and not to the unknown chlorosyl fluoride, ClFO, and F$_2$. Its thermal stability thus appears to be intermediate between that of ClF$_3$[15] and ClF$_5$.[16] The reaction chemistry of ClF$_3$O will be described in a separate paper.[19]

(19) C. J. Schack, C. B. Lindahl, D. Pilipovich, and K. O. Christe, *Inorg. Chem.*, **11**, 2201 (1972).

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CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
CANOGA PARK, CALIFORNIA 91304

Chlorine Trifluoride Oxide. II. Photochemical Synthesis

BY D. PILIPOVICH,* H. H. ROGERS, AND R. D. WILSON

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Chlorine trifluoride oxide, ClF$_3$O, was synthesized from several gaseous reaction systems using uv activation. The fluorination of both ClO$_2$F and ClO$_3$F, using ClF$_5$ or F$_2$ as fluorinating agents, gave excellent yields of ClF$_3$O. In addition, the direct photochemical synthesis of ClF$_3$O from the elements Cl$_2$, F$_2$, and O$_2$ was successfully achieved. Other systems yielding ClF$_3$O were ClF$_3$–O$_2$ and ClF–IF$_5$O. Attempts were unsuccessful to photochemically prepare either BrF$_5$O from BrF$_5$ and O$_2$ or BrF$_7$ from BrF$_5$ + F$_2$.

Introduction

Halogen fluorides can be readily synthesized by direct fluorination of the corresponding halogens at appropriate temperatures and pressures.[1] Consequently, little attention has been devoted to their photochemical synthesis. When the novel chlorine oxyfluoride, ClF$_3$O, was discovered[2,3] in 1965, its original synthesis involved handling of the treacherous[3] starting material, Cl$_2$O. Therefore, alternate approaches, such as photochemical reactions, were studied which might yield ClF$_3$O. Of initial interest to us was the use of uv irradiation to achieve the "deoxygenation" of either ClO$_2$F or ClO$_3$F. One of these, ClO$_2$F, had previously been shown[4] to degrade thermally to give ClF and O$_2$. A stepwise deoxygenation of these oxyfluorides *via* the intermediate (and unknown) chlorosyl fluoride, ClOF, might in the presence of F$_2$ yield ClF$_3$O. In addition, the alternate approach, *i.e.*, the photochemical addition of oxygen to various chlorine fluorides, was investigated. Of particular interest was whether ClF$_3$ could combine with oxygen to form ClF$_3$O and the direct synthesis of ClF$_3$O from the elements, Cl$_2$, F$_2$, and O$_2$. After the successful completion of our study, Bougon, Isabey, and Plurien independently discovered[5] the formation of ClF$_3$O when exposing a mixture of ClF$_3$ and OF$_2$ to uv irradiation. In this paper, we report the results of our original photochemical studies.

Experimental Section

Materials and Apparatus.—Perchloryl fluoride was purchased from Pennsalt Chemical Co. and used as received after verifying its purity through its infrared spectrum and vapor tension at −80°. Chloryl fluoride was synthesized by a modification of Woolf's procedure[6] and involved the fluorination of NaClO$_3$ with ClF$_3$. Fluorine was produced at Rocketdyne and Cl$_2$ and ClF$_3$ were obtained from the Matheson Co. The ClF$_3$ was purified by complexing with KF, removing volatiles at ambient temperature, and subsequently pumping off ClF$_3$ at temperatures above 140°. Chlorine pentafluoride was prepared according to the method of Pilipovich, *et al.*,[7] while chlorine monofluoride was synthesized from ClF$_3$ and Cl$_2$.[8] Bromine pentafluoride (Matheson) was treated with F$_2$ at ambient temperature until the material was colorless. It was purified by fractional condensation through traps kept at −64 and −95°. The BrF$_5$ was retained in the −95° trap and showed no detectable impurities. The preparation and purification of IF$_5$O[9] and ClF$_3$O[3] have previously been described.

All the results listed in this paper was obtained with a Hanovia high-pressure Hg lamp, No. 679-A-36 (power input 450 W). The spectral energy distribution of radiated Hg lines for the lamp includes (Å, W): 2967, 4.3; 2652, 4.0; 2537, 5.8; 2482, 2.3; 2380, 2.3; and 2224, 3.7, according to the manufacturer's specifications. In addition, this lamp emits lines of shorter wavelength down to about 1700 Å (quartz limit). The distance between the lamp and the cell window was about 2 in.

