PHOTOCHEMISTRY OF INTERHALOGEN COMPOUNDS

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Dedicated to the memory of the late Prof. Hans J. Schumacher on the occasion of his 100th birthday

Abstract

The chemical kinetics of the UV-photochemical formations of ClF, ClF_3 and ClF_3O were studied. Unfiltered radiation from a 450-watt UV lamp and a dual-temperature reactor were used allowing periodic analysis of the reaction mixture by gas chromatography. Most of the effort was devoted to the formation of ClF_3O from either ClF_3 / O_2 or the elements to obtain information relating to the optimum conditions and to the reaction mechanisms involved. The rate of ClF_3O formation was the same for both reactant systems. The rate was found to increase with oxygen concentration and to be independent of the irradiation time. It was also shown to be proportional to the intensity of the 184.7 nm band of the Hg spectrum, indicating that the dissociation of O_2 to two ground-state, ^3P, oxygen atoms is the primary photochemical process. The following mechanism is proposed which requires the photochemical dissociation of ClF_3 as well

$$O_2 + h\nu\,(184.7\ \text{nm}) \rightarrow O + O$$
$$ClF_3 + h\nu\,(200\ \text{to}\ 350\ \text{nm}) \rightarrow ClF_2 + F$$
$$O + ClF_2 \rightarrow ClF_2O$$
$$ClF_2O + F_2 \rightarrow ClF_3O + F$$

The photolysis of ClF_3 was investigated under similar conditions. A photochemical steady state was quickly achieved where $(F_2) = (ClF) = \alpha(ClF_3)$. The value of α is about 1 at low pressures and about 3 at high pressures. A mechanism that accounts for these results is proposed. At a wavelength of 365 nm, the quantum yield of the reaction $ClF + F_2 + h\nu \rightarrow ClF_3$ was found to be about 1 and that of the reaction $Cl_2 + F_2 + h\nu \rightarrow 2\ ClF$ to be considerably less than 1. The latter result is quite interesting because Cl_2 and F_2 are expected to undergo a chain reaction. The magnitudes of the quantum yields determined for the formations of ClF_3 and ClF have been verified in the independent investigations of H. J. Schumacher and coworkers.

Resumen

Se estudió en el ultravioleta la cinética de la reacción fotoquímica de formación de ClF, ClF_3 y ClF_3O. Se usó radiación de una lámpara ultravioleta de 450 watts y un reactor de temperatura dual para permitir el análisis periódico de la mezcla de reacción por cromatografía gaseosa. La mayor parte del esfuerzo se dedicó a obtener información sobre la formación de ClF_3O, ya sea a partir de mezclas de ClF_3 con O_2 o de sus elementos, con respecto a las condiciones óptimas y al mecanismo de reacción. La velocidad de formación de ClF_3O fue la misma en ambos sistemas. Se encontró que la velocidad aumenta con la concentración de oxígeno y es independiente del tiempo de irradiación. También se demostró que la velocidad es proporcional a la intensidad de la banda de 184,7 nm del espectro del Hg, lo que indica que el proceso fotoquímico primario consiste en la disociación del O_2 en dos átomos de oxígeno en estado fundamental ^3P. Se propone el mecanismo siguiente que requiere también la disociación fotoquímica del ClF_3.

$$O_2 + h\nu\ (184.7\ nm) \rightarrow O + O$$
$$ClF_3 + h\nu\ (200\ to\ 350\ nm) \rightarrow ClF_2 + F$$
$$O + ClF_2 \rightarrow ClF_2O$$
$$ClF_2O + F_2 \rightarrow ClF_3O + F$$

Se investigó la fotólisis de ClF_3 en condiciones similares. Fotoquímicamente se alcanza rápido el estado estacionario para el cual $(F_2) = (ClF) = \alpha\ (ClF_3)$. El valor de α es aproximadamente 1 a bajas presiones y aproximadamente 3 a altas presiones. Se propone un mecanismo que interpreta estos resultados. Se encontró que a la longitud de onda de 365 nm, la eficiencia cuántica de la reacción $ClF + F_2 + h\nu \rightarrow ClF_3$ es aproximadamente 1 y que la de la reacción $Cl_2 + F_2 + h\nu \rightarrow 2\ ClF$ es considerablemente menor que 1. El último resultado es muy interesante debido a que se espera que Cl_2 y F_2 experimenten una reacción en cadena. La magnitud de las eficiencias cuánticas determinadas para las formaciones de ClF_3 y de ClF se han verificado en investigaciones independientes de H. J. Schumacher y colaboradores.

Historical note

Chlorine fluorides and fluoride oxides are of significant interest as earth-storable oxidizers in high-performance liquid bi-propellant systems. As such, they were intensively studied in the nineteen-sixties and early nineteen-seventies for missile propulsion during the cold war and the race for the moon. The two highest performing oxidizers were ClF_5 for carbon-free fuels, such as hydrazine, and ClF_3O for fuels containing some carbon, such as monomethylhydrazine. Both, ClF_5 [1] and ClF_3O [2] were discovered and produced on a plant and pilot plant scale, respectively, at Rocketdyne. Because the pilot plant process used for the production of ClF_3O, involving the low-temperature fluorination of shock sensitive $ClONO_2$ with elemental fluorine [2], was dangerous and resulted in severe damage to Rocketdyne's pilot plant, safer processes, based on the photolytic reactions of either ClF_3 or its precursors with oxygen, were studied at Rocketdyne [3]. The kinetics of these reactions was investigated in more detail from 1970 to 1972 by Richard Wilson and the late Dr. Art Axworthy, but the results were never published. These studies were closely connected to the work and life-long research interests of the late Prof. H. J. Schumacher in Argentina, and many helpful discussions were held with Prof. Schumacher during this time period. When Dr. Carlos J. Cobos approached us to contribute a paper to a special issue of the Journal of the Argentine Chemical Society, commemorating the 100th Anniversary of Prof. Schumacher,

we could not think of any work which could have been closer to his interests and in which he also played an important role as an advisor.

Introduction

Chlorine trifluoride oxide, ClF_3O, was first prepared at Rocketdyne in 1965 by Pilipovich and Wilson [2]. The structure, properties, reaction chemistry, and methods of preparation of ClF_3O have since been investigated in detail [2-8]. A number of methods for the photochemical formation of ClF_3O using UV irradiation have been investigated [3,7,8]. These included the "deoxygenation" of the oxyfluorides $FC1O_2$ and $FClO_3$, the addition of oxygen to ClF_3, and the direct synthesis from the elements, Cl_2, F_2, and O_2 [3]. In addition, Bougon et al. [7] and Zuechner and Glemser [8] independently discovered ClF_3O when exposing a mixture of ClF_3 and OF_2 to UV irradiation. Although there are certain practical limitations on the large-scale preparation of materials by photochemical methods, the photochemical synthesis of ClF_3O is of interest as a non-hazardous route to ClF_3O.

In the previous study [3], the photochemical formation of ClF_3O from chlorine oxyfluorides was much faster (up to 29 cc/hr) than those from ClF_3 -O_2 (1 cc/hr) or from $C1_2$-F_2 -O_2 (4 cc/hr). However, the latter two systems would be the most convenient and practical. The photochemical formation of ClF_3O occurred only at reactor temperatures below about -40°C. This requirement for low temperature was attributed to rapid photochemical decomposition of ClF_3O that would occur unless most of it would condense on the cold wall of the reactor as it formed. It was possible, however, that the lower temperatures favored the reaction steps leading to ClF_3O over those forming ClF_3 and O_2. The rate of formation of ClF_3O was reduced drastically when the lamp housing was purged with oxygen (reducing the intensity of the Hg lines that are absorbed by oxygen before the light enters the reactor), and ClF_3O did not form at all when a Vycor or Pyrex filter was placed around the Hg lamp. Another feature of these reactions is their very small overall quantum yield. A 450-watt Hg lamp had to be placed within about 1 inch of the reactor window to obtain slow rates of ClF_3O formation. Perhaps the most unusual feature of this photochemical reaction [3] was that the rate of formation of ClF_3O from the elements was faster by a factor of about 4 than from a ClF_3-O_2 mixture under similar conditions (-60°C, 600 torr O_2). There is no obvious explanation for this observation because it was found that a mixture of the elements was converted almost quantitatively to ClF_3 and O_2 within about 30 minutes after irradiation was initiated. Also, the ClF_3 -O_2 system showed an apparent induction period of 1 hr, whereas the $C1_2$-F_2-O_2 system did not.

