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Kinetics of the Gas Phase Pyrolysis of Chlorine Pentafluoride[1]

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The kinetics of the photochemical formation of chlorine pentafluoride from ClF_3 and F_2 has been studied by Krieger, Gatti, and Schumacher.[2] Herein we report the results of our investigation of the gas phase thermal decomposition of ClF_5

$$ClF_5 \longrightarrow ClF_3 + F_2 \qquad (1)$$

where,[3] $\Delta H°_{600°K}$ = 18.5 kcal/mol, $\Delta S°(p)$ = 40.4 gibbs/mol, and $\Delta S°(c) = \Delta S°(p) - R - R \ln (RT)$ = 30.7 gibbs/mol.

Experimental Section

The electrically heated, stirred flow reactor (91 ml, monel) employed is described elsewhere.[4,5] Chlorine pentafluoride vapor of 98 wt % purity (the impurities were HF, ClF_3, and small amounts of CF_4) was passed through the reactor at an initial partial pressure of 32 Torr in a mixture with helium. The total pressure was 1 atm. The reactor was equipped with a by-pass to allow measurement of the ClF_5 concentration in the entering gas stream.

The gases leaving the reactor (or the by-pass) passed through a 10-cm nickel infrared cell with AgCl windows. The ClF_5 concentration was followed by measuring the absorbance at 12.5 μ pressure. The flow rates were measured with a soap bubble flow meter connected to the exit stream. The measured flow rates and reactor volume were corrected to reactor temperature. No correction was made for the partial dissolution of reactants and products in the soap solution or for the presence of water vapor from the soap solution.

Infrared analysis of the exit gas showed ClF_3 and ClF_5 as the major absorbers. Fluorine does not absorb in this pressure range (2–15 μ). The absorption bands for ClF_3 were masked by ClF_5. However, crude estimates of the moles of ClF_3 formed per mole of ClF_5 reacted were obtained for some of the experiments by measuring the ClF_3 absorbance at 15 μ. These results, presented in Table I, indicate that the stoichiometry is essentially that of eq 1. The possible de-

(1) This work was supported by the United States Air Force under Contract No. AF04(611)-10544.

(2) R. L. Krieger, R. Gatti, and H. J. Schumacher, *Z. Phys. Chem.*, 51, 240 (1966).

(3) JANAF Thermochemical Tables.

(4) J. M. Sullivan and T. J. Houser, *Chem. Ind.* (London), 1057 (1965).

(5) J. M. Sullivan and A. E. Axworthy, *J. Phys. Chem.*, 70, 3366 (1966).

Table I: Experimental Kinetic Data for the Pyrolysis of Gaseous Chlorine Pentafluoride

T, °C	τ, sec	Fraction reacted, α	k, sec^{-1}	$(ClF_3)_{calcd}$, Torr	$(ClF_3)_{obsd}$, Torr
252.2	24.9	0.119	0.00542		
252.2	113.0	0.378	0.00538	12.1	10.5
252.2	281.5	0.638	0.00626	20.4	20.1
252.2	449.0	0.648	0.00409		
268.5	196.8	0.694	0.0115		
279.4	36.2	0.483	0.0254		
279.4	115.3	0.731	0.0235		
283.2	23.6	0.471	0.0378		
283.0	36.3	0.571	0.0368		
288.0	9.5	0.301	0.0452	9.6	11.7
287.4	24.4	0.551	0.0503	17.7	20.5
288.0	27.9	0.610	0.0559	19.5	22.9
288.2	40.4	0.699	0.0572	22.4	24.9
287.4	42.4	0.703	0.0558	22.5	25.6
287.6	55.0	0.772	0.0614	24.7	31.4
293.0	11.6	0.394	0.0561		
291.8	11.9	0.394	0.0546		
293.0	14.6	0.457	0.0580		
291.5	24.1	0.603	0.0610		
293.3	32.4	0.669	0.0622		
293.0	38.4	0.705	0.0620		
293.5	41.7	0.740	0.0680		
293.0	62.8	0.806	0.0663		
294.0	81.3	0.844	0.0663		
307.5	7.96	0.532	0.143	17.0	15.0
306.8	9.76	0.624	0.169	20.0	22.2
307.0	11.9	0.677	0.176	21.7	25.4
307.5	12.9	0.664	0.153	21.2	16.2

composition of ClF_3 to ClF and F_2 is limited to less than 13% by thermodynamic considerations.

