produced. If $\phi_{2a} = 0$, then $\phi_1 = 1.00 = \phi_{2b} + \phi_3 + \phi_5 + \phi_6$ from which we get $\phi_5 = 0.60$. This happens to be identical with the yield for back-reaction in ethyl iodide calculated by Bunbury, Williams and Hamill from quite different experiments but with the analogous assumption that $\phi_{2a} = 0$.[4]

Linearity of Iodine Production with Time.—It frequently has been observed that ϕ_{I_2} is independent of amount of photolysis in a pure alkyl iodide. The mechanism proposed in equations 1–6 indicates that this observed independence is due to the fact that the measurements of I_2 were completed in a time short enough so that the natural ratio of HI/I_2 had not been decreased significantly by the occurrence of slow reaction 4. It would be predicted, therefore, that if a more reactive olefin than propylene were involved, a gradual decrease of ϕ_{I_2} with extent of photolysis should be observed. To test this prediction, we have photolyzed two samples of *t*-butyl iodide, each for eight three-minute periods, and in the second sample have interposed a 30-minute rest period between successive exposures to the lamp. The results are shown in Fig. 1 and the decrease in ϕ_{I_2} is evident.

Temperature Dependence.—The very large amount of isomerization observed at low temperatures evidently is correlated with the fact that both the absolute yield of HI and the HI/I_2 ratio are much greater at −60° than at room temperature. It also seems probable, but not certain, that ϕ_{I_2} has decreased at −60°.

The mode of formation of HI given in equation 2b will almost certainly be a function of temperature because of "cage effects," and it seems possible to explain both the increase in ϕ_{HI} and the decrease in ϕ_{I_2} in this way. The probability of back-diffusion of two separated radical partners depends strongly on the distance of the initial separation when the latter is small.[13] At low temperatures one expects that the liquid cage walls will be stronger and that the initial separation of iodine atom and propyl radical will be smaller. The probability of back-diffusion of partners should thus be much greater than at room temperature. Under these conditions ϕ_{2b} and ϕ_5 will increase, though possibly to an unequal degree, with consequent diminution of ϕ_{I_2}. The familiar nature of this picture thus gives some support to reaction 2b as the source of hydrogen iodide.

[13] R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950); J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **76**, 3274 (1954).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Kinetics of the Vapor Phase Photochlorination of Trifluorochloroethylene[1]

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The rate of the vapor phase chlorination of $CF_2{=}CFCl$ has been studied at room temperature. There is practically no dark reaction. The rate is independent of olefin pressure in the range of 25 to 400 mm. The rate has been found to depend on the 3/2 power of the chlorine pressure when the latter is low. The rate depends on the square root of the light intensity. The effect of added NO is normal and 10 mm. of this gas will completely stop the reaction. When O_2 at a partial pressure of 8 mm. or more is added to a mixture of a 100 mm. each of Cl_2 and $CF_2{=}CFCl$, an instantaneous reaction takes place at room temperature in a dark room. This reaction is accompanied by the emission of light. Apparently Cl_2 sensitizes the rapid oxidation of $CF_2{=}CFCl$ and very little activation energy is required. At 4 mm. O_2 it appears to inhibit the reaction slightly. A conventional mechanism is offered.

In connection with studies on various chemical and physical properties of fluorocarbons under way in this Laboratory, the kinetics of the photochemical chlorination of trifluorochloroethylene is being studied. The photochemical addition of chlorine to ethylene[2] and the chloroethylenes have been thoroughly studied.[3–11] However, there appear to be no data available on the corresponding reactions of substituted ethylenes containing fluorine. The heat of chlorination of trifluorochloroethylene previously has been determined in this Laboratory.[12] It is 48.8 kcal./mole while the heat of chlorination of ethylene is 43.6 kcal./mole.