The photolyses were carried out in a cell consisting of a stainless steel cylindrical body (3 in. long, 3 in. i.d., and 388 cm^3 volume). One end of the cell was sealed with a welded plate. The other end was a machined flange onto which a 4-in. diameter optical grade sapphire window was clamped. A vacuum seal was obtained by using Teflon O-rings. Provision was made to condense materials into the cell *via* a stainless steel coldfinger (3 in. long, $^3/_8$ in. o.d.) appended to the main cell body. An outlet was provided which was connected to a stainless steel–Teflon FEP vacuum line for product work-up. Cooling coils were brazed onto the outside of the cell body, and cold methanol was circulated to provide the cooling. The cell wall temperature was automatically controlled to within 3° of a preset temperature over the range −60° to ambient temperature. A removable metal lamphousing was positioned over the sapphire window and dry N$_2$ was passed over the window to cool the window, prevent condensation prior to the irradiation, and exclude atmospheric oxygen which might act as a filter for short wavelength uv radiation.

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TABLE I

PHOTOCHEMICAL FORMATION OF ClF_3O FROM HALOGEN OXYFLUORIDES

Expt no.	Reaction time, min	Temp, °C	Reactants,[b] cm^3	Products,[b] cm^3	Yield of ClF_3O, %[c]
1	60	15	ClF_5, 56.3; ClO_2F, 56.9	ClF_5; ClO_2F; ClF_3 (trace)	0
2	60	−40	ClF_5, 55.6; ClO_2F, 55.6	ClF_3O, 26; ClF_3 60	47
3	60	−40	ClF_5, 57.2; ClO_3F, 61.8	ClF_3O, 29; ClF_3 50; ClO_3F, 25	79
4	60	−60	F_2, 65.9; ClO_3F, 61.3	ClF_3O, 18; ClF_3, 10; ClO_3F, 33	64
5[a]	120	−60	ClO_3F, 120.5	ClO_3F, 50; ClF, 43; ClO_2F, 8; O_2	0
6[a]	60	−60	ClF, 67.5; O_2, 67	ClF, 51; ClF_3, 9; ClO_2F (trace); Cl_2	0
7[a]	60	−40	ClF_3O, 69.4	ClF_3O, 49.6; ClF_3; O_2	
8[a]	60	−60	ClF_3O, 61.7	ClF_3O, 56.8	
9[a]	180	−60	ClF_3, 31.5	ClF_3, 21.1; ClF, 10.2; F_2, 10.2	0
10	15	−60	ClF, 101.0; IF_5O, 51.4	ClF_3O, 5; ClF, 69.3; Cl_2; IF_5	10
11	60	−60	ClF, 95.0; IF_5O, 57.0	ClF_3O, 15; 79.5; Cl_2; ClO_2F, IF_5	26

[a] Control experiments. [b] All gas volumes in this paper are cm^3 at STP. [c] Based on moles of oxyfluoride reacted.

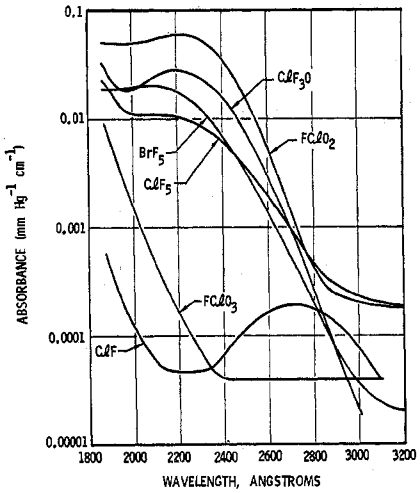

Figure 1.—Ultraviolet absorption spectra for ClF, ClF_5, ClF_3O, ClO_2F, ClO_3F, and BrF_5.

Photochemical Synthesis.—With the cell at ambient temperature and the condensing tube at −196°, the condensable reactants were loaded into the cell, followed by the addition of F_2 and/or O_2. The amount of each reactant introduced was determined by volumetric measurements made in the vacuum system external to the cell. The flow of N_2 was started over the cell window and the methanol cell-coolant flow was started. The condensing tube was allowed to reach the cell-body temperature, and after the reactants had mixed, the lamp was turned on. A shutter between the lamp and cell window was only removed when the lamp current had reached its full operating level. After the desired period of irradiation, the cell was warmed to ambient temperature and its contents fractionated in the vacuum line. The ClF_3O was trapped at −95°, measured volumetrically, and identified by its ir spectrum.[10] The other reaction products were similarly separated and identified by infrared spectroscopy, vapor pressure, and gas density measurements.