It is apparent from the above discussion that the photochemical formation of ClF_3O was of interest from both a theoretical and a practical point of view. Additional kinetic data for the reactions

$$2\ ClF_3 + O_2 + h\nu \rightarrow 2\ ClF_3O \qquad (1)$$

and

$$C1_2 + 3\ F_2 + O_2 + h\nu \rightarrow 2\ ClF_3O \qquad (2)$$

were obtained during this study, using improved experimental techniques. The goals of this

investigation were: (1) to gain further insight into the chemistry involved and (2) to obtain information that would be required for the photochemical production of ClF_3O (e.g., effects of O_2 concentration and irradiation zone temperature, and methods of reducing the induction period in the ClF_3-O_2 reaction). An ambient temperature reactor with a cooled condensing tip was used. The contents of the reactor were periodically sampled using a sensitive gas chromatographic (GC) technique. The following photochemical reactions were also investigated as a part of this program:

$$F_2 + Cl_2 + h\nu \rightarrow 2\ ClF \qquad (3)$$

$$F_2 + ClF + h\nu \rightarrow ClF_3 \qquad (4)$$

conditions. A large quantum yield would be in agreement with a These reactions were of interest because they occur in the early stages of the photochemical formation of ClF_3O from the elements. The thermal reaction between F_2 and Cl_2 ($F_2 + Cl_2 \rightarrow 2\ ClF$) had been studied previously [9], and a long-chain mechanism had been proposed. It was of interest to examine this mechanism under photochemical chain mechanism.

Krieger and Schumacher [10] reported in 1966 that the photochemical formation of ClF_5

$$F_2 + ClF_3 + h\nu \rightarrow ClF_5 \qquad (5)$$

gave quantum yields of up to 0.5. They proposed a mechanism in which the resulting ClF_5* activated complex reacts via three competing paths: $ClF_5^* \rightarrow ClF_4 + F$, $ClF_5^* + ClF_3 \rightarrow 2\ ClF_4$, and $ClF_5^* + M \rightarrow ClF_5$. A complex as large as ClF_5* would be expected to have a long enough life time that the first of these processes should not be important [11]. In any event, the photochemical formation of ClF_3 (Reaction 4) should involve an analogous mechanism with the reaction $ClF_3^* \rightarrow ClF_2 + F$ being relatively more important than would be $ClF_5^* \rightarrow ClF_4 + F$ in Reaction 5 (because of the fewer vibrational modes in ClF_3*). In addition, other reactions, such as

$$ClF_2 + F_2 \rightarrow ClF_3 + F \qquad (6)$$

might be expected to occur. Reaction 6 could lead to a chain reaction and quantum yields of greater than one for Reaction 4.

Experimental

Chlorine pentafluoride (Rocketdyne) was purified by treatment with anhydrous CsF for removal of any ClF_3, followed by fractional condensation through traps at -112 and -126°C. The material retained in the -126°C trap was used. Chlorine (The Matheson Co.) was purified by fractional condensation through traps kept at -142 and -196°C, using the -142°C fraction. Fluorine (Rocketdyne) was passed over NaF to remove HF. Chlorine trifluoride (The Matheson Co.) was purified by fractional condensation in a trap kept at -95°C. Chlorine monofluoride was prepared by heating an equivalent mixture of Cl_2 and ClF_3 to 150°C for several hours in a stainless-steel cylinder. The ClF was purified by fractional condensation through traps kept at -142 and -196°C using the material retained in the -196°C fraction. Chloryl fluoride (for GC

calibration) was prepared from $KC1O_3$ and ClF_3 by the method of Christe [12]. ClF_3O was prepared by fluorination of $ClONO_2$ [2]. All materials were handled in a 304 stainless-steel vacuum line [13] equipped with Teflon FEP U-traps and 316 stainless-steel bellows-seal valves (Hoke, Inc., 4251 F4Y). The system was well passivated with ClF_3.

The reactor was similar to that used previously to synthesize ClF_3O photochemically [3] but incorporated numerous improvements. It had both a front and rear sapphire window. A large "cold finger" was attached permitting the reactants and products to be condensed out even when the irradiation zone was at ambient temperature. In addition, a gas chromatographic method was employed for periodically analyzing the contents of the reactor during a given experiment. Pressures were measured with a Heise Bourdon tube gage (0 to 1500 torr, ± 0.1 percent) and a Wallace-Tiernan Bourdon tube gage (Model FA-145, 0 to 800 torr, 1 -torr divisions, accuracy of 1 part in 1000).

All photochemical studies were carried out in a 9 -cm, i.d., cylindrical stainless-steel reactor with a 7.6 -cm optical path. The front and rear windows were made of 3.2mm thick optical-grade sapphire. These -10cm-diameter windows were attached to the cell with Teflon O-rings and machined flanges. A closed end tube extending down from the bottom of the cell was 9-cm long and about 2.5-cm inside diameter. Copper coolant coils were brazed to the bottom 5 cm of this finger so that it could be cooled to condense the reactants and products. Similar coils were brazed to the main body of the cell so that water could be circulated to maintain the cell at about 20°C while the condensing tip was held at -60°C. Methanol was pumped rapidly through the lower set of coils in a closed loop, and the temperature of the tip was controlled by passing most of the coolant stream through a coil held at -80°C and the remainder through a coil held at near ambient temperature. The minimum "cold finger" temperature was taken as the temperature of the cold methanol.

The cell was connected to the vacuum line with a short section of 6.4-mm tubing that was also attached to the small internal volume Wallace-Tiernan gage for monitoring of the cell pressure. A small 1.5-mm-ID tube passed through the reactor wall and extended about 1 cm into the reactor so that representative GC samples could be withdrawn for analysis. The volume of the cylindrical portion of the reactor was 475 cc and the volume of the condensing tip was 60 cc. The gage and connecting line volumes totaled 40 cc.

All experiments were conducted using a Hanovia high-pressure Hg lamp, No. 679-A-36 (power input 450 W). According to the manufacturer's specifications, the spectral energy distribution of the radiated Hg lines included 296.7 nm, 4.3 watt; 265.2 nm, 4.0 watt; 253.7 nm, 5.8 watt; 248.2 nm, 2.3 watt; 238.0 nm, 2.3 watt; and 222.4 nm, 3.7 watt. In addition, this lamp emitted lines of shorter wavelengths down to about 170 nm (quartz limit). The lamp was cylindrical, the diameter of the quartz envelope being 2.8 cm.

In the experiments relating to the photochemical formation of ClF_3O, a very high light intensity was required and the lamp was placed with its centerline only 4.2 cm from the front window of the cell. The lamp was mounted in a metal housing that fitted over the front window of the cell and contained a sliding metal shutter to block the light during warm-up of the lamp. The housing was purged with dry nitrogen to cool the window and the lamp and to exclude atmospheric oxygen that has been shown to absorb wavelengths that are required for this reaction. The time-average light intensity was held constant by monitoring and controlling the current to the Hg lamp.

The experiments relating to the photochemical reactions of Cl_2 and ClF with F_2 were conducted with light of much lower intensity and only the 365-nm Hg band was used. The centerline of the lamp was placed 16 cm from the cell window and a Wratten 18A filter was used to isolate the 365-nm band. The filter was mounted between two Pyrex cells with optical path lengths of 1 cm through which cooling water was circulated. The intensity of the light reaching the reactor was determined by actinometer experiments in which the rate of photolysis of OF_2 was measured by following the pressure change associated with the reaction $OF_2 + h\nu \rightarrow F_2 + 0.5\ O_2$. Gatti, Staricco, Sicre, and Schumacher [14] have shown that this reaction has a quantum yield of 1.0 under these conditions.

