be about 0.0096. One reason that the rate constants at 22.7 for low concentrations of $C\ell O_3F$ were greater than for high concentrations could be the higher average pH values for the more dilute solutions.

Clathrate hydrate of perchloryl fluoride

On one occasion when the pressure of $C\ell O_3F$ was somewhat above one atmosphere while its solubility in water was being measured at 0°C, it was observed that the apparent solubility was abnormally high and that a solid formed. The solid had the general characteristics of clathrate hydrates formed by chlorine and several other gases.

Attempts were made to determine the composition of the solid hydrate by allowing crystallization to occur as water was held at 0° in the presence of gaseous perchloryl fluoride under pressure greater than one atmosphere. The results obtained were highly variable and the observed hydration numbers were much greater than the theoretical value, 7.67. In these experiments, conversion of water to the solid hydrate was incomplete. While the literature on clathrate hydrates is extensive, the number of papers is small in which the experimental hydration numbers indicate substantially complete conversion. In reviewing the subject, the author has been helped by references [6] to [12]. Apparently the best work on the subject is that of Galloway et al [6] who probably achieved the true equilibrium composition for hydrates of methane and ethane by forming the solids in a ball-mill, grinding the crystals as they formed.

A new procedure was used in the present study. Crystals of the solid hydrate were formed directly from a gaseous phase containing $C\ell O_3F$ at a much higher concentration than H_2O. The apparatus is shown in Fig. 1. It had an internal volume of 46.8 ml and could be weighed on a balance. Known weights of water and $C\ell O_3F$ were introduced and, before starting a run, the water was condensed at the bottom of the vessel, leaving no droplets on the finger. A refrigerant was placed in the finger, and the bottom of the vessel was held in a bath having a temperature close to 30°C. Under these conditions, water distilled and collected as the solid hydrate on the tip of the finger. In one run water condensed on the finger as liquid rather than solid. The most satisfactory results were obtained by using ice as the refrigerant. To start formation of the solid hydrate, a small flake of solid carbon dioxide was placed within the finger and pressed against the glass until a little solid formed by condensation of $C\ell O_3F$ and water vapor upon the cold spot. The finger was then filled with chopped ice and maintained in this condition until all of the liquid water had evaporated and condensed as solid hydrate. The vessel was then immersed in an ice bath and the valve was opened enough to allow perchloryl fluoride to escape until the pressure fell to that of the atmosphere. The valve was then closed and the vessel was dried and weighed to obtain the ratio of water to $C\ell O_3F$ in the hydrate. It was necessary to make a correction for the weight of gaseous perchloryl fluoride remaining at 0° and atmospheric pressure.

In some runs, refrigerants colder than 0°C were used. When these were cold enough to cause perchloryl fluoride to condense on the finger as liquid, the results were not satisfactory (see Table 6). The solid which formed was fluffy in appearance and had a tendency to fall away from the finger. With ice as the refrigerant, the solid hydrate looked like massive ice and adhered.

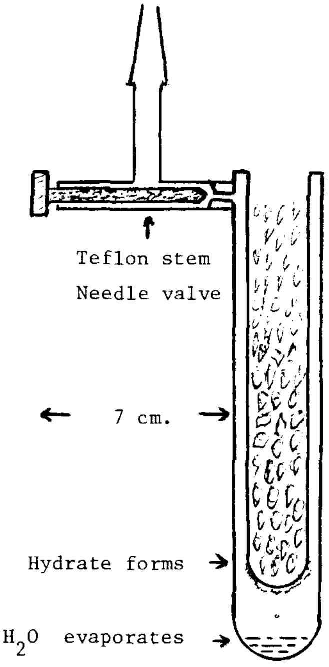

Fig. 1 apparatus for forming the solid hydrate of $C\ell O_3F$.