Absorption Spectra.—Uv spectra were obtained with a Cary Model 14 recording spectrophotometer. The cells were of 10-cm path length and constructed from 1-in. o.d. nickel tubing. Ultraviolet grade Linde sapphire windows were held in place with flanges and Teflon O-rings. Hoke M482m Monel bellows valves were used as cell closures. Prior to the introduction of the sample, the cell was passivated with F_2 and ClF_3.

Results

Uv Absorption Spectra.—The absorption spectra of some of the starting materials were recorded to obtain insight into the uv activation processes. These spectra are shown in Figure 1. The results for ClF_5 extend the work of Gatti, *et al.*,[11] to wavelengths shorter than 2640 Å. Likewise, the ClF spectrum extends that reported by Schmitz and Schumacher.[12] Schmitz and Schumacher have also reported[13] the uv spectrum of ClF_3.

Synthesis of ClF_3O from Halogen Oxyfluorides.—The results of the reactions of F_2, ClF, and ClF_5 with ClO_2F, ClO_3F, or IF_5O are given in Table I. The reaction temperatures employed ranged from +15 to −60°. The yield of ClF_3O at 15° was zero while at −60° yields as high as 79% were observed (based on 1 mol of ClF_3O from each mole of oxyfluoride reacted). Control experiments to determine the rate of decomposition of ClO_3F and ClF_3O were carried out. After 1 hr at −40 and −60°, ClF_3O had decomposed to the extent of 28.5 and 8.0%, respectively. Surprisingly, ClO_3F decomposed at a rate of about 29%/hr at −60°. Furthermore, the control experiment (expt 6, Table I) showed a low level of oxygenation of ClF to ClO_2F.

Synthesis of ClF_3O from the Elements.—The results for the synthesis of ClF_3O from the elements, Cl_2, F_2, and O_2, at −60° are shown in Table II. The conversions to ClF_3O increased with increasing reaction time ranging from a trace after 15 min to 44.6% after 360 min. Most of the Cl_2 and F_2 were converted to ClF_3 during the first 15 min of irradiation (expt 1). The effective irradiation wavelengths for the reaction were established through the use of different filters. No ClF_3O was formed using either a Pyrex or Vycor filter

TABLE II

PHOTOCHEMICAL FORMATION OF ClF_3O FROM THE ELEMENTS[a] AT −60°

Expt no.	Reaction time, min	Products,[b] cm^3			% Cl_2 converted to	
		ClF_3O	ClF_3	ClO_2F	ClF_3O	ClF_3
1	15	Trace	45.2		Trace	84
2	30	1.3	50.5	0.8	2.3	93
3	60	7.3	38.3	1.8	13.3	70
4	90	9.7	46.8	0.4	16.7	80
5	180	15.9	32.9	2.9	29.7	61
6	240	21.4	31.9		39.0	58
7	360	25.0	29.4	0.4	44.6	52
8[c]	60	0	37.7	3.9	0	71
9[d]	60	0	49.3	0.8	0	88
10[e]	180	7.5	40.1	4.9	13.2	71

[a] The ratio of $Cl_2:F_2:O_2$ in all experiments was 1:3:10 with the total amount of gas being about 400 cm^3 and the total pressure being about 780 mm (*i.e.*, approximately 28 cm^3 of Cl_2, 85 cm^3 of F_2, and 285 cm^3 of O_2). [b] Remainder of products were ClF, F_2, and O_2. These were not measured. [c] Pyrex filter used. [d] Vycor filter used. [e] Oxygen filter used.

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(10) K. O. Christe and E. C. Curtis, *Inorg. Chem.*, **11**, 2196 (1972).

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(12) H. Schmitz and H. J. Schumacher, *An. Asoc. Quim. Argent.*, **38**, 61 (1950).

(13) H. Schmitz and H. J. Schumacher, *ibid.*, **38**, 363 (1950).

and the yield of ClF_3O was drastically reduced by using a crude oxygen filter (*i.e.*, flowing oxygen rather than nitrogen for cooling the cell window).

Synthesis of ClF_3O from ClF_3 and O_2.—The results for the synthesis of ClF_3O from ClF_3 and O_2 at −60° are shown in Table III. Here again the conversions to ClF_3O increase with increasing reaction time with about 21% ClF_3O formed after 360 min. The amounts of ClF_3O formed from ClF_3–O_2 mixtures and from the elements are compared in Figure 2 as a function of the irradiation time. It may be seen that even though the elements are rapidly converted to a ClF_3–O_2 mixture, a much longer induction period occurs when starting with a ClF_3–O_2 mixture and about four times more ClF_3O forms from the elements during a 6-hr experiment.