A third lamp arrangement was made possible by the use of a special adapter flange. This placed a third sapphire window in front of the front window of the main reactor giving a sealed gas cell with an optical path of 2.5 cm. Gases could be flowed through this cell to absorb selected wavelengths before the light reached the reactor (a "gas filter"). This configuration required the lamp to be moved back this additional distance, resulting in a much reduced rate of ClF_3O formation, even when only N_2 was present in the filter cell.

The gas chromatographic system was a custom-built apparatus designed to handle highly reactive and corrosive materials [15]. A 20-foot, 3/16-inch, o.d., stainless-steel, specially prepared column containing 50-percent halocarbon oil No. 4-11V on Kel-F 300, 70-80 mesh, was employed. This column separated all species of interest at 25°C, except O_2, F_2 and N_2 which eluted as a common initial peak. The column was wrapped in aluminum foil. The detector was a Gow-Mac thermoconductivity cell, Model 9285, with a conventional Wheatstone bridge electrical circuit. The detector block and filaments were made of nickel. Helium was used as the carrier gas. Before entering the system, the helium was passed through a 3/8-inch, stainless-steel U-trap maintained at -80°C to remove water vapor. The pressure before entering the column was 20 psi maintained by throttling a Hoke needle valve. The helium exit flow was 36.9 cc/min. The inlet system utilized a Beckman two-way gas sampling valve which was lubricated with halocarbon oil 13-21. The sampling loops were replaced by two stainless-steel U-tubes of 5.3- and 10-cc volume. The Beckman gas sampling valve was attached to the vacuum system and the reactor (through low-volume 1/16inch, i.d., tubing) using 1/8-inch, stainless-steel Hoke valves with V-stems and Teflon packings. The retention times were 2.8, 3.9, 9.9, 13.2, 15.9, 18.9, and 24.1 minutes for F_2, ClF, $C1_2$, $FClO_2$, ClF_3, ClF_5, and ClF_3O, respectively. During most of the study, the electrometer output was recorded linearly on a Speedomax G recorder and the peaks were integrated with a planimeter. After most of the photochemical studies were completed, a Hewlett-Packard integrator, Model 3371B, was added to the system to give automatic peak integration. The output from the integrator was fed to a time-share computer terminal where the peak areas and retention times were printed and could be punched on tape for machine processing. Calibration factors were obtained for F_2, ClF, Cl_2, $FC1O_2$, ClF_3, ClF_5, and ClF_3O over a partial pressure range of from 100 to 200 torr down to about 0.5 torr or less and were found to be independent of sample pressure.

In the studies of ClF_3O formation, the reactor tip was held at about -60°C to maintain the ClF_3 at its vapor pressure of about 10 torr and to condense most of the ClF_3O as it formed. When studying the reaction $F_2 + ClF + h\nu \rightarrow ClF_3$, the tip was cooled with a slush bath (before the coils were installed on the reactor) to condense the ClF_3 as it formed. The reaction $F_2 + Cl_2 + h\nu \rightarrow 2\ ClF$ was studied with the entire cell at 20°C.

With the cell and cold finger at ambient temperature, the evacuated cell, after passivation with ClF_3, was filled to the desired pressure with freshly purified ClF_3. A sample of the ClF_3 was taken from the reactor for GC-analysis to verify its purity. The cell was then charged with O_2 to the desired pressure. The ClF_3 and O_2 were allowed to mix at ambient temperature for 20 min at which time a second sample was taken for GC-analysis. Cooling of the cold finger was then initiated and when the desired temperature of -60°C was obtained, the lamp was turned on to warm up. When the lamp reached full power as determined by the volt-meter in the power source circuit, the shutter was removed and the reaction initiated. GC samples were taken at various time intervals throughout each experiment. Samples were taken at ambient temperature, which meant interruption of the UV irradiation and the warm-up of the cold finger to ambient before sampling. After removal of the sample, the cell was re-cooled, and after reaching the desired temperature and waiting long enough for the system to equilibrate, irradiation was restarted. Occasionally, samples were taken with the UV lamp on and the cold finger at -60°C to determine the composition of the gas in the cell during irradiation.

Before each sample was removed from the cell for analysis, sufficient sample was drawn through the sampling system and discarded to purge the sampling line and valves. Less than 5 cc of the sample at reactor pressure was required for this. Therefore, the smallest amount of sample required for analysis (using the smaller loop) was 10 to 15 cc of gas or about 2 to 3 percent of the sample in the cell. In most of the experiments, however, the large loop was employed with the first filling of the loop being discarded. This procedure used about 7 percent of the contents of the cell per analysis. The pressure in the reactor and the GC loop were measured on the Wallace-Tiernan gage before the sample was introduced into the column.

When ClF_3O was prepared from the elements, the procedure was identical except that Cl_2 was condensed into the cell and then the F_2 and O_2 were introduced.

Results and Discussion

Formation of ClF_3O from ClF_3 and O_2: The previous study [3] of the photochemical formation of ClF_3O from ClF_3 and O_2 indicated an induction period for this reaction and a rate (effective quantum yield) that is smaller than the rate of ClF_3O formation from the elements. It was postulated that the observed induction period might result from the time required for some of the ClF_3 to decompose to F_2 and ClF. That is, that F_2 or ClF might be catalysts for the photochemical formation of ClF_3O (large amounts of ClF form within the first 5 to 10 minutes from the elements at this high light intensity). For this reason, the photolysis of ClF_3 was investigated under these, for photochemical studies somewhat unusual, conditions of very high light intensity and full spectral output of the Hg lamp.

Photolysis of ClF_3: Because the previous method of synthesizing ClF_3O from ClF_3 and O_2 involved cooling the photochemical reactor to -60°C, resulting in the ClF_3 concentration being fixed at its vapor pressure (about 10 torr at this temperature), the present investigation was conducted with the reactor at 20°C and the condensing tip at a nominal -60°C. When ClF_3 vapor alone is irradiated, the only observed products are F_2 and ClF in approximately equal quantities, in addition to ClF_3 at its vapor pressure. The rate of formation of ClF and F_2 is initially very rapid (>l torr per minute), but the concentrations appear to approach a photochemical

steady state with a half-time to steady state of about 20 minutes (Fig. 1). At the low-pressure steady state, $(ClF)_{ss} = (F_2)_{ss} = 3\ (ClF_3)_{ss}$.

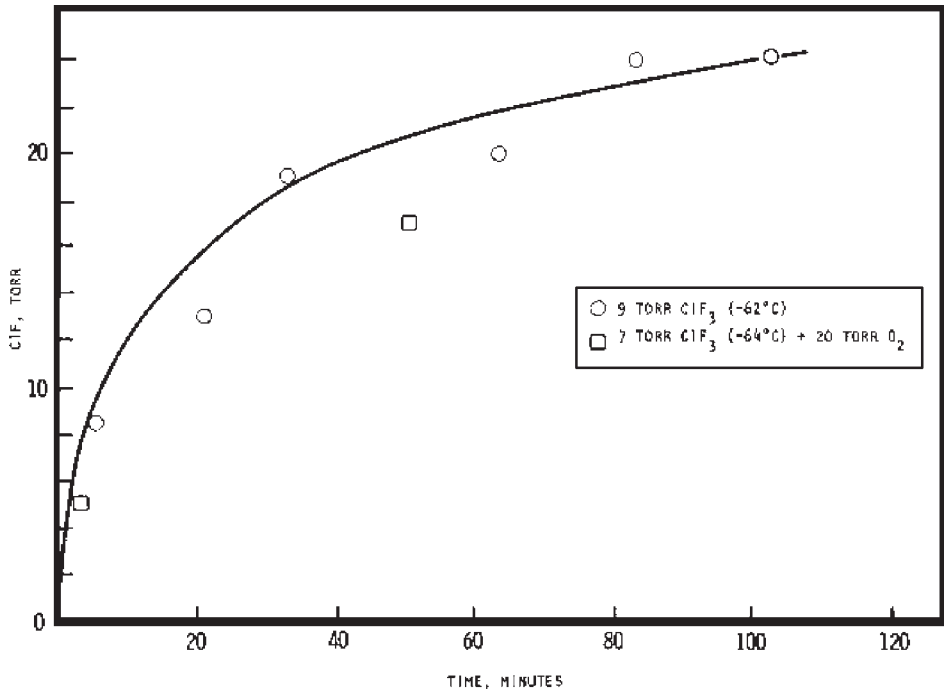


Fig. 1*.Rate of formation of ClF from the photolysis of ClF_3 at low total pressure (irradiation zone at 20°C, condensing tip at -64°C).*