Results

The experimental results[6,7] for the thermal decomposition of ClF_5 over the temperature range 252–307° are presented in Table I. For a first-order decomposition in a stirred flow reactor, the rate constant k is given by

$$k = \alpha/\tau(1 - \alpha) \quad (2)$$

where α is the fraction reacted and τ is the average residence time in the reactor.[8] In Figure 1, a plot of $\alpha/(1 - \alpha)$ *vs.* τ for the data at 293° shows that the reaction follows first-order kinetics up to at least 84% decomposition. The data in Figure 1 were obtained at 291.5–294.0° and converted to 293° using the measured activation energy of 36.8 kcal/mol. The data in Table I give a linear Arrhenius plot. A least-squares fit of the data to the Arrhenius equation gives

$$k = 10^{13.02} \exp(-36{,}800/RT) \text{ sec}^{-1} \quad (3)$$

The limit of error for the activation energy is

$$E = 1.0 \text{ kcal/mol} \quad (4)$$

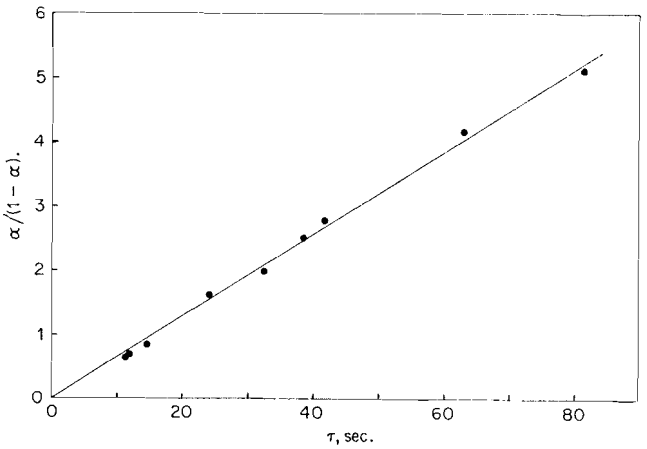


Figure 1. First-order plot at 193°.

Discussion

Reaction Mechanism. Three possible mechanisms may be written which are compatible with the observed rate expression, *i.e.*, first-order in ClF_5 with no apparent inhibition as the products accumulate.

A. Unimolecular Elimination of F_2

$$ClF_5 \longrightarrow ClF_3 + F_2 \quad (5)$$

B. Radical Chain Mechanism

$$ClF_5 \longrightarrow ClF_4 + F \quad (6)$$

$$F + ClF_5 \longrightarrow ClF_4 + F_2 \quad (7)$$

$$ClF_4 \longrightarrow ClF_3 + F \quad (8)$$

$$F + ClF_4 \longrightarrow ClF_3 + F_2 \quad (9)$$

C. Nonchain Radical Mechanism

$$ClF_5 \longrightarrow ClF_4 + F \quad (6)$$

$$ClF_4 \longrightarrow ClF_3 + F \quad (8)$$

$$F + ClF_4 \longrightarrow ClF_3 + F_2 \quad (9)$$

$$2F + M \longrightarrow F_2 + M \quad (10)$$

$$2ClF_4 \longrightarrow 2ClF_3 + F_2 \quad (11)$$

It will be shown in the following discussion that none of these mechanisms can be completely eliminated on the grounds of giving unreasonable Arrhenius parameters, but the nonchain radical mechanism appears to be the most likely mechanism. The expected[9] A

(6) The results presented herein differ from those presented in ref 7 because an error was found in the computational procedure used to convert absorbance to concentration. The amount by which this changed the reported kinetic parameters does not indicate the experimental uncertainty in these parameters.

(7) A. E. Axworthy and J. M. Sullivan, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1956, p 185.

(9) S. W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1968.

factor for direct molecular elimination of fluorine, reaction 5, is 10^{13} to 10^{14} sec^{-1}. Three-center reactions of this type are not common, and for ClF_5 would be expected to involve a "stiff" transition state. The structure of ClF_5 is square pyramidal with the central chlorine and the four equivalent fluorine atoms approximately in a plane.[10] The unique fluorine atom would probably be involved in reaction 5 since this would permit the closest approximation to the planar ClF_3 structure[11] in the transition state. If ClF_5 does decompose through reaction 5, the reverse of this reaction has an A factor of $10^{6.3}$ 1. mol^{-1} sec^{-1}. This is unusually low for a bimolecular association reaction but is not unreasonable if the transition state is very stiff compared with ClF_5.

Although reaction 5 cannot be ruled out on the basis of the observed A factor, it is not unlikely that the activation energy required to form the three-center transition state is considerably greater than the experimental value of 36.8 kcal/mol (the shortest distance between two F atoms in ClF_5 is 2.36 Å compared with 1.41 Å in F_2). If $A_5 \cong A_{ob} = 10^{13.0}$, the criterion for reaction 5 to be negligible (less than 1%) is $E_5 > E_{ob} + 2\theta = 41.8$ kcal/mol, where $\theta = 2.3\ RT = 2.5$ kcal/mol at 550°K.