Experimental Method

A manometric method was employed to indicate the progress of the reaction. The reaction cell was a Pyrex cylinder 15 cm. long and 3 cm. in diameter. It had optically flat windows and two outlets. One outlet was closed in all runs except those using oxygen. The other was sealed to a stopcock and a number 18/7 ball joint. A small side arm was sealed on just below the stopcock and was used for condensing the reactants by means of liquid nitrogen. The cell, including the side arm, was enclosed in a light tight box which was fitted with optically flat windows. A standard taper joint (10/30 capillary) was attached to the exit line just above the lid of the box. A manometer was connected to this.

Matheson chlorine (purity 99.5%) was taken from a tank, degassed and distilled at Dry Ice temperature into a Pyrex storage bulb. Trifluorochloroethene was furnished through the courtesy of the Kinetics Chemical Division of the du Pont Company. It was scrubbed with 10% KOH solution and a 10% H_2SO_4 solution to remove the inhibitor. After

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[1] This research is being supported by United States Air Force Research and Development Command Contract Number AF 18(600)-1151.

[2] T. D. Stewart and B. Werdenbaum, THIS JOURNAL, **57**, 1702 (1935).

[3] R. G. Dickinson and J. L. Carrico, *ibid.*, **56**, 1475 (1934).

[4] K. L. Müller and H. J. Schumacher, *Z. physik. Chem.*, **35B**, 285 (1937).

[5] K. L. Müller and H. J. Schumacher, *ibid.*, **35B**, 455 (1937).

[6] C. Schott and H. J. Schumacher, *ibid.*, **49B**, 107 (1941).

[7] R. Schmitz and H. J. Shumacher, *ibid.*, **51**, 281 (1942).

[8] R. Schmitz and H. J. Schumacher, *ibid.*, **52**, 72 (1942).

[9] H. J. Schumacher, *Angew. Chem.*, **53**, 501 (1940).

[10] F. S. Dainton, D. A. Lomax and M. Weston, *Trans. Faraday Soc.*, **53**, 460 (1957).

[11] J. Adam, P. Goldfinger and P. A. Gosselain, *Bull. soc. chim. Belg.*, **65**, 549 (1956).

[12] J. R. Lacher, J. J. McKinley, C. H. Walden, K. R. Lea and J. D. Park, THIS JOURNAL, **71**, 1334 (1949).

drying it was stored in a flask. All stopcocks were greased with Dow Corning Silicone High Vacuum grease for runs up to 60.

In an effort to prevent the film formation which occurred in the cell, especially at high chlorine pressures, some Halocarbon grease from Halocarbon Products Corporation was obtained. About $^1/_8$ of this grease was distilled off at 200° and under reduced pressure. The residue had fairly good physical properties and was used on the chlorine storage bulb, the measuring bulbs and the cell stopcock. This prevented film formation.

The amount of reactants to be used in a given run was determined by measuring the pressure they exerted in a vessel having a calibrated volume. In reading the pressure a quartz Bodenstein gauge was used. Using liquid nitrogen, the reactants were condensed into the side arm attached to the reaction cell. On closing the stopcock, the gases were allowed to come to the desired temperature before irradiation began. The reaction was followed by means of a manometer filled with Kel-F polymer oil No. 10. This manometer was connected to a mercury manometer and the outside pressure could be adjusted periodically.

A G. E. 400 watt mercury lamp and a 1,000 watt tungsten lamp were used as light sources. They were operated from a constant voltage transformer and were set in the focal plane of a quartz lens. Four collimating holes 15 mm. in diameter were used to obtain a parallel beam. The light intensity was measured by means of a General Electric photovoltaic cell (No. 8PVI) and a potassium ferrioxalate actinometer.[13] The output from the photocell was led directly to a galvanometer or microammeter, and the intensity was found to be directly proportional to the deflection. The lamps were allowed to warm up for 0.5 hr. before use. Except for one run, the light from the mercury lamp was not filtered. A Corning blue filter, No. 5850, was used in one run to remove two strong Hg lines of 546 and 578 mμ. The rate was 15% slower. This is understandable as the filter did not transmit all of the active light. The mercury lamp was used to study the dependence of rate on olefin pressure, and this was checked using a tungsten lamp and a Corning filter No. 5113. The intensity of the mercury lamp, however, was too low for the dependence on light intensity to be studied. It was necessary to use the tungsten lamp for this. Two sets of runs were made, one using Corning filter No. 5850, and the other No. 5113. No. 5850 transmits appreciably from 300 to 480 mμ with a peak at 368 mμ. It starts transmitting again at 660 mμ and at 740 transmits about 77%. No. 5113 transmits from 360 mμ to about 470 mμ with a peak of 38% at about 408 mμ. It transmits again weakly at 2,000 mμ.