When similar ClF_3 photolysis experiments were conducted with either N_2 or O_2 added at high partial pressures, the ClF formation rates shown in Fig. 2 were obtained. When O_2 was present at a high concentration, ClF_3O was also formed at a rate of about 1 torr per hour, which will be discussed below. The ratio (ClF) ss /(ClF_3) ss is decreased at these pressures to a value of about one, and the half-time to steady state is also decreased by a factor of three to about 6 minutes. This indicates that, as might be expected, the primary photochemical process in the photolysis of ClF_3 is not pressure-dependent but the rates of certain of the reverse processes controlling the position of the photochemical steady state increase with pressure.

Figure 3 shows that when the gas filter cell was installed in front of the reactor, the ClF concentration at steady state was decreased by about a factor of two, but the half-times to steady state are about the same. This would be in agreement with a simplified model in which the rate of photochemical dissociation of ClF_3 decreases by a factor of two (because the lamp was moved back) and the rate constants for the reverse reactions of ClF do not change [16]. It will be seen that these results generally fit a mechanism that is proposed for the photolysis of ClF_3 in which the forward reaction is photochemical but the back reactions (to reform ClF_3) are mainly dark reactions.

The rate of ClF formation from ClF_3 was the same whether the gas filter contained O_2 or N_2 at atmospheric pressure (Fig. 3). This is, no doubt, because O_2 absorbs strongly only at very

short wavelengths where the output of the lamp is small, while ClF_3 absorbs strongly at longer wavelengths where O_2 does not compete.

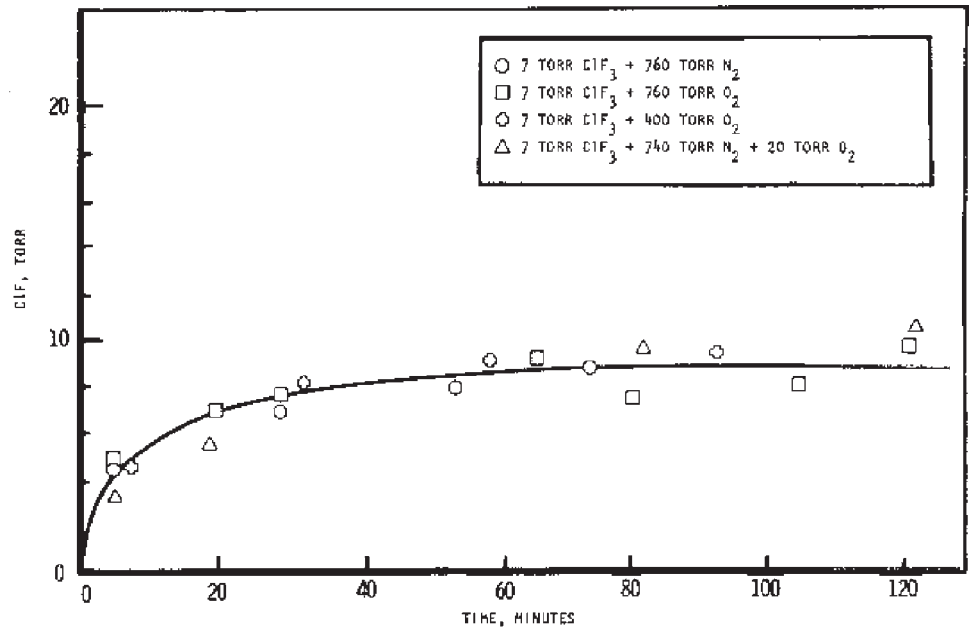


Fig. 2. *Rate of formation of ClF from the photolysis of ClF_3 at high total pressures.*

Absorption Spectra: The UV absorption spectra of species of interest to the program are plotted in Fig. 4. The reported absorption spectrum of ClF_3O [3] is similar to that shown here for ClF_3. The curve for F_2 and the (smoothed) curve for O_2 were taken from the literature. The long wavelength curve for ClF_3 represents the results of Schmitz and Schumacher [17]. The spectra for ClF and for ClF_3 at shorter wavelengths were measured by us. The ClF results [18] are in agreement with a spectrum determined previously in this laboratory [3], and the position of the maxima is in agreement with Schmitz and Schumacher [19]. The curves for ClF and ClF_3 are extended to the absorption values at 365 nm reported by San Roman and Schumacher [20].

Mechanism of ClF_3 Photolysis: San Roman and Schumacher [20] have established that when a mixture of F_2, ClF, and ClF_3 is irradiated with monochromatic light at a wavelength of 365 nm, a steady state is not reached, but rather the formation of ClF_3 goes to completion with a quantum yield of one. Their proposed mechanism includes:

$$F_2 + h\nu \rightarrow 2\ F \qquad (9)$$

$$F + ClF + M \rightarrow ClF_2 + M \qquad (10)$$

$$F + ClF_2 + M \rightarrow ClF_3 + M \qquad (11)$$

or

$$ClF_2 + ClF_2 \rightarrow ClF_3 + ClF \qquad (12)$$

before the steady state is reached. Decomposition of ClF_3 would not be expected during its photolysis at 365 nm. It should also be noted that the In the full spectrum irradiation of ClF_3, ClF_3 is the strongest absorber at the shorter light intensity is much greater in our experiments than in those of San Roman and Schumacher [20]. wavelengths. This can account for the formation of large concentrations of CIF and F_2.

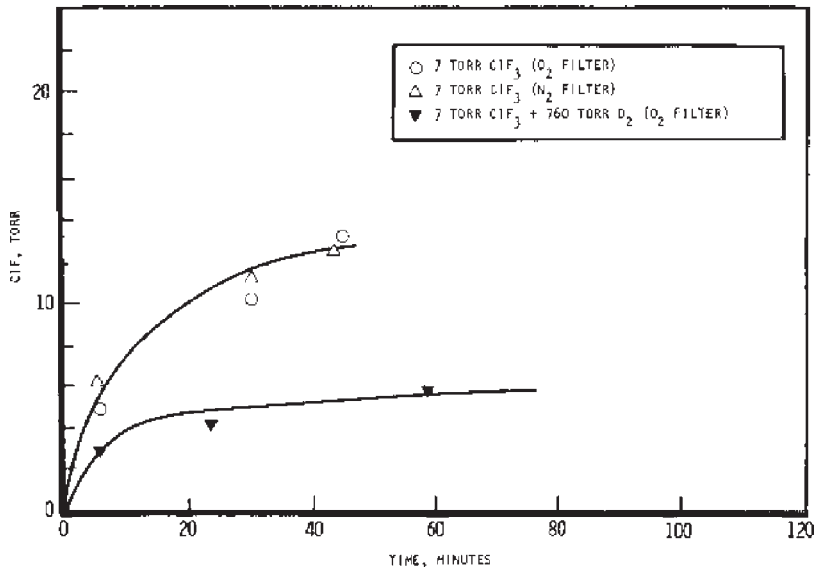


***Fig. 3**. Effect of gas filter on the formation of CIF from the photolysis of ClF_3.*

The primary photochemical process in the photolysis or ClF_3 is expected to be:

$$ClF_3 + h\nu \rightarrow ClF_2 + F \qquad (13)$$

However, as pointed out by Krogh and Pimentel [21], there is sufficient energy [22] in quanta of these wavelengths for the ClF_2 formed to dissociate in a concerted mechanism to give:

$$ClF_3 + h\nu \rightarrow ClF + 2\,F \qquad (14)$$

The following dark reactions would be expected to be important in the photolysis of ClF_3:

$$F + ClF + M \rightarrow ClF_2 + M \qquad (10)$$
$$F + ClF_2 + M \rightarrow ClF_3 + M \qquad (11)$$
$$ClF_2 + ClF_2 \rightarrow ClF_3 + ClF \qquad (12)$$
$$F + F + \text{wall} \rightarrow F_2 \qquad (15)$$

The most likely process for the formation of F_2 is (15). The homogeneous recombination of F atoms will not compete with reaction (10).

