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On the Reactions of Chlorine Fluorides with Hydroxyl Compounds

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A systematic study was carried out of the reactions of ClF, ClF_3, ClF_5, and ClO_2F with a monofunctional ($HONO_2$) and a bifunctional (HOH) hydroxyl compound. The nature of the observed reaction products depends upon which reagent is used in excess but can be rationalized for both hydroxyl compounds on a common basis. The observed analogies and additional experimental data allow some generalizations concerning the nature of some of the intermediate reaction products.

Introduction

Most of the studies dealing with chlorine fluorides have been concentrated on three aspects: their syntheses and physical properties, their use as fluorinating agents, and their ability to form adducts. Their reaction chemistry, in particular that involving hydroxyl compounds, has been largely neglected. This may have been partially due to the violent nature of most of the reactions and the great experimental difficulties encountered in working with most of these systems. Thus, only the reactions of ClF, ClF_3, and ClO_2F with H_2O,[1,2] of ClF with an excess of $HONO_2$,[3] and of an excess of ClF_5 with H_2O[4] have been reported. In this paper, we wish to report the results of a systematic study of ClF, ClF_3, ClF_5, and ClO_2F with monofunctional ($HONO_2$) and bifunctional (HOH) hydroxyl compounds with either reagent in excess.

Experimental Section

Caution! Most of these reactions are extremely vigorous and can produce shock-sensitive materials. They should be carried out on a small scale only with appropriate shielding and safety precautions.

Materials and Apparatus.—The materials used in this work were manipulated in a Monel vacuum line equipped with Teflon FEP U traps. For reactions involving an excess of halogen fluoride, the line was well passivated with ClF_3. Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Chlorine monofluoride was prepared by heating an equimolar mixture of Cl_2 and ClF_3 to 150° for several hours in a stainless steel cylinder. Chlorine trifluoride (The Matheson Co.) and ClF_5 (Rocketdyne) were commercial materials. The preparation of $ClF_2^+AsF_6^-$ has previously been described.[5] Chloryl fluoride was prepared from $KClO_3$ and F_2 by the method[6] of Woolf and Cl_2O was prepared from HgO and Cl_2 by the method[7] of Schack. Nominally anhydrous $HONO_2$ was prepared from fuming nitric acid by distillation from concentrated H_2SO_4. All volatile materials were purified prior to use by fractional condensation. Their purities were determined by measurements of their vapor pressures and infrared spectra. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer in the range 4000–400 cm^{-1} using a 5-cm stainless steel cell fitted with AgCl windows. Mass spectra were recorded on a quadrupole mass spectrometer (Electronic Associates Inc. Model Quad 300) using a stainless steel–Teflon FEP inlet manifold.

Reaction of Excess ClF with $HONO_2$.—Anhydrous $HONO_2$ was condensed into one U of a double-U Teflon FEP trap, weighed (5.70 mmol), and cooled to −196°. Chlorine monofluoride (12.8 mmol) was condensed at −196° into the second U of the trap. The U containing $HONO_2$ was allowed to warm up to the melting point (−42°) of $HONO_2$. Then, the temperature of the U containing ClF was gradually increased and both compounds were allowed to interact slowly. First, a brownish color developed. The contents of both U's were combined in one U and kept at −78° for 10 min. The formation of a white solid was observed. The mixture was allowed to warm up to 23° and was kept at this temperature for 30 min. It was cooled again to −196°, at which temperature no noncondensable material was observed and was then during warm up subjected to fractional condensation. The individual fractions were measured by volume and/or weight and identified by their vapor pressures and infrared and mass spectra. The reaction products consisted of $ClONO_2$ (5.7 mmol), HF, and unreacted ClF (7.0 mmol).

Reactions of ClF with Excess HOH.—Chlorine monofluoride (2.34 mmol) and HOH (1.17 mmol) were combined at −196° in a Teflon FEP ampoule. Upon warming of the ampoule from −196 to −78°, melting of the mixture occurred and a dark brown liquid was formed. After keeping the mixture at −78° for 20 hr, the reaction products were separated and consisted of Cl_2O (0.65 mmol), Cl_2 (0.42 mmol), ClO_2 (0.21 mmol), HF, and O_2.