Using the potassium ferrioxalate actinometer and measuring the deflection of the galvanometer attached to this photovoltaic cell, a determination was made of the number of quanta absorbed by chlorine when present in the reaction cell. It was found that for the tungsten lamp with filter No. 5113, the number of quanta absorbed is approximately a linear function of the chlorine pressure. At pressures above 100 mm., significant deviation from linearity occurs.

In order to check the extent of a dark reaction, enough Cl_2 and $CF_2{=}CFCl$ were condensed into the reaction cell to make, on evaporation, 134.7 and 109.1 mm., respectively. The total pressure as a function of time is illustrated in Fig. 1. After a period of 12,000 sec., the pressure dropped only 1.7 mm. Using unfiltered Hg light, the pressure changes with time as shown in the figure. During the initial illumination, the pressure changed slowly with time. The induction period was observed on practically all the runs made. By studying the infrared spectra of the reaction product, it was concluded that it was entirely $CF_2Cl{-}CFCl_2$. This is further substantiated by the fact that in runs with equal amounts of Cl_2 and $CF_2{=}CFCl$ carried to the end of the pressure fall, the final pressure was one-half of the initial.

Since the reaction probably proceeds by a chain mechanism, a run with light was made in which a small amount of NO (Matheson 99.0% purity) was added. The partial pressures of Cl_2, $CF_2{=}CFCl$ and NO were 113.2, 115.7 and 11.0 mm. The pressure change on illumination is also shown in Fig. 1. This amount of NO practically stops the reaction.

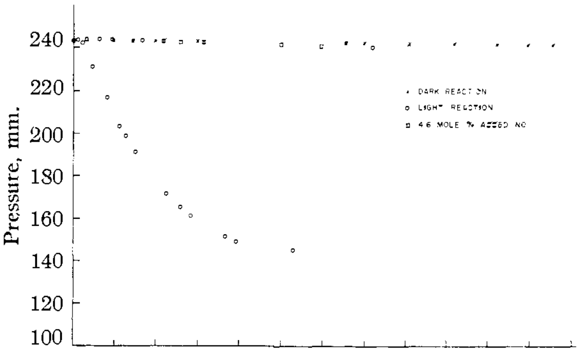

Fig. 1.—Total pressure as a function of time for dark reaction, reaction with 4.6 mole % added NO and light, and reaction with light.

In view of the fact that Schmitz and Schumacher[8] found that a trace of O_2 strongly inhibited the photochemical chlorination of vinyl chloride, the effect it might have here was studied. In order to get the oxygen (commercial) into the cell, a small standard taper joint was sealed to the second outlet. Small bulbs having calibrated volumes could be attached. In making a run the reaction cell and calibrated bulb were evacuated, the O_2 was introduced to the desired pressure. After closing a stopcock connecting the bulb and cell, the latter was evacuated. The Cl_2 and $CF_2{=}CFCl$ were then condensed, using liquid nitrogen, into the sidearm on the cell. The oxygen was then expanded into the cell in a darkened room. The experiments performed are summarized in Table I. Enough Cl_2 and $CF_2{=}CFCl$ were condensed in the cell to give final pressures of 100 mm. each.

