Kinetics of the Chlorine Fluoride Reaction[1]

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Abstract: The rate of reaction of chlorine with fluorine to form chlorine fluoride was measured in the temperature range 80–128°, and the spontaneous ignition limit of the stoichiometric mixture was studied at pressures ranging from 15 to 280 mm and temperatures ranging from 130 to 170°. The reaction is first order with respect to fluorine and one-half order with respect to chlorine. The activation energy obtained from rate studies is 19,800 cal. The activation energy obtained by application of Semenov thermal explosion theory to the explosion limit is higher. Neither argon nor the variation of the surface-to-volume ratio affects the observed kinetics. A mechanism is proposed.

Mixtures of chlorine and fluorine will burn to form chlorine fluoride.[2] Wicke and Friz[3] measured the heat of formation of chlorine fluoride by observing explosions of mixtures of the reactants in closed vessels. The flame is an unusually simple one. There is no appreciable variation in the molecular weight of the mixture during combustion. The maximum adiabatic flame temperature is about 1400°K. Only five different molecular species, Cl_2, F_2, Cl, F, and ClF, are expected to be found in the flames. Of these, only the product is active in the infrared. Because the flame is simple, we have chosen it for exhaustive study. We have reported[2b] spatial flame speeds in tubes. The maximum flame speed was observed in lean mixtures (those containing 45.2% chlorine by volume). The occurrence of the maximum flame speed in such mixtures was puzzling. The maximum adiabatic flame temperature is achieved with slightly rich mixtures (51.4% chlorine), and, since fluorine has a lower dissociation energy than chlorine, one might expect the kinetics to be given by an expression of the form[4] $d[ClF]/dt = k[F_2]^{1/2}[Cl_2]$. Such a rate expression maximizes the rate, at a given temperature, in very rich mixtures, those containing 67% chlorine. Thus, both flame temperature and the anticipated kinetics suggested that the flame speed maximum should occur in rich mixtures.

Some predictions of the kinetic behavior of this system have been made from various theoretical considerations.[5,6] In view of the unexpected dependence of flame speed on composition, we felt that an experimental study of the kinetics of the reaction was in order. A few preliminary experiments were carried out to define the range of temperatures and pressures which could be used in the study. These experiments outlined a spontaneous ignition region. Working outside this region, we were able to measure the rate, concentration dependence, and activation energy of the reaction. The results are reported here, and a mechanism which rationalizes the results is proposed.

Experimental Section

Materials. Chlorine was obtained from Air Products and Chemicals, Inc. The manufacturer claimed a purity of 99.5%. The molecular weight determined by gas density measurements was found to be 70.92 (theory, 70.91).

Fluorine was obtained from Air Products and Chemicals, Inc., which claimed a purity of 98% for the product. Hydrogen fluoride was removed by means of a standard Matheson Co. sodium fluoride trap. The purity of the resulting product was estimated by permitting it to react with mercury, which does not react with the most probable remaining impurity, oxygen. The gas was thus found to contain at least 97% fluorine and was used without any further treatment.

Apparatus and Procedure. The rate studies were carried out by combining the reactants in a stainless steel mixing chamber, expanding a portion of the mixture into a thermostated reaction vessel, and withdrawing samples at suitable intervals for infrared analysis. The samples were small compared with the volume of the bomb. The mixing chamber, a Heise Bourdon Tube Co. Model H43545C pressure gauge, the reaction vessel, reactant bottles, a nitrogen purge bottle, a vacuum pump, and a vent line were all connected to a common manifold which also contained an outlet for attachment of the infrared sample cell.

The mixing chamber was a 42-l. stainless steel tank. Gases were mixed either by the jet mixing which accompanied the introduction of the second gas, natural convection driven by a heating tape wrapped about the base of the chamber and heated to about 60° for 12–24 hr, or by removal from the system and tumbling of the mixing tank. Mixing by any of these three techniques was adequate as was evidenced by the fact that the results were reproducible regardless of the mixing technique used. On occasion, there were spontaneous explosions while the reactants were being mixed. They probably resulted from static sparks. Such occurrences are not unusual[7] in studies involving fluorine.