A second reaction carried out at 25° showed as the only products ClO_2, Cl_2, and O_2 in a mole ratio of 1:2:0.25 and HF.

Reaction of ClF with Cl_2O.—Chlorine monofluoride (2.33 mmol) and Cl_2O (1.63 mmol) were combined at −196° in a Teflon FEP U trap. The mixture was allowed to warm to −78° and was kept at this temperature for 15 hr. The color of the liquid reaction mixture had changed after this period from an original dark brown to yellow. The products were separated and consisted of ClO_2F (0.81 mmol), Cl_2 (1.65 mmol), and unreacted ClF (1.50 mmol).

Reaction of $HONO_2$ with Excess ClF_3.—In order to establish the stoichiometry of the reaction, $HONO_3$ (8.60 mmol) was combined with a large excess of ClF_3 (18.5 mmol) at −196°. Upon warm up, a violent reaction occurred which required moderation by cooling and a brownish color developed. After completion of the reaction at −78°, the products were separated and shown to consist of NO_2F, ClO_2F, ClF, HF, and 10 mmol of unreacted ClF_3 as expected for a 1:1 reaction. Since ClF_3 forms an adduct with NO_2F which complicates the separation of the reaction products, subsequent experiments were carried out with ratios of the starting materials close to 1:1. Typically, ClF_3 (10.5 mmol) was slowly admitted into a Teflon FEP U trap containing $HONO_2$ (10.5 mmol) at a temperature slightly above the melting point of $HONO_2$. Initially, an orange color (indicating the presence of ClO_2) developed, followed by solidification of the mixture. When no further ClF_3 uptake took place at −78°, the remaining ClF_3 was added at −196°. The reaction was completed by temperature cycling between −78 and −196° and no noncondensable material was observed at −196°. Fractional condensation of the reaction products showed NO_2F (10 mmol), HF (9 mmol), ClO_2F (5.9 mmol), and ClF (4.4 mmol).

Reaction of ClF_3 with Excess $HONO_2$.—Nominally anhydrous $HONO_2$ (10.4 mmol) and ClF_3 (3.45 mmol) were combined at −78° in a Teflon FEP U trap. The ClF_3 was added in increments, and after each addition, the mixture was allowed gradually to warm up until reaction occurred. During the ClF_3 additions, the reaction mixture turned orange, indicating the formation of ClO_2. After completion of the ClF_3 addition, the mix-

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ure was kept for 8 hr at −78°. The reaction mixture consisted of ClO_2 (1.7 mmol), $ClONO_2$ (1.7 mmol), HF (10 mmol), N_2O_5, and O_2. No unreacted ClF_3 was recovered.

Reaction of Excess ClF_5 with $HONO_2$.—Chlorine pentafluoride (4.0 mmol) and $HONO_2$ (3.36 mmol) were condensed at −196° into the separate bends of a double-U Teflon FEP trap. The $HONO_2$ was warmed to its melting point and ClF_5 vapor was allowed to contact the liquid $HONO_2$ phase. A vigorous reaction took place. At first, a brown color developed, and upon addition of all the ClF_5, two liquid layers formed. The upper one containing most of the material was colorless, whereas the lower one was brown. The mixture was allowed to interact for several minutes at −78° and was then allowed to warm to ambient temperature, at which point the brown color disappeared. Recooling of the mixture to −196° showed the absence of noncondensable material. The reaction products consisted of ClO_2F (1.66 mmol), ClF_5 (2.4 mmol), NO_2F (3.3 mmol), and HF.

Reaction of ClF_5 with Excess $HONO_2$.—Chlorine pentafluoride (1.39 mmol) and $HONO_2$ (6.76 mmol) were combined at −196° in a Teflon FEP U trap. A vigorous reaction took place upon melting, which was moderated by intermittent cooling with liquid N_2. After completion of the reaction, the brown liquid product was kept at 23° for 10 min and then recooled to −196°. The reaction products consisted of O_2 (0.42 mmol), ClO_2F (0.55 mmol), $ClONO_2$ (0.29 mmol), ClO_2 (0.36 mmol), N_2O_5, and HF.