TABLE I

MIXTURES OF $CF_2{=}CFCl$, O_2 AND Cl_2

P_{O_2} calcd.	P_{Cl_2} calcd.	$P_{CF_2=CFCl}$ calcd.	P_{total} calcd.	P_{total} after flash	Δ	P_{final}	Δ
0.0	99.6	100.2	199.8	195.5	− 3.3	97.0	−102.8
4.0	102.8	102.7	209.5	189.9	−19.6	125.8	− 83.7
8.0	103.3	100.1	208.4	169.5	−38.9	147.5	− 60.9
12.3	100.2	100	212.5	167.1	−45.4	142.0	− 70.5
16.1	100	100	216.1	175.7	−40.4	156	− 60.1
23.8	99.7	99.5	223.0	194.0	−29.0	179.7	− 43.3
31.9	100.7	100.3	233.1	194.3	−38.8	181.9	− 51.2
40.7	99.7	99.0	239.4	227.0	−12.4	215.4	− 24.0
73.4	101.9	101.2	276.5	295.7	+19.2	289.6	+ 13.1

It was found that for oxygen pressures between 4.0 and 40.7 there would be a precipitous fall in pressure at about the time the side arm reached room temperature. When the oxygen was 73.4 mm., there was a pressure rise. For all pressures of oxygen above 4.0 mm. there was a flash of light which preceded the rapid change in pressures. With 4.0 mm. of oxygen the mixture did not flash. In Table I the first, second and third columns give the calculated partial pressures of O_2, Cl_2 and $CF_2{=}CFCl$ present in the cell at room temperature. The fourth column gives their sum assuming no reaction to be taking place. The fifth column gives the observed pressure after the initial rapid reaction was complete. The difference between the observed and calculated total pressure is in column 6. The reaction cell was then illuminated using the same optical system as before, until all pressure changes ceased. The final pressure, column 7, when subtracted from the pressures listed in column 4, gives the total pressure change (column 8). In all runs with added oxygen the final product gases had a yellow color indicating that all the chlorine had not been consumed. Apparently, O_2 at these low pressures and in the presence of Cl_2 will react rapidly with $CF_2{=}CFCl$ in the dark. This suggests very little activation energy is required. The flash of light was quite often accompanied by a brown deposit which was soluble in a variety of organic solvents. Sometimes particles of carbon seemed to be formed. In a separate experiment the weight of the solid product was found to be 2.8%, the total weight of the reactants. No analysis of the products has yet been possible. The infrared spectra of the gaseous products are consistent

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[13] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (*London*), **A235**, 518 (1956).