The reaction vessel was constructed from a 35-cm length of 15-cm i.d. Monel 400 pipe with a Monel 400 cap turned from a 6-mm plate welded into each end. A single 0.25-in. Gyrolock tube fitting was welded into one of the end caps, and from this fitting a 10-cm length of Monel seamless tubing connected the reaction vessel to a Monel 400 Hoke 413 HT packless valve to which the tubing was silver soldered. The entire reaction vessel including the valve body and connecting tubing was immersed in a thermostated oil bath whose temperature was maintained to within 0.5°.

At appropriate times 50-mm samples were withdrawn into a sample cell, made of aluminum, with sodium chloride windows.

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[1] This work was supported in part by grants to Dr. Dahneke from the Department of Health, Education, and Welfare and the Ford Foundation. The paper is taken in part from Dr. Dahneke's Ph.D. thesis, 1967.

[2] (a) O. Ruff and E. Ascher, *Z. Anorg. Allgem. Chem.*, **176**, 258 (1928); (b) E. A. Fletcher and L. L. Ambs, *Combust. Flame*, **12**, (2), 115 (1968).

[3] E. Wicke and H. Fritz, *Z. Elektrochem.*, **57**, 9 (1953).

[4] S. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 320.

[5] S. W. Benson and G. R. Haugen, *J. Am. Chem. Soc.*, **87**, 4036 (1965).

[6] R. M. Noyes, *ibid.*, **88**, 4311, 4318, 4324 (1966).

[7] E. A. Fletcher and D. B. Kittelson, *Combust. Flame*, **12** (2), 119 (1968).

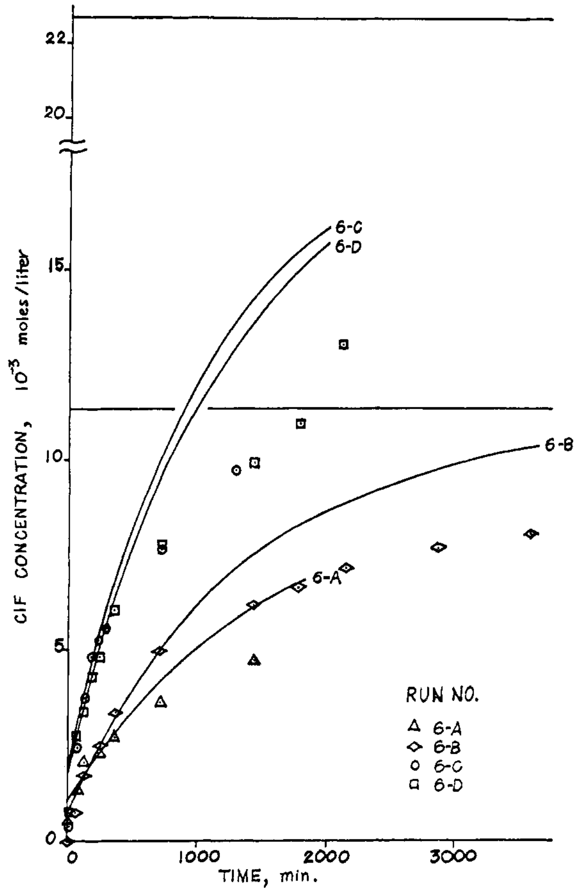

Figure 1. Kinetic data at 80.6°. Horizontal lines are asymptotes.