Reaction of ClF_5 with Excess HOH.—Chlorine pentafluoride (2.00 mmol) and HOH (5.00 mmol) were combined at −196° in a Teflon FEP U trap. A vigorous reaction started upon melting of the ClF_5, which was controlled by intermittent cooling with liquid N_2. The yellow to orange mixture was kept at 23° for 3 hr before being recooled to −196°. The products consisted of ClO_2 (1.35 mmol), ClO_2F (0.35 mmol), ClO_3F (0.18 mmol), O_2 (<0.5 mmol), and HF.

Reaction of ClO_2F with Excess $HONO_2$.—Chloryl fluoride (2.35 mmol) and $HONO_2$ (2.16 mmol) were combined at −196° in a Teflon FEP U trap. The mixture was allowed to warm up and to react. The resulting homogeneous brown solution was kept for 30 min at 23°, at which temperature gas evolution was observed. The reaction products were O_2 (0.25 mmol), ClO_2 (0.48 mmol), ClO_2F (1.86 mmol), N_2O_5, $HONO_2$, and HF. Since only 0.49 mmol of ClO_2F reacted, the amount of $HONO_2$ available (2.16 mmol) presented a true excess.

Hydrolysis of $ClF_2^+AsF_6^-$ in HF Solution.—To a mixture of $ClF_2^+AsF_6^-$ (21.7 mmol) and anhydrous HF (5 ml liquid), wet HF (5 ml containing 20.6 mmol of H_2O) was slowly added at −78°. At first a brownish red color developed which gradually changed to yellow. After keeping the mixture at −78° for 1 hr, the volatiles were removed *in vacuo*. The solid residue was shown by infrared spectroscopy to consist of $ClO_2^+AsF_6^-$ and $ClF_2^+AsF_6^-$.

Results and Discussion

The following reaction systems were studied: excess $ClF + HONO_2$, excess $ClF_3 + HONO_2$, excess $ClF_5 + HONO_2$, ClF_3 + excess $HONO_2$, ClF_5 + excess $HONO_2$, ClO_2F + excess $HONO_2$, and ClF_5 + excess HOH. The reactions between excess ClF_5 and HOH,[4] between ClF and excess $HONO_2$,[3] and between ClF, ClF_3, or ClO_2F and HOH with either reagent in excess[1,2] have previously been reported. In order to establish the nature of some of the intermediate products, the $ClF-Cl_2O$ system, the low-temperature reaction of ClF with an excess of water, and the hydrolysis of $ClF_2^+AsF_6^-$ in HF solution were also studied. Consequently, complete experimental data are now available for a systematic evaluation of the reactions between chlorine fluorides and mono- and bifunctional hydroxyl compounds. The following equations (some of them expressed in multiples for easier comparison) summarize the observed reactions:

excess ClF + HOX

$$4ClF + 4HONO_2 \longrightarrow 4HF + 4ClONO_2 \quad (1)$$

$$5ClF + 2HOH \longrightarrow 4HF + ClO_2F + 2Cl_2 \quad (2)^{1,2}$$

ClF + excess HOX

$$4ClF + 4HONO_2 \longrightarrow 4HF + 4ClONO_2 \quad (3)^{3}$$

$$4ClF + 2HOH \longrightarrow 4HF + 2Cl_2 + O_2 \quad (4)^{1,2}$$

$$4ClF + 2HOH \xrightarrow{\text{low temp}} 4HF + 2Cl_2O \quad (4a)$$

$$10ClF + 5HOH \xrightarrow{25°} 10HF + 2ClO_2 + 4Cl_2 + {}^1/_2O_2 \quad (4b)$$

excess ClF_3 + HOX

$$2ClF_3 + 2HONO_2 \longrightarrow 2HF + ClO_2F + ClF + 2NO_2F \quad (5)$$

$$2ClF_3 + 2HOH \longrightarrow 4HF + ClO_2F + ClF \quad (6)^{1,2}$$

ClF_3 + excess HOX

$$4ClF_3 + 12HONO_2 \longrightarrow 12HF + 2ClO_2 + 2ClONO_2 + 5N_2O_5 + {}^1/_2O_2 \quad (7)$$