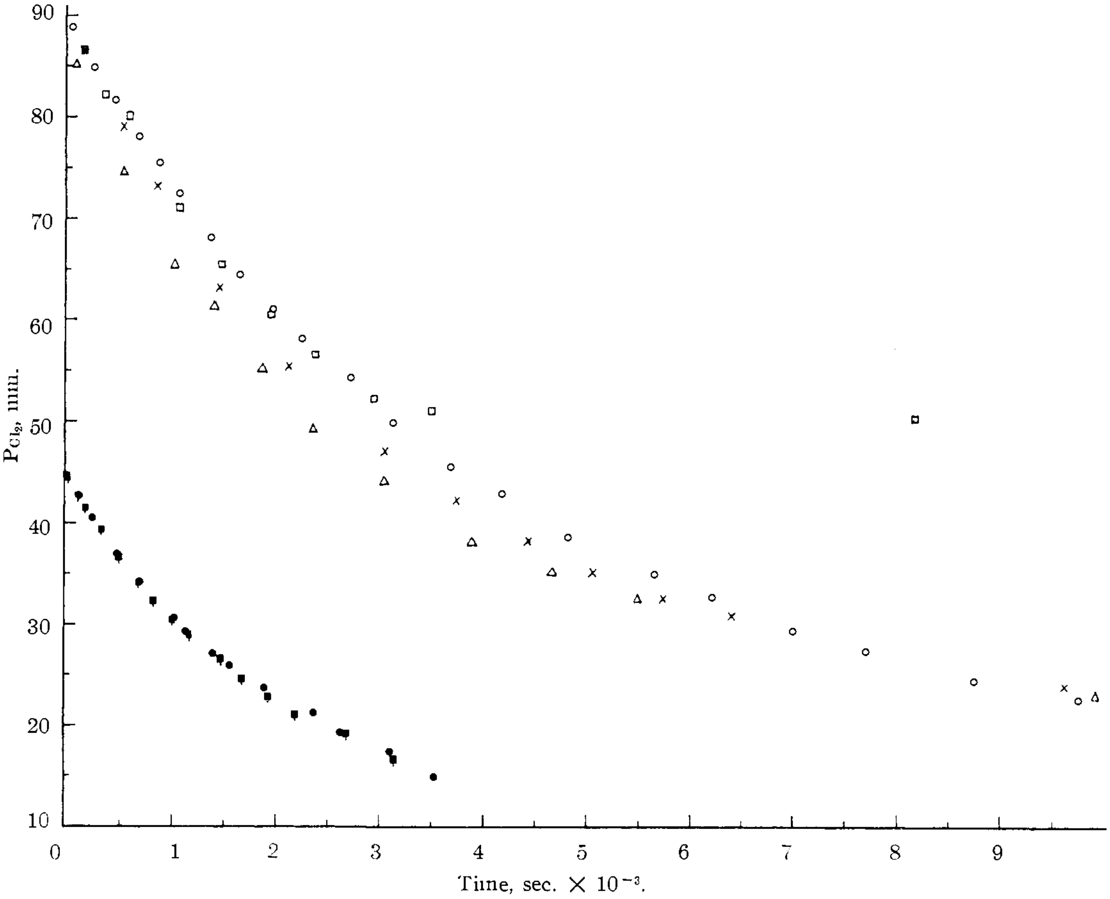

Fig. 2.—The partial pressure of chlorine as a function of time with the light intensity held constant while varying the olefin pressure.

	Initial conditions (silicone grease)			Initial conditions (halocarbon grease)	
	P_{Cl_2}, mm.	$P_{CF_2=CFCl}$, mm.		P_{Cl_2}, mm.	$P_{CF_2=CFCl}$, mm.
○	98.8	99.2	●	50.4	197.3
×	101.3	198.5	■	50.7	52.4
△	100.2	389.9			
□	100.3	51.2			

with the presence of CF_3Cl. When the reaction is carried out in a 5-liter flask, the flash is quite intense. Dickenson and Carrico[3] found that Cl_2 sensitized the photoöxidation of $CCl_2{=}CCl_2$. The products were CCl_3COCl and phosgene. However, mixtures of $CCl_2{=}CCl_2$ and O_2 were stable in the dark. Swarts[14] found that CFBr=CFBr oxidized very rapidly in the air to give CBr_2FCOF. Myers[15] combined O_2 with liquid $CF_2{=}CFCl$ in a steel cylinder to give a volatile product which hydrolyzed to oxalic acid. Hurka[16] also has studied the oxidation of $CF_2{=}CFCl$. He obtained good yields of $CClF_2COF$ at room temperature in the absence of a catalyst. However, in the presence of light, Cl_2 or *t*-BuOCl, a violent uncontrollable reaction occurs and carbon, halogenated methanes and phosgene are produced.

Two series of runs were carried out at constant light intensity, one with the mercury lamp and the other with the tungsten lamp and filter 5113. The purpose was to obtain information on the order of the reaction. The initial conditions are summarized in Table II.