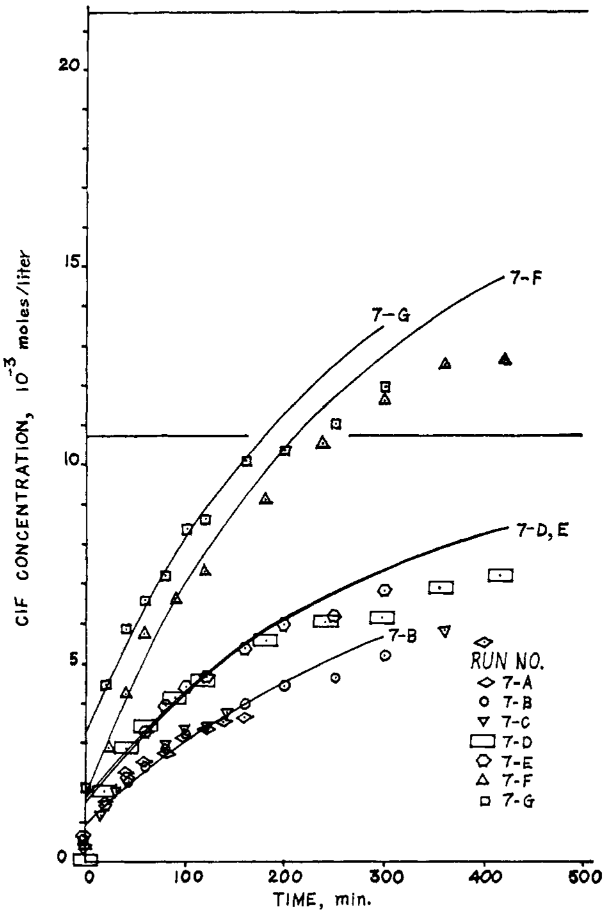

Figure 2. Kinetic data at 100.4°.

The reaction was assumed to have been frozen at the time of sampling inasmuch as it proceeds very slowly at room temperature. The cell was 10 cm long between the windows. The inside diameter was tapered from 3.8 cm at one end to 2.5 cm at the other. The windows were sealed to the aluminum body with gaskets made from Neoprene O rings. This arrangement worked satisfactorily. An analysis usually took about 15 min. On one occasion, a subsequent analysis of a sample made 70 min after the first showed a loss of ClF amounting to only about 9% of the original sample.

The partial pressure of ClF in the sample cell was determined by analysis with a Perkin-Elmer Model 112-U infrared spectrometer using a NaCl prism. Chlorine trifluoride was sought but was not found among the reaction products. The spectrometer was calibrated by a procedure recommended by Downie,[8] *et al.*, using H_2O, CO_2, and NH_3 as calibrating gases. All ClF absorption measurements were made at 784 cm^{-1}. The shape and center of the band were found to depend upon the total sample pressure. Nitrogen was therefore added to raise the total sample pressure to 50 mm. The ClF required for calibrating the procedure was obtained by permitting a mixture of reactants to react at 100° for 9 days. To answer the question about possible variations due to the effects of any particular gas other than nitrogen being used for pressurization, the absorbances of three samples of ClF mixed with Cl_2 were measured and the results compared with the results obtained with N_2 as the added gas. There was no appreciable difference between the two.

The explosion limits of stoichiometric mixtures were measured approximately as part of a preliminary study. The results are given here because they are of interest to anyone contemplating work with this system and because they lend themselves to interpretation by the well-known thermal ignition theory. The mixtures were expanded slowly into the reaction vessel until explosion was observed as measured by a flick on the needle of the pressure gauge. The mixing chamber valve was immediately closed and the pressure subsequently read after the gas had returned to the bath temperature. It is this pressure which is reported as the pressure limit at each temperature. Flames never flashed back to the mixing chamber, evidently because the valve openings are smaller than the quenching diameters.

Results

Rate Studies. Except where otherwise noted, the surface-to-volume ratio in all experiments was 0.321 cm^{-1}. Figure 1 shows the variation of ClF concentration with time for each of four runs at 80.6°. The initial partial pressures (millimeters) of reactants in each of the runs follow. The partial pressure of F_2 is given first in each pair: 6-A, 125, 125; 6-B, 125, 250; 6-C, 250, 250; 6-D, 250, 250. The curves which appear in this figure, and in Figures 2 and 3 as well, are calculated from the kinetic expression which was ultimately selected to describe the results. The agreement is quite good, but the ClF concentration apparently tended to drop off near the end of long experiments. We attribute this observation to the reaction of ClF with water vapor which became absorbed on the walls of the sampling lines when there were long intervals between samples. This discrepancy disappeared when extra care was taken to avoid it or when the time between samplings was short. Figure 2 shows the variation of ClF concentration with time at 100.4°. The partial pressures of reactants are: 7-A, 125, 125; 7-B, 125, 125; 7-C, 125, 125; 7-D, 125, 250; 7-E, 125,

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[8] A. R. Downie, M. C. Magoon, T. Purcell, and B. Crawford, *J. Opt. Soc. Am.*, 43, 941 (1953).