$$4ClF_3 + 6HOH \longrightarrow 12HF + 2Cl_2 + 3O_2 \quad (8)^{1,2}$$

$$[\equiv 2ClO_2 + ClOCl + {}^1/_2O_2] \quad (8a)$$

excess ClF_5 + HOX

$$ClF_5 + 2HONO_2 \longrightarrow 2HF + ClO_2F + 2NO_2F \quad (9)$$

$$ClF_5 + 2HOH \longrightarrow 4HF + ClO_2F \quad (10)^{4}$$

ClF_5 + excess HOX

$$2ClF_5 + 8HONO_2 \longrightarrow 8HF + 4N_2O_5 + 2ClO_2F \quad (11)$$

$$2ClO_2F + 2HONO_2 \longrightarrow 2HF + N_2O_5 + 2ClO_2 + {}^1/_2O_2 \quad (11a)$$

or

$$2ClF_5 + 10HONO_2 \longrightarrow 10HF + 4N_2O_5 + 2ClONO_2 + 2O_2 \quad (11b)$$

$$2ClF_5 + 5HOH \longrightarrow 10HF + 2ClO_2 + {}^1/_2O_2 \quad (12)$$

ClO_2F + excess HOX

$$2ClO_2F + 2HONO_2 \longrightarrow 2HF + 2ClO_2 + N_2O_5 + {}^1/_2O_2 \quad (13)$$

$$2ClO_2F + HOH \longrightarrow 2HF + 2ClO_2 + {}^1/_2O_2 \quad (14)^{1,2}$$

Cl_2O + excess ClF

$$2Cl_2O + ClF \longrightarrow ClO_2F + 2Cl_2 \quad (15)$$

Several reactions require some specific comments. According to ref 1 and 2 eq 6 can be followed by additional more or less slow reactions resulting in the formation of some Cl_2 and O_2 and of traces of ClO_3F. Equation 8 might be rewritten by substituting the observed amounts of Cl_2 and O_2 by the appropriate chlorine oxides (eq 8a). This assumption is supported by the fact that in the $ClF-H_2O$ system, depending upon the reaction conditions, either Cl_2 and O_2 (eq 4) or ClO_2, Cl_2, and O_2 (eq 4b) or Cl_2O (eq 4a) can be obtained as the principal products. The reaction products observed for the reaction of ClF_5 with excess $HONO_2$ can be rationalized by assuming that ClO_2F is formed as the primary product (eq 11) which reacts only slowly with additional $HONO_2$, according to (eq 11a), thus leaving an appreciable amount of ClO_2F unconverted. This assumption was confirmed by reaction 13, which showed that this reaction is indeed slow. In addition, a side reaction generating $ClONO_2$ and oxygen occurs (eq 11b). For reaction 12, substantial amounts of ClO_3F and ClO_2F were found in the reaction product. The observation of some ClO_2F is not surprising since it has previously been shown[2] that the hydrolysis of ClO_2F is quite slow. The hydrolysis of some of the ClO_2F produces nascent oxygen, which, in turn, can rapidly oxidize ClO_2F to ClO_3F. Since ClO_3F is resistant to hydrolysis,[8] it will build up as a product.

A general comparison between the reactions of $HONO_2$ and those of HOH shows an excellent agreement. The reaction products and the changes in the oxidation states of Cl are analogous for each equation pair. The only exceptions are reactions 1 and 2. The difference is due to the fact that $ClONO_2$, under the given conditions, does not interact with ClF, whereas Cl_2O even at −78° does, yielding ClO_2F and Cl_2 (eq 15). The fact that the products differ depending upon which reagent is used in excess is not surprising. If an excess of the fluorinating agent is used, ClO_2F is always one or often the only chlorine-containing reaction product independent of the oxidation state of the chlorine fluoride starting material. The only exception is again reaction 1 for the above-mentioned reason, *i.e.*, inability of ClF to fluorinate $ClONO_2$ under the given conditions. If an excess of the hydroxyl compound is used, the main reaction products are chlorine oxides (most frequently ClO_2) and chlorine nitrate. In the case of excess $HONO_2$, any NO_2F present will form N_2O_5 and HF. In the case of ClF the formation of several intermediates was experimentally confirmed suggesting for the low-temperature reaction of ClF with HOH the sequence