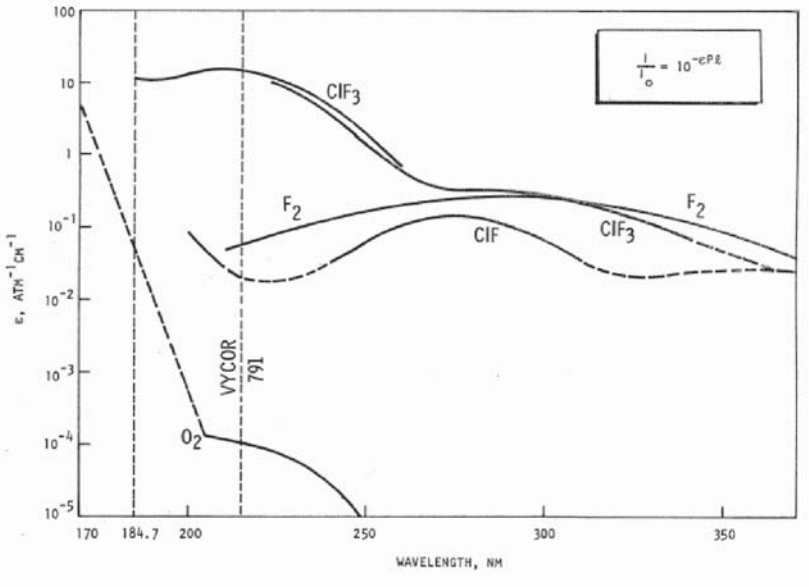


Fig. 4*.UV absorption spectra.*

This proposed mechanism for the photolysis of ClF_3 can account for the decrease in the rate of ClF formation as the ClF concentration increases and for the lower steady-state concentrations of ClF and F_2 at higher total pressures. As the concentration of ClF increases, the rates of Reactions (10) and (11) increase relative to that of (15), leading to a continued decrease in the rate of formation of F_2 and ClF. Thus, a mechanism in which most of the back reaction occurs via dark reactions, is in agreement with the observed results for the photolysis of ClF_3. However, the heterogeneous formation of F_2 can continue at a finite rate at the steady state, and the steady state will be reached when the rates of the reverse photochemical reactions, $F_2 + h\nu \rightarrow 2\ F$ and $ClF + h\nu \rightarrow Cl + F$, followed by $Cl + F_2 \rightarrow ClF + F$, equal the rate of F_2 formation.

Estimates were made of the total amount of light absorbed by the ClF_3. These were based

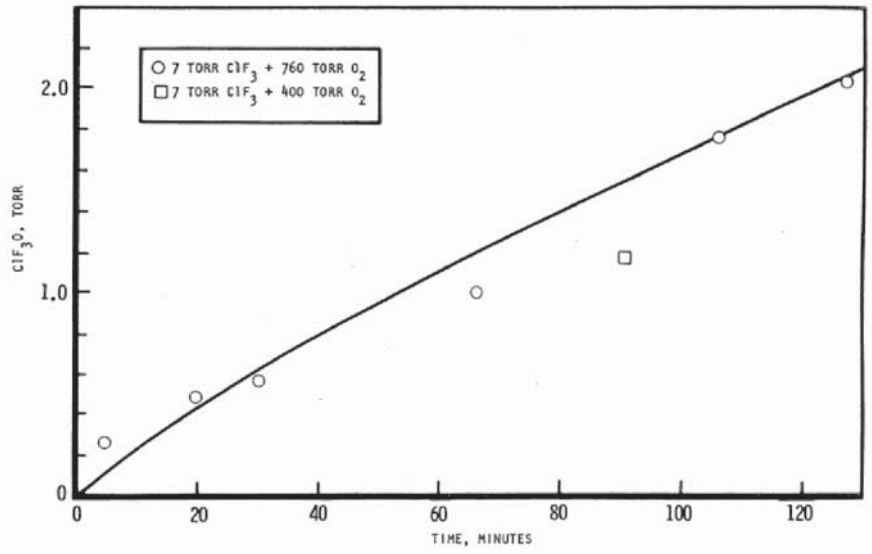


Fig. 5*.Rate of formation of ClF_3O from ClF_3 and O_2 at short reaction times.*

on the spectral output of the lamp, the geometry of the apparatus, and the absorption spectra of ClF_3. It appears that the quantum yield for the photolysis of ClF_3 under these conditions is very small, even in the early stages of the reaction, being on the order of only 0.03.

Kinetics of ClF_3O Formation: In the two high oxygen concentration experiments of Fig. 2, some ClF_3O was also formed. These results are plotted in Fig. 5. At 400 torr O_2, the ClF_3O concentration was measured only in one case, because short GC scans were used at the 2 earlier points for determining only the ClF concentration. Under these conditions (reactor at 20°C, tip at -64°C), the rate of formation of ClF_3O was nearly linear with time and there was no indication of an induction period. In some of the earlier experiments (such as those shown in Fig. 5), a small amount of ClF_3O formed very rapidly during the first 2 or 3 min of irradiation. This was traced to the presence of a similar amount of $FC1O_2$ in the reactor before irradiation was initiated. It was found previously [3] that $FC1O_2$ rapidly forms ClF_3O under conditions, similar to these. In all of the remaining experiments that are reported here, the reactants were purified to the point where no appreciable amount of $FC1O_2$ was present initially.

The observation that ClF_3O can be formed with the irradiation zone at 20°C establishes that the dark reactions leading to ClF_3O are relatively temperature independent (or there are no competing reactions which does not seem likely). Thus, the previous suggestion appears to be valid that cooling of the reactor tip is required to condense out the ClF_3O before it can be decomposed by the light. It is possible, of course, that part of this temperature effect was caused by an actual change in the reaction mechanism at low temperature. The results of the present study show that ClF_3O can be produced, although at a very slow rate, photochemically in an ambient temperature reactor if a method for the rapid removal of the ClF_3O from the irradiation zone is provided as, for example, in a re-circulating reactor.

It was suggested previously that F_2 or ClF might catalyze the photochemical formation of ClF_3O from ClF_3 and O_2 and that the time required for the formation of these species from ClF_3 could account for the induction period of about 1 hour that was observed in that study [3]. However, the results reported above on the photolysis of ClF_3 indicate that these species reach their maximum values in about 15 min at the higher pressures. In addition, the results shown in Fig. 5 indicate that the induction period that was reported was not real but must have resulted from some limitations of the analytical methods employed. In any event, a few ClF_3-O_2 experiments were run with ClF and F_2 added initially. The results obtained were similar to those shown in Fig. 5, indicating that these species either do not affect the rate or are formed rapidly enough that their initial addition does not give an observable effect.