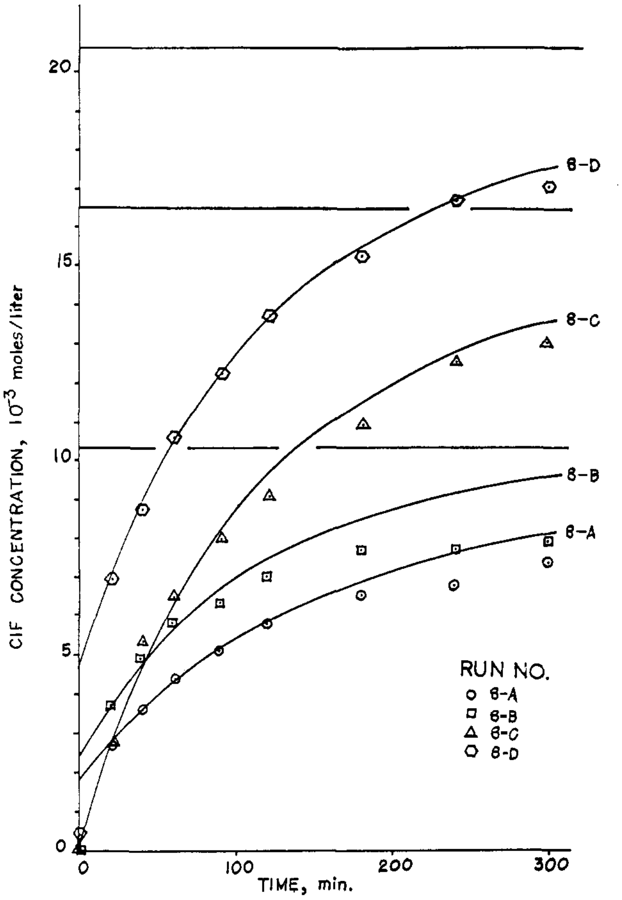

Figure 3. Kinetic data at 115.6°.

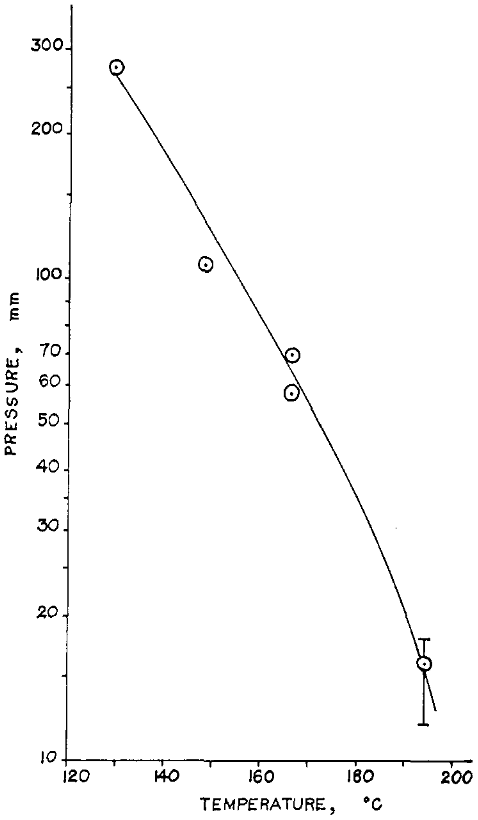

Figure 4. Explosion limits of stoichiometric Cl_2–F_2 mixtures in the cylindrical Monel bomb.

250; 7-F, 250, 250; 7-G, 250, 250. Runs 7-F and 7-G are identical except that in run 7-F the surface-to-volume ratio was doubled to 0.642 cm^{-1} by the addition of Monel wire. As can be seen in Figure 2, the variation of the surface-to-volume ratio had no effect on the kinetics. Run 7-A differs from the others in having had 250 mm of argon added to the reacting mixture. Except for the added argon, this run is identical with runs 7-B and 7-C. As can be seen from the figure, the addition of argon apparently had no effect on the kinetics of the reaction. Figure 3 shows the results of a group of experiments at 115.6°. The partial pressures of the reactants are 8-A, 125, 125; 8-B, 125, 250; 8-C, 200, 200; 8-D, 250, 250. The surface-to-volume ratio in 8-C is 0.642 cm^{-1}. Although it is not evident in this figure, the variation of the surface-to-volume ratio had no apparent effect on the rate of the reaction either. In addition, one experiment was done at 127.8°, in which the partial pressures of the reactants were (125, 125) and the surface-to-volume ratio was 0.321 cm^{-1}.