Columns one and two give the initial partial pressure of chlorine and trifluorochloroethylene; the third, the room temperature. The chlorine pressure is graphed as a function of time in Fig. 2 for the first four runs (Table IIa made using silicone grease) taking the initial time as that instant when P_{Cl_2} was 90 mm. This was done in order to escape an inhibition period which varied from run to run. In Fig. 3 two runs (Table IIb made using halocarbon grease) are graphed the initial times being the time when P_{Cl_2} = 45 mm. In these two series the initial chlorine pressure is constant while the olefin pressure is allowed to vary. The rate of the reaction determined by the slopes of the curves is independent of the olefin pressure. This is also true of the photochemical chlorination of ethylene and the chloroethylenes. In the run where only 51.1 mm. of olefin was used, the rate does not fall off until half of it is consumed. These data show that the rate is independent of olefin pressure as long as it is above 25 mm.

In determining the dependence of the rate on the chlorine pressure, only runs made with halocarbon grease were used. The total pressure was graphed as a function of time. After drawing the best curve through the points, the slope, dP/dt was recorded as a function of the chlorine pressure at regular intervals throughout the reaction. The logarithm of this slope was then plotted against the logarithm of chlorine pressure. The results are shown in Fig. 3 for several runs. It is seen that a slope of 1.5 is obtained. The runs in which silicone grease was used gave more erratic lines in the individual runs, some slopes approaching 2 and others 1.5, due perhaps to film formation. No attempt was made to combine runs.

In order to determine the dependence of rate on light intensity, two series of runs were made at 27–29°. The light intensity was varied by inserting screens in the light path.

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(14) F. Swarts, *Bull. Acad. Roy. Belg.*, [3] **34**, 307 (1897).

(15) R. L. Myers, *Ind. Eng. Chem.*, **45**, 1783 (1953).

(16) V. R. Hurka, U. S. Patent 2,676,983 (April, 1954).

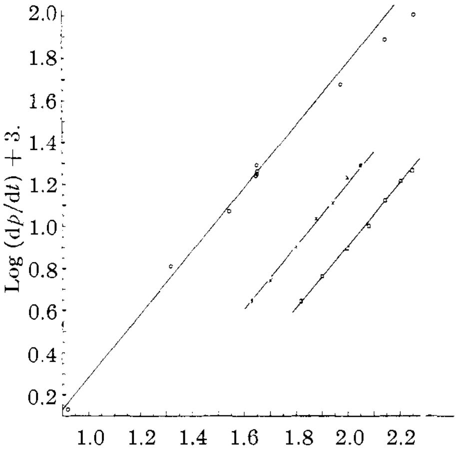

Fig. 3.—Log (dP/dt) + 3 as a function of log P_{Cl_2}: Points marked O taken from Table IIb. Points marked × and □ taken from two individual runs during the course of a reaction. Scale for log P_{Cl_2} shifted 0.4 and 0.6 unit to the right, respectively, for × and □. Lines are drawn with a slope of 1.5.

In the first, the rate was taken at P_{Cl_2} = 90 mm. and the second, P_{Cl_2} = 45. The first series was made with tungsten lamp and filter 5850 and silicone grease. The second tungsten lamp and filter 5113 and halocarbon grease. The results are shown in Fig. 4 and show that the rate depends on the square root of I_0.

TABLE IIa

PHOTOCHEMICAL CHLORINATION SUMMARY OF INITIAL CONDITIONS

P_{Cl_2}, mm.	$P_{CF_2=CFCl}$, mm.	t, °C.
100.3	391	28.4
101.3	199.2	27.5
98.1	98.1	28.5
100.4	51.1	29
48.2	96.4	31
10.3	10.3	29.5
10.2	10.4	30

TABLE IIb

P_{CF_2CFCl}, mm.	P_{Cl_2}, mm.	Temp., °C.	Deflection	Rate, mm./sec. × 10^{+3}	At P_{Cl_2}, mm.
197.2	27.8	28	1.86	6.98	22.2
199.8	40.5	28	1.90	11.66	35
199.5	10.4	29	1.86	1.5	9.1
198.2	99.7	29	1.81	47.5	94
199.1	150	27	1.74	77.5	137.2
197.8	197	26	1.83	101	180.7
199.7	50.6	26	1.80	17.3	45
199.2	50.2	26.5	0.13	6.10	45
199.1	50.3	27	.018	2.27	45
197.3	50.2	28	.44	9.64	45
197.3	49.9	29	1.86	19.5	45
197.3	50.4	25	1.88	17.9	45
52.4	50.7	25	1.84	18.4	45
194.6[a]	49.8	25	1.80	18.4	45

[a] Made with 44 mm. of adduct present initially.