If the radical chain mechanism predominates, the following conditions obtain at steady state

$$k_{ob} = k_6 + (k_6k_7k_8/k_9)^{1/2} \quad (12)$$

$$(F) = (k_6k_8/k_7k_9)^{1/2} \quad (13)$$

$$(ClF_4) = (k_6k_7/k_8k_9)^{1/2}(ClF_5) \quad (14)$$

$$R_6 = R_9 \text{ and } R_7 = R_8 \quad (15)$$

where R_6 represents the rate of reaction 6, etc.

At long chain length, $k_{1c} = (k_6k_7k_8/k_9)^{1/2}$. If $A_7 \cong A_9$, $A_{1c} = (A_6A_8)^{1/2} \cong (10^{14} \cdot 10^{14})^{1/2} = 10^{14}$. This is in fair agreement with A_{ob}.

The activation energy at long chain length is given by $^1/_2(E_6 + E_7 + E_8 - E_9)$. Because ΔH for $ClF_5 = ClF_3 + 2F$ is 57.0 kcal/mol,[12] $E_6 + E_8 = 57.0 + E_{6R} + E_{8R}$ where E_{6R} and E_{8R} are the activation energies for the reverse of reactions 6 and 8, respectively. Thus for the long-chain mechanism, $E_7 = 2E_{ob} - 57.0 - E_{6R} - E_{8R} + E_9 = 16.6 - E_{6R} - E_{8R} + E_9$. If as expected $E_{6R} \cong E_{8R} \cong E_9 \cong 0$, $E_7 \cong 16.6$ kcal/mol. $E_7/\theta = 6.6$ which is only slightly above the expected maximum value for a fast bimolecular propagation step.[13]

An additional requirement for the long-chain mechanism is that $R_6 \ll R_7 = R_{ob}$. If $A_6 \cong 10^{14}$, E_6 must be greater than about $E_{ob} + 3\theta$ or 44 kcal/mol. Thus, for a long-chain mechanism to prevail, $E_6 \geq 44$, $E_7 \cong 16.6$, and $E_8 \cong 57.0 - E_6 < 13$ kcal/mol. These values cannot, *a priori*, be considered as unreasonable; hence the long-chain mechanism cannot be eliminated.

If $39 < E_6 < 45$, a short chain mechanism could occur. This would lead to a linear Arrhenius plot only if both terms in eq 12 have the same activation energy. This would be the case, however, because it was shown above that the A factors for these two terms should be of the same magnitude, requiring that their activation energies be about the same for a short-chain mechanism to occur.

The termination process in the chain mechanism must involve the reaction of F and ClF_4 (*e.g.*, reaction 9). The occurence of the other possible termination reactions, 10 and 11, does not give first-order kinetics. However, the termination reaction

$$F + ClF_4 \longrightarrow ClF_5 \quad (6R)$$

could be added to the chain mechanism without affecting the above discussion. Krieger,[2] *et al.*, conclude that $R_{6R} = R_9$ under their conditions.

The major factor which determines whether the radical chain reaction occurs is, of course, the rate of the fluorine atom abstraction reaction, 7. There are indications[13] that these types of reactions (*e.g.*,[14] $QF + \cdot NF_2 \rightarrow NF_3 + Q\cdot$) have high activation energies and, therefore, do not occur. On this basis, the chain mechanism appears less likely to occur than the non-chain radical mechanism.

If the decomposition reaction proceeds *via* the non-chain radical mechanism, the observed activation energy (36.8 kcal/mol) is a measure of the bond dissociation energy for the first bond in ClF_5—providing that, as expected, $E_{6R} \cong 0$. Hence, the dissociation energy of the second bond (eq 8) would be 57.0 − 36.8 = 20.2 kcal/mol.[12] This value for ΔH_8 appears reasonable. In the first place, if we consider the reaction

$$ClF_5 + ClF_3 \rightleftarrows 2ClF_4 \quad (16)$$

then $\Delta H_{16} = \Delta H_6 - \Delta H_8 = (\Delta H_6 + \Delta H_8) - 2\Delta H_8 = 57.0 - 2\Delta H_8 = +16.6$ kcal/mol. Since ΔS_{16} should be small, $\log K_{16}^{eq} \cong -16.6/\theta$ which at 600°K gives $K_{16}^{eq} = 10^{-6.4}$. A larger value of ΔH_8 would permit the ClF_4 radical to reach very appreciable concentrations at moderate temperatures; this presumably is not the case.

Secondly, the high quantum yields (up to 0.5) obtained in the photochemical synthesis[2] at ~1 atm and 30° puts a lower limit on ΔH_8 (and thus an upper limit on ΔH_6). The half-life of ClF_4 is given by $\tau_{1/2} = 0.7\ (A_8)^{-1} \times 10^{+\Delta H_8/\theta} \cong 7 \times 10^{-15} \times 10^{+\Delta H_8/1.38}$

(10) G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

(11) R. D. Burbank and F. N. Bensey, *ibid.*, **21**, 602 (1953).