In all the runs except 8-C, a small amount of ClF formed in the reacting mixtures during their preparation and before sampling could be begun. In run 8-C the reactants were very quickly and vigorously mixed and used immediately. As can be seen in Figure 3, the experimental curve for this run extrapolates back to zero ClF concentration at zero time, lending confidence to our interpretation of the observation.

Explosion limits observed with equimolar mixtures of chlorine and fluorine are shown in Figure 4. The point at 194° may be subject to the error indicated. It was observed during a very rapid addition of the mixture to the reaction vessel.

Interpretation of the Results

Kinetics. The rate equation was assumed to have the form

$$d[ClF]/dt = k[F_2]^a[Cl_2]^b$$

In accordance with standard procedures, the rate equation was integrated for various values of a and b to give the quantity kt as a known function of a, b, the initial concentration of reactants, and the instantaneous concentration of ClF. Plots were then made of kt as determined from these variables *vs.* t. If the correct values of a and b have been chosen, the plot will be a straight line having the slope k. Furthermore, plots for all experiments at the same temperature but having different initial concentrations will be superimposed if the initial concentrations are known. The following sets of (a, b) were tested: $(\frac{1}{2}, \frac{1}{2})$, $(1, \frac{1}{2})$, $(\frac{3}{2}, \frac{1}{2})$, $(2, \frac{1}{2})$, $(1, 1)$. Of these, the set $(1, \frac{1}{2})$ was distinctly superior. It was the only one which superimposed the plots for all tests at a given temperature. For example, Figures 5 and 6 show plots for the kinetic data at 100.4°. Note that in Figure 5, for which $(a, b) = (1, \frac{1}{2})$, what scatter there is is due primarily *not* to different slopes (rate constants) but to different intercepts (zero-time concentrations of ClF). In examining Figure 6, for which $(a, b) = (1, 1)$, one should note that all runs but 7-B are superimposed. Except for run 7-B, all these runs had identical Cl_2 concentrations; only the F_2

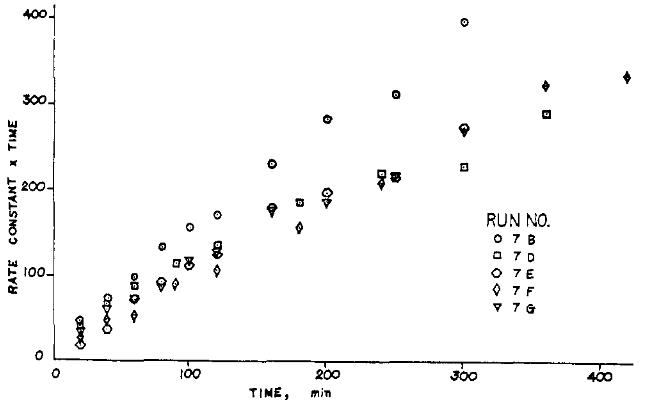

Figure 5. Plot of the integrated form of the rate equation for the case $(a, b) = (1, ^1/_2)$.

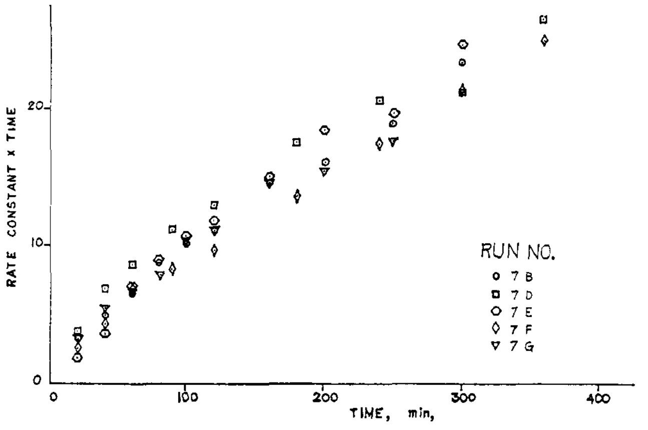

Figure 6. Plot of the integrated form of the rate equation for the case $(a, b) = (1, 1)$.