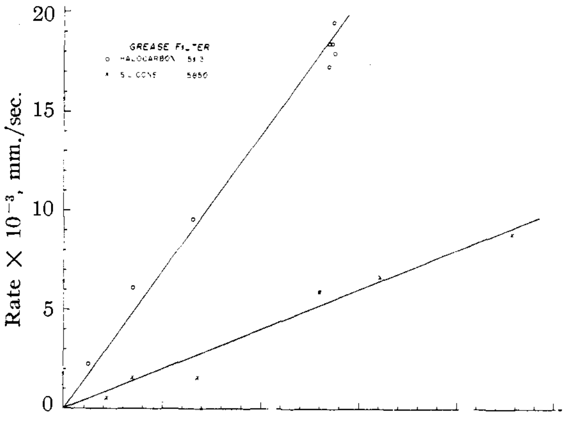

Fig. 4.—Rate as a function of $I_0{}^{1/2}$. Runs marked O made with halocarbon grease, P_{Cl_2} = 45 mm.; runs marked × made with silicone grease, P_{Cl_2} = 90 mm.; rate scale for runs marked × $^1/_{10}$ of marked scale.

Discussion

Under these conditions the rate has been found to depend on only the $^3/_2$ power of the chlorine pressure and on the square root of the light intensity when it is varied. Since the light absorbed is proportional to the chlorine pressure, the rate equation will take the form

$$-\frac{dP}{dt} = k_0{}^1(P_{Cl_2})^{3/2} = k_0 I_a{}^{1/2}(P_{Cl_2})$$

This equation is the same as that found for the chloroethylenes[4,10,11] and that derived for the general case of photochemical additions.[17]

The simplest mechanism consistent with this rate law is

$$Cl_2 + h\nu \longrightarrow 2{\cdot}Cl \quad (1)$$

$$\cdot Cl + Tf \longrightarrow Tf{\cdot}Cl \quad (2)$$

$$\cdot TfCl + Cl_2 \longrightarrow TfCl_2 + \cdot Cl \quad (3)$$

$$\cdot TfCl + \cdot TfCl \longrightarrow \text{products} \quad (4)$$

The reverse of step two cannot take place in any appreciable degree since the chlorine atom concentration would be raised to such an extent that the radical–radical reactions $2{\cdot}Cl + M \rightarrow Cl_2$ and $\cdot Cl + \cdot TfCl + M \rightarrow TfCl_2$ or $Tf + Cl_2$ would take place appreciably. This could be observed by a dependence of the rate on the trifluorochloroethylene pressure which was not found. The reverse of step three cannot be appreciable either as in one run (Table IIb) 44 mm. of product was added and no effect was found on the rate. It cannot be decided on the basis of our present data whether step four produces the dimer or is a disproportionation reaction.

These experiments also can be used to calculate the chain length. In a run where the chlorine pressure was 45 mm., I_0 was 14.1×10^{12} quanta/sec. and 2.47×10^{12} quanta absorbed, the chain length or quantum yield was 3.64×10^5. In another run at the same chlorine pressure, the light flux was 3.34×10^{12} quanta/sec. and 0.585×10^{12} quanta/sec. were absorbed. The chain length was 7.64×10^5. k_0 was found to be 2.0×10^2 eins$^{-1/2}$ sec.$^{-1/2}$. Steady-state treatment shows k_0 to be equal to $k_3\sqrt{2}/k_4$.

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[17] P. A. Gosselain, J. Adam and P. Goldfinger, *Bull. soc. chim. Belg.*, **65**, 533 (1956).