(12) If the new value for the dissociation energy of F_2 [W. Stricker, *Z. Naturforsch*, **22a**, 1137 (1967)] is confirmed, the sum of the first two bonds in ClF_5 will be lowered to 53.5 kcal/mol.

(13) See p 122 of ref 9.

(14) Unpublished data from this laboratory.

sec. The time required to suffer at least one collision with an F atom is $\sim 10^{-10}\ (X_F)^{-1}$ sec, where X_F is the mole fraction of F atoms in the photochemical reactor. Thus $\Delta H_8 > 1.36\ (4.15 - \log X_F)$. An upper limit for X_F can be estimated by calculating the value at which F atom recombination, reaction 10, equals the rate of the photochemical dissociation of F_2 which was about 0.01 Torr/sec at the highest F_2 pressure. Using the smallest reported rate constant[15] for k_{10} at room temperature, 5×10^7 l.^{2} mol^{-2} sec^{-2}, the calculated maximum value of X_F is 10^{-5}. Thus $\Delta H_8 > 12.5$ kcal/mol.

It may be seen from the above discussion that at least three mechanisms are compatible with the observed kinetic parameters. We favor the nonchain radical mechanism on the grounds that reactions 5 and 7 might be expected to be too slow.

Photochemical Mechanism. Krieger, Gatti, and Schumacher[2] studied the kinetics of the photochemical formation of ClF_5 from ClF_3 and F_2 (365 mμ, 16 to 70°) and obtained the complex rate expression

$$\frac{d(ClF_5)}{dt} = kI_{abs}\left[k'\frac{(ClF_3)}{(M)} + 1 + \frac{k''}{(M)}\right]^{-1} \quad (17)$$

where

$$(M) = (F_2) + 0.40(ClF_5) + 0.22(N_2) + 0.18(He) \quad (18)$$

They explain their results on the basis of the following reaction scheme

$$F_2 \xrightarrow{h\nu} 2F \quad (19)$$

$$F + ClF_3 + M \longrightarrow ClF_4 + M \quad (8R)$$

$$ClF_4 + F \longrightarrow ClF_5^* \quad (20)$$

$$ClF_4 + F \longrightarrow ClF_3 + F_2 \quad (9)$$

$$ClF_5^* + ClF_3 \longrightarrow 2ClF_4 \quad (21)$$

$$ClF_5^* + M \longrightarrow ClF_5 \quad (22)$$

$$ClF_5^* \longrightarrow ClF_4 + F \quad (23)$$

Reaction 21 is required to account for the observed inhibition by ClF_3. Each of the competing paths for ClF_5^*, reactions 21, 22, and 23, occurred to an appreciable extent (>10 %) in every experiment. Two consequences of the photochemical investigation are of interest to the present study (in addition to the lifetime of ClF_4 discussed above). First, from the photochemical results the average lifetime of the activated ClF_5^* is calculated to be 10^{-9} sec^{-1}. Hence, the thermal reaction should be in the pressure-dependent region. Secondly, the photochemical mechanism predicts an acceleration of the thermal reaction as the product ClF_3 accumulates. It may be seen from Figure 1 that the thermal reaction follows first-order kinetics out to at least 84% reaction, with no indication of acceleration at higher fractions of decomposition. From the photochemical rate parameters, a 20% increase in the first-order rate constant would be predicted at 80% decomposition. Further thermal experiments at various pressures and initial ClF_3 concentrations would be required to establish definitely whether the thermal reaction is pressure dependent or inhibited slightly by ClF_3.

The lifetime of the photochemically activated ClF_5^* is shorter than would be predicted for a thermally activated molecule of this complexity.[16,17] Classical RRK theory predicts a lifetime[18] of $10^{-5.7}$ sec at 600°K and $10^{-4.6}$ sec at 300°K. The fluorine atoms formed from the photochemical decomposition of F_2 at 365 mμ contain 20 kcal/mol of excess translational energy, since there are no accessible electronic states. If all of this energy were introduced into the ClF_5^*, its predicted lifetime would be reduced to $10^{-8.5}$ sec, near the observed value. This excess energy from the photochemical fluorine atom would also account for the reactivity of ClF_5^* toward ClF_3. A major problem with this suggested difference between the thermal and photochemical reactions is that the photochemically formed F atoms should cycle through reaction 8R many times and lose their excess energy before forming ClF_5^*.

(15) R. W. Diesen, *J. Phys. Chem.*, **72**, 108 (1968).

(16) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Company, Inc., New York, N. Y., 1960.

(17) A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press Inc., New York, N. Y., 1955.

(18) The value $c_v = c_p - 8$ was used in making the calculation. For details see p 112 of ref 9.