TABLE III
PHOTOCHEMICAL FORMATION OF ClF_3O FROM ClF_3 AND O_2[a] AT −60°

Expt no.	Reaction time, min	Products,[b] cm³		% ClF_3 converted to ClF_3O	% ClF_3 recovered as ClF_3
		ClF_3O	ClF_3		
1	60	0	29.4	0	98
2	90	1.3	32.5	3.9	97
3	180	3.2	29.1	9.6	87
4	360	6.6	25.3	20.8	79

[a] $ClF_3:O_2$ ratios of about 1:10 were used in all experiments with the total amount of gas being about 340 cm³ and the total pressure being about 670 mm (*i.e.*, approximately 31 cm³ of ClF_3 and 310 cm³ of O_2). [b] Remainder of products were ClF, F_2, and O_2. These were not measured.

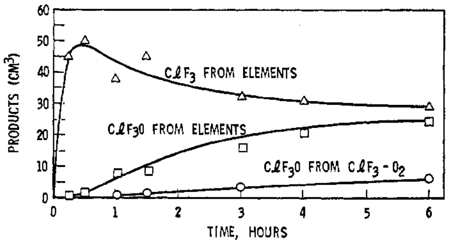

Figure 2.—Photochemical conversion as a function of irradiation time at −60°.

Attempted Synthesis of BrF_5O.—Mixtures of BrF_5 and O_2 (mole ratio of 1:9), after exposure to uv irradiation for 1 to 3 hr at −40 to −60°, consisted exclusively of the unchanged starting materials. Similarly, the photolysis of BrF_5–F_2 mixtures (mole ratio of 1:9) did not result in the formation of any novel compound, such as BrF_7. The unreacted BrF_5 was quantitatively recovered after completion of the experiment.

Discussion

The results obtained in this study demonstrate that uv photolysis constitutes a convenient high-yield synthesis for ClF_3O. The starting materials used for the photolysis reactions are quite different from those used in the chemical syntheses.[3] They are more readily available and safer to handle than $ClONO_2$ or the shock-sensitive[3] Cl_2O.

A wide choice of starting materials exists for the photochemical synthesis of ClF_3O. It appears that the photolysis of almost any system capable of producing active oxygen and either ClF, ClF_3, or ClF_5 will produce ClF_3O. Thus, ClF_3O has been prepared from any of the following reaction systems: Cl_2–F_2–O_2, ClF_3–O_2, ClO_2F–ClF_5, ClO_3F–ClF_5, ClO_3F–F_2, and ClF–IF_5O. It may be seen from the data in Tables I, II, and III that starting with the elements or the ClF_3–O_2 mixture results in better yields of ClF_3O but the halogen oxyfluorides give much faster rates of formation of ClF_3O (in cm³/hr). The failure to observe ClF_3O in the ClF–O_2 system (expt 6, Table I) is most likely due to the short reaction time (60 min). Thus, a 1-hr initiation period was required for the ClF_3–O_2 system (expt 1, Table III) before any ClF_3O could be detected in the products. The number of possible reaction systems has recently been further extended by the independent work of Bougon, *et al.*[5] The latter authors reported the preparation of ClF_3O by photolysis of the ClF_3–OF_2 system.

When considering the results obtained in the present investigation, it should be noted that some of the reactants and products were present in quantities which caused their partial condensation on the reactor walls. The vapor pressure data presented in Table IV indicate the amount of each species which will remain uncondensed at −40 and −60° and thus can participate in the photochemical reaction. It can be seen, for example, that at −60° most of the ClF_3O condenses and, hence, is not subject to decomposition by the irradiation. These vapor pressure considerations might also explain why ClF_3O photolyzes more rapidly at −40 than at −60° (expt 7 and 8 of Table I) and why ClO_3F photolyzes faster than ClF_3O (expt 5 and 8 of Table I).

TABLE IV
VAPOR PRESSURE AND CALCULATED MAXIMUM VOLUME OF VAPOR IN REACTOR

	Vapor pressure, mm		Vapor volume, cm³ at STP[f]	
	−40°	−60°	−40°	−60°
ClF_3O[a]	22	5	13.1	3.3
Cl_2[b]	>400	>100	>230	>65
ClF_5[c]	220	72	131	47
ClF_3[b]	47	10	28	7
ClF[b]	>760	>760	>490	>450
ClO_3F[d]	1000	398	597	260
ClO_2F[e]	143	37	91	23

[a] Reference 3. [b] D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947). [c] Reference 7. [d] R. L. Jarry, *J. Phys. Chem.*, **61**, 498 (1957). [e] H. Schmitz and H. J. Schumacher, *Z. Anorg. Allg. Chem.*, **249**, 238 (1942). [f] In 388-cm³ reactor, assuming ideal vapor pressure.