Data in Table 6 show a minimum hydration number close to 7.75. This may be a good value. At present one cannot be sure that a lower hydration number is unattainable. Structures of other clathrate hydrates indicate that a spherical molecule of diameter less than 5.1Å may have a hydration number as low as 5.75. A molecule of diameter within the range 5.1 to 5.8Å may have the minimum hydration number, 7.67 [6][9][10][11]. The density of solid perchloryl fluoride (2.19 g/ml at -190°C)[3] indicates a molecular diameter of 5.29Å or somewhat less and suggests the probable minimum hydration number to be 7.67.

vessel was held in a bath having a temperature of about 30°C. Under these conditions, water distilled and collected as the solid hydrate on the tip of the finger. In one run water condensed on the finger as liquid rather than solid. The most satisfactory results were obtained by using ice as the refrigerant. Before filling the finger with chopped ice, a small flake of solid carbon dioxide was placed within the finger and pressed against the glass until a little solid formed by the condensation of $C\ell O_3F$ and water vapor upon the cold spot. Distillation was then continued, with the finger cooled by ice, until all liquid had evaporated. The vessel was then immersed in an ice bath and the valve was opened enough to allow perchloryl fluoride to escape until the pressure fell to that of the atmosphere. The valve was then closed, and the vessel was dried and weighed to obtain the ratio of water and $C\ell O_3F$ in the solid hydrate. It was necessary to make a correction for gaseous perchloryl fluoride remaining at 0° and atmospheric pressure.

In some of the runs, refrigerants colder than 0°C were used. When these were cold enough to cause perchloryl fluoride to condense on the finger as a liquid, the results were not satisfactory (see Table 6). The solid which formed was fluffy in appearance and had a tendency to fall away from the finger. With ice as the refrigerant, the solid looked like ice and adhered.

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A sample of the solid hydrate was held in the vessel shown in Fig. 1 with the valve open to the atmosphere at 756 torr. As the temperature rose slowly, the solid decomposed to give liquid solution plus $C\ell O_3F$ gas within the range 2° to 3°C.

In another experiment 0.2842 g. of water and 0.1386 of $C\ell O_3F$ were placed in a glass bulb of about 1 ml volume. The vessel was then hermetically sealed. Two liquid phases were present at 22°C. When the bulb was shaken vigorously while cooled by ice-water, one of the phases became

TABLE 6

Hydration number of perchloryl fluoride

H_2O, g.	Initial $C\ell O_3F$, g.	Temp. of coolant in finger, °C	Approx. initial pressure, Atm.	$C\ell O_3F$ in solid hydrate, g.	Hydration number, $H_2O/C\ell O_3F$
.2013	.5808	0.0	2.7	.1451	7.89
.2013	.9395	0.0	4.3	.1557	7.35
.2031	.7986	0.0	3.7	.1490	7.75
.2034	.8580	-10 to -15	3.9	.1487	7.78
.1577	.3611	-35 to -45	1.4a	.0881	10.18
.2034	1.3725	-78	0.2a	.1082	10.69
.1577	.4620	-78	0.2a	.0755	11.88

[a] Liquid $C\ell O_3F$ was present on the finger.

solid. As the vessel warmed slowly the solid melted at approximately 20.5°C This temperature is probably close to the invariant point involving four phases: gas, solid hydrate, liquid rich in $C\ell O_3F$, liquid rich in water.

REFERENCES

1 A. Engelbrecht and H. Atzwanger, Monatsh. Chem., 83 (1952) 1087.

2. A Engelbrecht and H. Atzwanger, J. Inorg. Nucl. Chem., 2 (1956) 348.

3 John F. Gall, Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Ed., Vol. 9, pp. 598-610, Interscience Publishers, John Wiley and Sons, New York (1966).

4 H. C. Mandell, Jr. and G. Barth-Wehrenalp, J. Inorg. Nucl. Chem., 12 (1959) 90.

5 G. H. Cady and S. Misra, Inorg. Chem., 13 (1974) 837.

6 T. J. Galloway, W. Ruska, P. S. Chappelear and R. Kobayashi, Ind. Eng. Chem. Fundam., 9, (1970) 237.

7 W. M. Deaton and E. M. Frost, Jr., "Gas Hydrates and Their Relation to the Operation of Natural Gas Pipelines", Monograph 8, U.S. Bureau of Mines (1946).

8 J. H. van der Waals and J. C. Plateeuw, "Clathrate Solutions", Advances in Chemical Physics, I. Prigogine, ed., Vol. II, pp. 1-58, Interscience, New York and London, 1959.

9 M. von Stackelberg and H. R. Müller, J. Chem. Phys., 19 (1951) 1319; Z. Elektrochem., 58 (1954) 25.

10 W. F. Claussen, J. Chem. Phys., 19 (1951) 259, 662, 1425.

11 L. Pauling and R. E. Marsh, Proc. Natl. Acad. Sci. U.S.A., 38 (1952) 112.

12 S. Sh. Byk and V. I. Fomina, Russian Chem. Reviews, 37 (1968) 469.