$$ClF + HOH \longrightarrow HF + HOCl \quad (16)$$

$$HOCl + ClF \longrightarrow HF + ClOCl \quad (17)$$

In the presence of an excess of ClF, fluorination of Cl_2O can occur according to eq 15. This reaction was shown to be quantitative at temperatures as low as −78°. In the presence of an excess of water at −78°, Cl_2O is the principal product. In addition to Cl_2O formation, reaction 4b also occurs at −78° and becomes at 25° the dominant reaction. Under the reaction conditions of ref 1 and 2, ClO_2 can decompose further to Cl_2 and O_2 (eq 4). The fact that pure Cl_2O does not readily disproportionate at temperatures between −78 and 25° to ClO_2 and Cl_2 suggests the participation of less stable intermediates such as possibly HOCl or ClO radicals in the ClO_2 formation step.

In the case of ClF_3 and ClF_5 the first reaction should be again the elimination of HF. This reaction is extremely fast and exothermic and often proceeds explosively, even at low temperature

$$ClF_n + HOX \longrightarrow ClF_{n-1}OX + HF \quad (18)$$

The next steps could involve either the reaction of $ClF_{n-1}OX$ with additional HOX

$$ClF_{n-1}OX + HOX \longrightarrow ClF_{n-2}(OX)_2 + HF \quad (19)$$

or an intramolecular fluorination, *i.e.*, XF elimination

$$ClF_{n-1}OX \longrightarrow ClF_{n-2}O + XF \quad (20)$$

Reaction 19 should also be followed by steps such as (20) or by X_2O elimination if there are no or only relatively unreactive fluorine atoms left in the molecule

$$ClF_{n-2}(OX)_2 \longrightarrow ClF_{n-2}O + X_2O \quad (21)$$

Thus, by either sequence, one might expect to obtain FClO as a intermediate in the reactions of ClF_3. However, the following facts indicate that this intermediate would be quite unstable. The photochemical synthesis[9] and reaction chemistry[10] of ClF_3O are best interpreted in terms of an unstable FClO intermediate. In addition, an attempt was made to prepare and isolate FClO, according to

$$ClF_2^+AsF_6^- + HOH \xrightarrow{\text{HF soln}} ClO^+AsF_6^- + 2HF \quad (22)$$

$$ClO^+AsF_6^- + FNO \longrightarrow NO^+AsF_6^- + FClO \quad (23)$$

However, instead of $ClO^+AsF_6^-$, only $ClO_2^+AsF_6^-$ and unreacted $ClF_2^+AsF_6^-$ were found for (22).

Similarly, one might have expected to observe ClF_3O, which is known to be stable,[11,12] as an intermediate in the reactions of HOX with an excess of ClF_5. The fact that it was not observed either suggests an alternate sequence such as

$$ClF_5 + 2HOX \longrightarrow ClF_3(OX)_2 + 2HF \quad (24)$$

$$ClF_3(OX)_2 \longrightarrow ClO_2F + 2XF \quad (25)$$

or indicates that ClF_3O is much more reactive toward HOX than is ClF_5.

In many of these systems, the final products show that the Cl-containing starting material has disproportionated in the course of the reaction. Suitable intermediates which could readily disproportionate might be ClO, HOCl, HOClO, and FClO.

In summary, it appears that the reactions of chlorine fluorides with a monofunctional ($HONO_2$) and a bifunctional (HOH) hydroxyl compound can be rationalized on a common basis. The observed reaction patterns should be very useful for predicting the products of the reactions of chlorine fluorides with other hydroxyl compounds. The partial hydrolysis of chlorine fluorides does not offer a synthetic route toward chlorine oxyfluorides, except for ClO_2F.

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