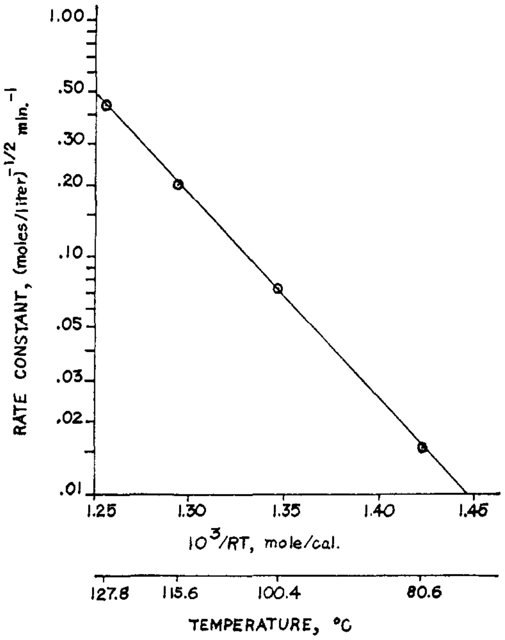

Figure 7. Variation of rate constant with temperature for the reaction $Cl_2 + F_2 \rightarrow 2ClF$.

Table I. Rate Constants for the ClF Reaction

Run	Temp, °C	Initial ClF concn, mol l.$^{-1}$ (est)	k, (l. mol^{-1})$^{1/2}$ min^{-1}
6-A	80.6	0.00104	0.0160
6-B		0.00076	0.0152
6-C		0.00209	0.0154
6-D		0.00185	0.0142[a]
			0.0155 av
7-B	100.4	0.00101	0.0751
7-D		0.00161	0.0746
7-E		0.00147	0.0761
7-F		0.00160	0.0697
7-G		0.00325	0.0727
			0.0736 av
8-A	115.6	0.00178	0.199
8-B		0.00233	0.199
8-C		0.00000	0.203
8-D		0.00452	0.191[a]
			0.200 av
O-A	127.8	0.00226	0.435

[a] Point disregarded in computing average.

concentration was changed. Thus, this plot suggests that the rate is first order with respect to F_2 and less than first order with respect to Cl_2. Detailed results of the tests of the data are available elsewhere.[9] The data at all the temperatures studied are best fitted by the expression $d[ClF]/dt = k[F_2][Cl_2]^{1/2}$.

The rate constants themselves were calculated by first determining the zero-time concentrations from plots which made use of the integrated rate expression. Then, using the zero-time concentration as the boundary condition necessary to integrate the rate expression, the integrated expression was fitted to the earlier data points by the method of least squares to find the best value of k. The curves shown in Figures 1-3 were obtained using these rate constants. Table I gives the rate constants observed at 80.6, 100.4, and 115.6°. It includes, also, the result of one experiment which was carried out at 127.8°. To compute the average values of k at each temperature, we disregarded the results of two experiments, 6-D and 8-D, because their deviations from the averages were large compared with the others.

The activation energy was then determined by application of the Arrhenius equation to the rate constants. The expression $k = k_0 \exp(-E/RT)$ was fitted to the average values of k by the method of least squares. The activation energy is 19,800 cal. The rate constant is given by

$$k = 2.76 \times 10^{10} e^{-19{,}800/RT} \text{ (l. mol}^{-1})^{1/2} \text{ min}^{-1}$$

where R is in cal mol^{-1} deg^{-1}. Figure 7 is a plot of this equation which shows the average k's at each of the four temperatures studied. The fit of the data is quite good. The average deviation of the experimental points from those computed is 2.2%.