The most convenient and practical reaction system for the photochemical synthesis of ClF_3O is obviously the one starting from the elements Cl_2, F_2, and O_2. As can be seen from Table II and Figure 2, the synthesis of ClF_3O from the elements produces ClF_3 at a rapid rate during the first half-hour with yields around 90%. This implies that the synthesis of ClF_3O from the elements is closely related to that starting from ClF_3 and O_2, although the different rates and the existence of a 1-hr initiation period for the ClF_3–O_2 system are unexpected. The purpose of the present study was not to study the kinetics of any particular reaction, but rather to screen different reaction systems for their potential as a practical synthesis of ClF_3O. An independent, detailed kinetic study of these systems is in progress in our laboratory and will be published at a later time.[14] Consequently, the discussion of the possi-

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(14) A. Axworthy and K. Mueller, unpublished results.

ble reaction mechanisms will be limited in this paper to the most apparent aspects.

The selection of reaction temperatures below −25° is beneficial for the synthesis of ClF_3O. At reaction temperatures of −40° and below, the vapor pressure of ClF_3O is quite low, thus minimizing its photolytic decomposition according to

$$ClF_3O \xrightarrow{h\nu} ClF_3 + {}^1/_2O_2$$

This decomposition path has been noted also during its pyrolysis and is consistent with the observation (expt 1, Table I) that at 15° no ClF_3O is formed from a system capable of producing it at a lower temperature.

The photolysis of either ClO_2F or ClO_3F in the presence of F_2 or ClF_5 gave ClF_3O in high yields. The observed (expt 5, Table I) degradation of ClO_3F to ClF, ClO_2F, and O_2 indicates a stepwise decomposition of ClO_3F, according to

$$ClO_3F \longrightarrow ClO_2F + {}^1/_2O_2$$
$$ClO_2F \longrightarrow ClOF + {}^1/_2O_2$$
$$ClOF \longrightarrow ClF + {}^1/_2O_2$$

The following data support this assumption. The decomposition of ClO_3F yields a substantial amount of ClO_2F, while the oxygenation of ClF to ClO_2F (expt 6, Table I) is very inefficient. Thus, the product of the first decomposition step of ClO_3F should be ClO_2F.

Some indications concerning the nature of the key intermediates were obtained from experiments involving the use of various filters during uv irradiation (Table II). The insertion of a Vycor filter (10% transmittance at 2250 Å) precluded the formation of ClF_3O from the elements. This result suggested the importance of oxygen activation in the "fixation" step. This assumption was substantiated by passing O_2 between the lamp and the cell, which vastly decreased the ClF_3O yield (compare expt 5 and 10, Table II).

Having thus established the importance of oxygen activation, it would be tempting to propose the combination of ClF_3 with an oxygen atom to form ClF_3O. This, however, appears unlikely since the rate of formation of ClF_3O from ClF_3 and O_2 is much slower, particularly during the initial stages of the reaction, than the rate of formation from Cl_2, F_2, and O_2 (see Figure 2). It has been noted (expt 9, Table I) that ClF_3 slowly generates ClF upon uv irradiation and it is possible that ClF, and not ClF_3, combines with O. The suggested reaction sequence would be

$$ClF_3 \rightleftarrows ClF + F_2$$
$${}^1/_2O_2 \longrightarrow O$$
$$ClF + O \rightleftarrows ClOF$$
$$ClOF + F_2 \longrightarrow ClF_3O$$

The unknown compound, ClOF, would be a plausible intermediate for both the oxygenation of ClF_3 and the deoxygenation of ClO_2F or ClO_3F (see above).

In the ClO_3F- and ClO_2F-containing systems, the postulated ClOF intermediate might be formed in two different ways: (1) by direct deoxygenation of ClO_2F or ClO_3F, and (2) by recombination of ClF with atomic oxygen. If (2) were the preferred reaction path, the rate of ClF_3O formation should be comparable for both the ClF_3–O_2 and the ClO_3F–F_2 systems, since both ClO_3F and ClF_3, upon photolysis, yield ClF at comparable rates (expt 5 and 9, Table I). However, this is not the case. The rate of ClF_3O formation for the ClO_3F–F_2 system is much higher than that found for the ClF_3–O_2 system. Therefore, it appears that at least some of the unstable ClOF intermediate must be fixed by fluorine during the deoxygenation of ClOF or ClO_2F. Attempts were unsuccessful to extend the above described technique toward the syntheses of the yet unknown molecules, BrF_5O and BrF_7.

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