Effect of Oxygen Pressure: A series of carefully controlled photochemical experiments was conducted to determine how oxygen concentration, time, and reactants (ClF_3-O_2 versus $C1_2F_2$ -O_2) affect the rate of ClF_3O formation. The results are shown in Fig. 6. In all of these experiments, the reactor was held at 20°C and the condensing tip at -60 ±1°C. Thus, the partial pressure of ClF_3 remained constant at 10 torr since a tenfold excess of liquid ClF_3 was present.

In all cases, the rate of ClF_3O formation was found to be linear with time with no indication of an appreciable induction period. The rate increased with increasing oxygen pressure. The rate

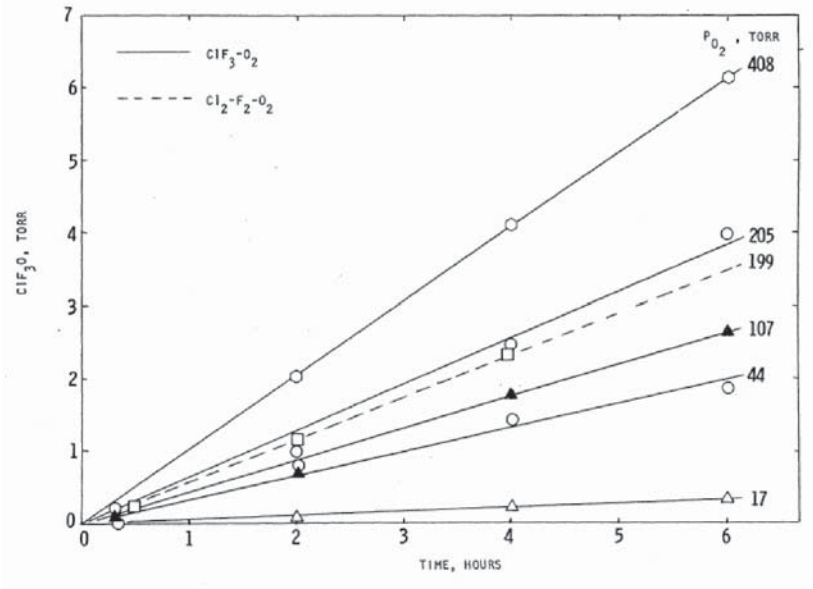


***Fig. 6**.ClF_3O formed as a function of time and oxygen partial pressure (P_{ClF3} = 10 torr).*

of ClF_3O formation (slope in Fig. 6) is plotted as a function of oxygen pressure in Fig. 7. At low oxygen pressures the rate rapidly increases with oxygen pressure but slows down at higher pressures.

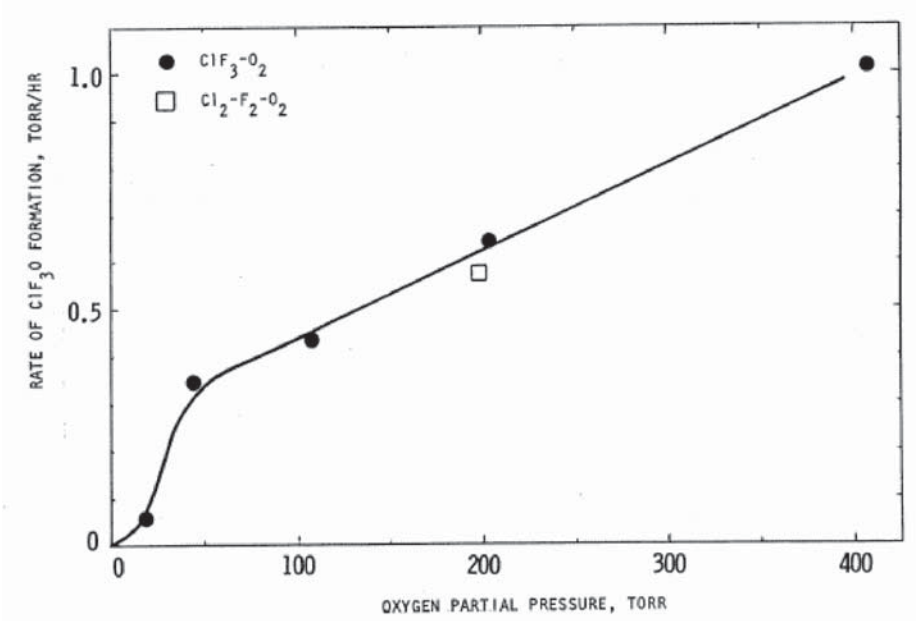


***Fig. 7.**Rate of ClF_3O formation as a function of partial pressure of oxygen (P_{ClF3} = 10 torr).*

Formation of ClF_3O from the Elements: It was found in the previous investigation [3] that when the elements are irradiated under certain conditions, the F_2 and Cl_2 are converted to ClF in a few minutes and most of the ClF is converted to ClF_3 within the first 20 minutes. Thus, starting

with F_2 and Cl_2 in a mole ratio of 3:1 should be nearly equivalent to starting with ClF_3. The ClF_3 condenses at -60°C, as it forms, resulting again in a ClF_3 partial pressure of 10 torr and photochemical steady-state concentrations of F_2 and ClF. Experiments conducted using periodic GC analyses, established that this series of events indeed occurs in the cooled-tip reactor used in this study.

It can be seen from the experiments shown in Fig. 6 and 7 that equivalent results are obtained when starting with either the elements or with the corresponding ClF_3-O_2 mixtures. This is in agreement with the above theoretical considerations but not with the results reported in [3].

Effective Wavelengths: It was shown in [3] that placing a Pyrex or Vycor sleeve around the lamp prevented the formation of ClF_3O from the elements and flowing oxygen between the lamp and the reactor window reduced the rate of ClF_3O formation by about a factor of two. These observations strongly indicated that the photochemical dissociation of O_2 is the initiating process in the formation of ClF_3O. If ClF_3 dissociation were the only required photochemical process, this should occur readily even with the Vycor filter, and the oxygen purge should have no effect (Fig. 4).

Because quartz will transmit the 171 nm Hg band of the lamp, it is possible that excited, ^1D, oxygen atoms might be important in the formation of ClF_3O. At a wavelength of 184.9 nm, O_2 dissociates into two ground-state, ^3P, oxygen atoms. The formation of a ^1D oxygen atom requires a wavelength of 175.9 nm or shorter [23]. It can be seen from Fig. 4 that the absorption coefficient of oxygen [24] is on the order of 0.1 atm^{-1} cm^{-1} at 184.9 nm and is about two orders of magnitude higher at 171 nm. It can be calculated that light of wavelength 184.9 nm has a distance for half absorption in oxygen at atmospheric pressure of about 3 cm while for 171 nm radiation, the distance is only 0.33 mm. Thus, an oxygen purge between the lamp and window [3] would absorb all of the 171 nm band and about one-half of the 184.9 nm radiation. This suggests that the formation of ^3P oxygen atoms from O_2 is the major photochemical process occurring in the formation of ClF_3O from ClF_3-O_2 and Cl_2-F_2-O_2.

This was put on a more quantitative basis by use of the gas filter. To install the filter, it was necessary to move the lamp about 2.8 cm farther from the reactor window. This and the introduction of an extra window in the light path reduced the light intensity. When nitrogen, which is transparent at the wavelengths of interest was passed through the filter cell, the rate of ClF_3O formation from ClF_3-O_2 was 0.175 torr/hr at an oxygen partial pressure of 441 torr. This rate is lower by about a factor of six than would have been obtained without the cell with the lamp in its original position, indicating that the rate is strongly dependent on the light intensity. Passing oxygen through the filter at atmospheric pressure (at a high flow rate to prevent the accumulation of a significant concentration of ozone) reduced the rate of ClF_3O formation by a factor of 1.77 over that obtained with nitrogen. It can be calculated that for 43 percent of the effective wave-length to be absorbed in this cell, the absorption coefficient must be close to 1- 10.1 atm^{-1} cm^{-1}. Again, this is about the absorption coefficient of oxygen at 184.9 nm.