The Reaction Mechanism. Most observed reaction rates can be rationalized by several schemes. The one we have chosen to describe here seems to be the most likely first candidate.[10] The reactions which

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(9) B. E. Dahneke, Ph.D. Thesis, University of Minnesota, 1967.

should be considered are the following

$$\mathrm{F_2 + M \xrightarrow{k_1} 2F + M} \qquad \Delta H = 38 \text{ kcal} \qquad \text{(I)}$$

$$\mathrm{F + Cl_2 \xrightarrow{k_2} ClF + Cl} \qquad \Delta H = -3 \text{ kcal} \qquad \text{(II)}$$

$$\mathrm{Cl + F_2 \xrightarrow{k_3} ClF + F} \qquad \Delta H = -23 \text{ kcal} \qquad \text{(III)}$$

$$\mathrm{Cl + F + M \xrightarrow{k_4} ClF + M} \qquad \Delta H = -61 \text{ kcal} \qquad \text{(IV)}$$

$$\mathrm{F + F + M \xrightarrow{k_5} F_2 + M} \qquad \Delta H = -38 \text{ kcal} \qquad \text{(V)}$$

$$\mathrm{Cl + Cl + M \xrightarrow{k_6} F_2 + M} \qquad \Delta H = -58 \text{ kcal} \qquad \text{(VI)}$$

$$\mathrm{Cl + ClF \xrightarrow{k_7} Cl_2 + F} \qquad \Delta H = 3 \text{ kcal} \qquad \text{(VII)}$$

The effect of the back reaction (VII) is to decrease the rate of the reaction because of the increase in product concentration as well as because of the decrease in reactant concentrations. The present data sometimes suggest that this reaction may play a role in the mechanism, but there are enough exceptions to these trends so that we are convinced that the effect is due entirely to experimental error. It is therefore assumed that VII can be neglected. Reactions IV, V, and VI are the chain terminating reactions.

To simplify the remaining set of equations, it is necessary to make order of magnitude estimates of the remaining rate constants and concentrations. The estimates used in the discussion which follows are found in Table II.

Table II. Magnitudes Used in the Synthesis of the Mechanism

Quantity	Units	Magnitude	Source of estimate
k_1	l./mol min	10^{-4}	*a*
k_2	l./mol min	10^{10}	Ref 6[b]
k_3	l./mol min	10^{10}	Ref 6[b]
k_4	(l./mol)^2/min	10^{13}	Comparison with k_5 and k_6
k_5	(l./mol)^2/min	10^{12}	k_1 and equil const
k_6	(l./mol)^2/min	10^{13}	Ref[c] and equil const
[M]	mol/l.	10^{-2}	Ideal gas law
[F$_2$]	mol/l.	10^{-2}	Ideal gas law
[Cl$_2$]	mol/l.	10^{-2}	Ideal gas law

[a] D. J. Seery and D. Britton, *J. Phys. Chem.*, **70**, 4074 (1966). [b] An activation energy of 3 kcal and a preexponential factor of 10^{13} ml/(mol sec) were assumed. [c] R. A. Carabetta and H. B. Palmer, *J. Chem. Phys.*, **46**, 1333 (1967).

In addition, it is necessary to estimate the orders of magnitude of the fluorine and chlorine atom concentrations. Livingston's[11] notation is used in the discussion which follows; *i.e.*, for step i in the mechanism, A + B → C + D, for example

$$v_i \equiv -\mathrm{d[A]/d}t = k_i\mathrm{[A][B]}$$

The steady-state approximation is applied to the concentrations of Cl and F. Thus

$$\mathrm{d[Cl]/d}t = v_2 - v_3 - v_4 - 2v_6 = 0 \qquad (1)$$

and

$$\mathrm{d[F]/d}t = 2v_1 - v_2 + v_3 - v_4 - 2v_5 = 0 \qquad (2)$$

Addition of these two equations and solution for [F] gives

$$[\mathrm{F}] = \frac{(k_4{}^2[\mathrm{Cl}]^2 + 4k_5k_1[\mathrm{F_2}] - 4k_5k_6[\mathrm{Cl}]^2)^{1/2} - k_4[\mathrm{Cl}]}{2k_5} \qquad (3)$$