The importance of the short wavelengths in effecting this reaction indicates that the optimum conditions for the photochemical synthesis of ClF_3O would be with a lamp that puts out a large fraction of its radiation at about 184.9 nm. It is likely, however, that longer wavelengths are also required to dissociate ClF_3 (see mechanism discussion).

Physical and Chemical Processes: A number of miscellaneous experiments were conducted on the formation of ClF_3O from ClF_3 and O_2 to investigate certain features of the reaction. Because small GC samples could be withdrawn periodically from this reactor, it was possible to obtain detailed information that could not be obtained from the previous batch reactor.

Condensation Rate of ClF_3O: It was found that the average half-time for a ClF_3O molecule to diffuse or convect through oxygen to the cooled tip and condense was about 3 to 5 minutes. These measurements were made with the light off but convection should be even faster with the light on.

Photolysis of ClF_3O: The results varied depending on the conditions, but the half-life of the ClF_3O photochemical decomposition was determined to be between 20 to 60 minutes with light of this intensity and spectral distribution. These results indicate that about 5 to 20 percent of the ClF_3O formed in this reactor will be decomposed before condensing out in the cooled tip.

Effective Vapor Pressures: It has been established that temperatures of -40°C or lower are required for the photochemical formation of ClF_3O with higher rates obtained at -60°C. It has been postulated [3] that the lower temperatures are required to reduce the vapor pressure of the ClF_3O to the point where most of it will condense out as it forms. This is not a completely satisfactory explanation, however, because the calculated [25] (extrapolated) vapor pressure of ClF_3O [2] is 3.6 torr at -60°C and 17.0 torr at -40°C. At these partial pressures, significant decomposition should occur and constant formation rates, such as those shown in Fig. 6, would not be expected.

The usual procedure was to warm the reactor to ambient temperature before withdrawing a GC sample to determine the composition of the entire contents of the cell. However, a few samples were drawn while the light was on with the tip being cooled. These showed the ClF_3 to be at a partial pressure of about 10 torr and the F_2 and ClF at their expected steady-state concentrations. However, the partial pressure of uncondensed ClF_3O was always quite low, being on the order of only 0.1 to 0.2 torr. This suggests that the ClF_3O dissolves in the condensed ClF_3 at -60°C.

The following series of measurements were made to determine if the extrapolated vapor pressures are correct and if the ClF_3O does indeed dissolve in condensed ClF_3. Purified ClF_3O was introduced into the evacuated and passivated reactor at a pressure of 10.3 torr. The tip then was cooled to -61.8°C for 1 hr and a GC sample drawn. The vapor pressure of ClF_3O determined in this manner was 2.8 torr. After warming to ambient, ClF_3 was added to a partial pressure of 97 torr. After cooling the tip for 1 hr at -59.5°C, the measured partial pressures of ClF_3O and ClF_3 were 0.1 and 12 torr, respectively, indicating that ClF_3O does dissolve in the condensed ClF_3 at this temperature. After warming to ambient and then cooling the tip to -40.3°C for 1 hr, the GC measurements indicated that the partial pressures were 1.95 to 45.5 torr, respectively. The calculated vapor pressure of ClF_3O is 16.5 torr at this temperature, again indicating that most of it is dissolved in the ClF_3.

The vapor pressures of ClF_3, calculated from the equation given in [26], are 10.9 and 46.5 torr at -59.5 and -40.3°C, respectively. These are in fair agreement with the measured values of 12 and 45.5 torr.

Comparison with Previous Results: A comparison of the results of Fig. 5 with those of Fig. 2 of Ref. 3 shows that the two studies are not in agreement although similar reactors were employed and the UV lamps were of the same type. It is possible, of course, that the differences result from the fact that the present study employed a reaction temperature of 20°C with an attached condensing tube at -60°C, while the entire reactor was kept at -60°C in the previous study. This does not seem likely, however, in terms of the various physical and chemical processes that were discussed above. That is, both reactors would be expected to contain the same chemical species at similar concentrations at each point in time, regardless of which reactant system is used. The following explanations are more likely.

The study in Ref. 3 was not a careful kinetic investigation, but rather was designed to investigate the general conditions under which ClF_3O can be prepared photochemically. The present study shows that the rate of ClF_3O formation is very sensitive to the light intensity. Therefore, changes in the lamp to window distance could account for the differences that were observed between the ClF_3-O_2 and $C1_2$-F_2-O_2 reactant systems. Also, more than one 679-A-36 lamp was employed in the first study, and it is possible that a different lamp was used for each series. Normally, this would be of no consequence because the lamps gave the same average intensity. However, the rate of ClF_3O formation is dependent on the intensity of the 184.9 nm band of Hg. Calvert and Pitts (pages 699 and 700 of Ref. 24) point out that as the quartz envelopes around these types of lamps age, the intensity of the shorter wavelength radiation drops off dramatically.

It is likely, therefore, that the difference between the two curves in [3] results from a difference in light intensity (at 184.9 nm). This could have been caused either by a different lamp-to-window distance or by the use of an "older" lamp in the experiments plotted on the lower curve. These same considerations probably account for the fact that the maximum rate in the present study (about 1 torr of ClF_3O/hr) is much less than the maximum of 8 torr/hr obtained in Ref. 3 for the $C1_2$ -F_2 -O_2 system. A new lamp was probably used in the latter experiments.

Finally, it should be noted that the previous experiments were of the batch type in which each point on the curve represents a single filling of the reactor and removal and work up of the products. It is not surprising, therefore, that the curves in [3] are not as linear as those obtained in this study in which each curve represents a single experiment.

Mechanism of ClF_3O Formation: The oxygen filter experiments appear to establish quite conclusively that the reaction of a ^3P oxygen atom, formed by the photolysis of O_2, is involved in the first step of the formation of ClF_3O from a mixture which contains, at the photochemical steady state, ClF_3, ClF, F_2, and O_2. The use of O_2 photolysis as a source of oxygen atoms is not new. Oxygen atoms from the photolysis of O_2 have been reacted with O_2 to form O_3, with CO to form CO_2, and with H_2 to form OH [27]. By absorption in the continuum below 175 nm, O_2 molecules are dissociated into ^1D and ^3P oxygen atoms [27-29]. The ^1D atom appears to be the more reactive species in the above cases [27].

Beyond the evidence of the involvement of ^3P oxygen atoms, this is a particularly difficult system for which to obtain information relating to the actual reaction mechanism. This study establishes rather clearly the conditions required for the photochemical synthesis of ClF_3O from these reactants, but a definitive mechanism has not been established. The decrease in effect of O_2 concentration at the higher O_2 concentrations is in approximate agreement with the 184.7 nm Hg

band being of importance in the dissociation of O_2 molecules. The half-absorption distance for this wavelength in oxygen is about 3 cm-atm. Thus, 50 percent is absorbed in the 7.5 cm cell at about 0.4 atm of O_2. At higher oxygen pressures, the total amount of the 184.7 irradiation that is absorbed no longer increases rapidly with oxygen pressure.

It is not convenient to determine the effect of ClF_3 concentration on the rate because increasing the temperature of the condensing tip to increase the ClF_3 vapor pressure increases the partial pressure of ClF_3O. This may cause significant losses of ClF_3O by photolysis. Likewise determining the effective wave-length region(s) is difficult. It has been established that short wavelengths around 184.7 nm are required, but it has not been proven that this wavelength would be sufficient in the absence of the longer wavelength radiation that leads to the steady-state reactions such as Reactions 9 through 13.

ClF_3 and O_2 and from the elements [3]: By analogy to the reactions that might occur in the formation of ClF_3O from ClO_3F and $C1O_2F$, the following mechanism has been proposed for the formation of ClF_3O from

$$ClF_3 + h\nu \leftrightarrow ClF + F_2 \quad (16)$$
$$O_2 + h\nu \rightarrow O + O \quad (17)$$
$$ClF + O + M + h\nu \rightarrow FClO + M \quad (18)$$
$$FClO + F_2 \rightarrow ClF_3O \quad (19)$$

According to this mechanism, FClO [30] is the principal intermediate.

It was found during this program, that the photolysis (and reformation) of ClF_3 is a fast process compared with the formation of ClF_3O. Therefore, ClF_2 radicals and F will be at moderate steady-state concentrations. The following mechanism is proposed as an alternative to the FClO mechanism: An equally plausible mechanism is one in which the photochemical dissociation of ClF_3

$$ClF_3 + h\nu \rightarrow ClF_2 + F \quad (20)$$
$$O_2 + h\nu \rightarrow O(^3P) + O(^3P) \quad (21)$$
$$F + ClF_2 + M \rightarrow ClF_3 + M \quad (22)$$
$$ClF_2 + ClF_2 \rightarrow C1F_3 + ClF \quad (23)$$
$$O + O + M \rightarrow O_2 + M \quad (24)$$
$$O(^3P) + ClF_2 \rightarrow C1F_2O \quad (25)$$
$$ClF_2O + F_2 \rightarrow ClF_3O + F \quad (26)$$

The key reaction in this scheme is Reaction 25 (which may require a third body). This mechanism would be in agreement with the required high light intensity and with the observation of Tolberg and coworkers [31] that ClF_3O does not form readily from the reaction of ^1D or ^3P oxygen atoms with either ClF_3 or ClF.

Photochemical Formation of ClF: At the start of this study, preliminary measurements were made of the kinetics of the photochemical formation of ClF_3 from ClF and F_2 at 25°C using only the isolated 365 nm radiation band from the Hg lamp. This reaction was of interest for comparison with the results that had been obtained by Krieger and Schumacher [10] at this wavelength for the similar reaction $F_2 + ClF_3 + h\nu \rightarrow ClF_5$.

F_2 were initially at equal concentrations of 300 torr. The GC The ClF and sampling tube had not yet been installed in the reactor so the rate was followed by measuring the pressure change. The final products were determined by fracionation and IR spectroscopy. Under these conditions, an initial quantum yield of about 1.3 was obtained. The quantum yield decreased rapidly during the course of the irradiation. An appreciable quantity of $C1_2$ was found in the products along with ClF_3 and unreacted ClF and F_2.

After this first reaction condition was investigated, it was learned that San Roman and Schumacher were just completing a detailed study of this reaction. They found that with F_2 in excess, the quantum yield is exactly one. At equal F_2 and ClF concentrations, however, they also found that $C1_2$ formed and the apparent quantum yield decreased with time of irradiation [20, 32]. San Roman and Schumacher proposed that Reactions 9 through 12 account for the main course of the reaction with F_2 in excess [20].

Comparing the mechanisms that have been proposed for the photochemical formations of ClF_3 and ClF_5 [10,20] it may be seen that the reaction analogous to one of the most important reactions in the formation of ClF_5 does not compete in the formation of ClF_3. The reaction $F + ClF_2 \rightarrow ClF_3$ is fast compared to $F + ClF_2 \rightarrow F_2 + ClF$, whereas the reactions $F + ClF_4 \rightarrow ClF_5$ and $F + ClF_4 \rightarrow F_2 + ClF_3$ are believed to occur at comparable rates.

Another feature of these reaction mechanisms is that although ClF_2 and ClF_4 are sufficiently stable to give moderate quantum yields, the reactions $ClF_4 + F_2 \rightarrow ClF_5 + F$ and $ClF_2 + F_2 \rightarrow ClF_3 + F$ do not occur. These could have lead to quantum yields of greater than one. Therefore, these exothermic reactions of F_2 must have appreciable activation energies as does the reaction $NF_2 + F_2 \rightarrow NF_3 + F$ ($\Delta H = -22$ kcal/mol) which has an activation energy of 14 kcal/mol [33].

Photochemical Formation of ClF: Also early in this study, two initial experiments were conducted to determine the quantum yield of the reaction $F_2 + C1_2 + h\nu \rightarrow 2$ ClF at 365 nm. Since no mol change is involved, only the average quantum yield over the course of the reaction could be obtained without the GC sampling system. At 365 nm the extinction coefficient for Cl_2 is about 25 times that of F_2 so that most of the light was absorbed by Cl_2. The initial pressure of Cl_2 was 100 torr in each experiment and the F_2 was at 100 torr in the first experiment and 615 torr in the second. The measured quantum yields, based on moles of $C1_2$ consumed per quantum absorbed, were only 0.08 and 0.20, respectively. Only ClF was formed in the first experiment. ClF and ClF_3 were formed in the second in the ratio of about 5 to 1.

After the GC sampling system was installed on the reactor, an experiment was run with F_2 and $C1_2$ to determine if the rate of ClF formation decreases rapidly with time as the concentration of ClF increases. A similarly small average quantum yield was obtained but the initial rate was relatively large followed by a very rapid decrease in rate with time. Reaction had virtually ceased before less than 20 percent of the reactants had been consumed. This is a strong indication that the photochemical $C1_2$- F_2 reaction is inhibited by the product ClF.

There is no obvious explanation for the low quantum yields obtained in the photochemical formation of ClF. The results of Fletcher and Dahneke [9] indicate that the thermal F_2-$C1_2$ reaction proceeds via a long-chain mechanism [34] at 100°C. There is little doubt that C1 atoms are formed throughout the reactor in the photochemical system and most of these somehow reform Cl_2 before they can react with F_2 to form ClF via the reaction:

$$C1 + F_2 \rightarrow ClF + F \quad (27)$$

The homogeneous three-body recombination of atoms should be too slow to compete with Reaction 27, as also would be diffusion of C1 atoms to the wall. The only apparent mechanism that might account for the low quantum yields obtained is the following:

$$C1_2 + h\nu \rightarrow Cl + C1 \quad (28)$$
$$C1 + ClF \leftrightarrow Cl_2 + F \quad (29)$$
$$F + ClF + M \rightarrow ClF_2 + M \quad (30)$$
$$Cl + ClF_2 \rightarrow 2\ ClF \quad (31)$$
$$C1_2 + h\nu \rightarrow C1_2 \quad (32)$$

This mechanism requires that Reactions 30 and 31 be much faster than Reaction 27. The equilibrium constant for Reaction 29 is only about 0.05, so Reaction 27 would have to have an effective collision number in excess of about 10^6 or 10^7 for Reaction 30 to dominate. At steady-state, the ratio F_2/ClF_2 should be on the order of 10^7. Thus, if the collision number of Reaction 27 is greater than about 10^9, both Reactions 30 and 31 could be faster than Reaction 27. At 300°K, increasing the activation energy by 1.4 kcal/mol decreases the rate by a factor of 10. Thus, if Reaction 27 has a normal frequency factor and an activation energy of greater than 13 kcal/mol, the rate of Reaction 27 could be low enough to give quantum yields of less than one. This mechanism would predict that much higher quantum yields would be obtained at 254 nm, where the dissociation of F_2 would be the dominant process.

They have also obtained low quantum yields on the order of those that are reported here [32]. The photochemical F_2-Cl_2 reaction has been independently investigated in detail by Schumacher and coworkers at 365 nm

Acknowledgments

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$$d(ClF)/dt = k_1 - k_2 (ClF) \qquad (A\text{-}1)$$

and

$$k_2 t = \ln\left[\frac{k_1}{k_1 - k_2(ClF)}\right] \qquad (A\text{-}2)$$

By setting Eq. (A 1) equal to zero

$$(ClF)_{ss} = k_1/k_2 \qquad (A\ 3)$$

and from Eq. (A-2) and (A-3)

$$(t_{1/2})ss = \ln 2/k_2 \qquad (A\ 4)$$

It can be seen that the results shown in Fig. 1, 2, and 3 are in approximate agreement with Eq. (A-3) and (A-4) if k_1 is only a function of light intensity and k_2 is independent of light intensity but increases weakly with pressure over the range of 40 to 400 torr.
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