Subtraction of eq 1 from 2 and solution for [F] gives

$$[\mathrm{F}] = \frac{(k_2{}^2[\mathrm{Cl_2}]^2 + 4k_5[\mathrm{M}](k_1[\mathrm{F_2}][\mathrm{M}] + k_3[\mathrm{Cl}][\mathrm{F_2}] + k_6[\mathrm{Cl}]^2[\mathrm{M}]))^{1/2} - k_2[\mathrm{Cl_2}]}{2k_5[\mathrm{M}]} \qquad (4)$$

From the numbers in Table II and eq 3 and 4, one can estimate the magnitudes of [F] and [Cl]. They are both of the order 10^{-10} mol l.$^{-1}$. Expansion of (4) in a binomial expansion and neglect of higher order terms gives

$$[\mathrm{F}] = \frac{k_1[\mathrm{F_2}][\mathrm{M}] + k_3[\mathrm{F_2}][\mathrm{Cl}] + k_6[\mathrm{Cl}]^2[\mathrm{M}]}{k_2[\mathrm{Cl_2}]} \qquad (5)$$

Equations 3 and 5 can be combined to eliminate [F] and, after elimination of terms of negligible order

$$[\mathrm{Cl}]^2 = \frac{(k_1k_2/k_3k_4)[\mathrm{Cl_2}]}{1 + (k_2k_6/k_3k_4)([\mathrm{Cl_2}]/[\mathrm{F_2}]) + (k_3k_5/k_2k_4)([\mathrm{F_2}]/[\mathrm{Cl_2}])} \qquad (6)$$

The rate equation can be written

$$\mathrm{d[ClF]/d}t = v_2 + v_3 + v_4 \qquad (7)$$

which becomes, using eq 2

$$\mathrm{d[ClF]/d}t = 2v_1 + 2v_3 - 2v_5 \qquad (8)$$

In eq 8, only the $2v_3$ term is significant as can be shown by means of order of magnitude estimates. Thus

$$\mathrm{d[ClF]/d}t = 2k_3[\mathrm{F_2}][\mathrm{Cl}] \qquad (9)$$

Substitution for [Cl] from eq 6 gives

$$\mathrm{d[ClF]/d}t = \frac{2(k_1k_2k_3/k_4)^{1/2}[\mathrm{F_2}][\mathrm{Cl_2}]^{1/2}}{\{1 + (k_2k_6/k_3k_4)([\mathrm{Cl_2}]/[\mathrm{F_2}]) + (k_3k_5/k_2k_4)([\mathrm{F_2}]/[\mathrm{Cl_2}])\}^{1/2}} \qquad (10)$$

According to the estimates in Table II, (k_3k_5/k_2k_4) is of the order 10^{-1}. The term (k_2k_6/k_3k_4) is of the order unity. However, it may be less, since k_2 is associated with the breaking of a stronger bond than is k_3, and k_6 may be less (and k_5 much less) than k_4. A value of this ratio as large as 0.25 could have been masked by experimental error since it would have corresponded to a small variation in the rate constant. If the last two terms in the denominator on the right-hand side of eq 10 are small, it becomes identical with the observed result where

$$k = 2(k_1k_2k_3/k_4)^{1/2} \qquad (11)$$

The rate of the reaction now becomes

$$\mathrm{d[ClF]/d}t = 2.76 \times 10^{10}e^{-19{,}800/RT}[\mathrm{F_2}][\mathrm{Cl_2}]^{1/2} \qquad (12)$$

One additional point is worth making, since it supports the proposed mechanism. The rate constants of the elementary reactions can be expressed in the Arrhenius form. It thus follows from eq 11 that the activation

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(10) We are greatly indebted to R. S. Brokaw, who, in a private communication, suggested the essential features of this mechanism as a result of the conversation with E. A. F.

(11) R. Livingston in "Technique of Organic Chemistry," Vol. VIII, S. L. Freiss and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1953, Chapter 1, Part 5.

energy for the over-all reaction should be given by

$$E = (E_1 + E_2 + E_3 - E_4)/2 \qquad (13)$$

where the subscripted E's are the activation energies of the corresponding elementary reactions. These energies are known or can be estimated. Thus, E_1 is about 28 kcal.[12] Both E_2 and E_3 can be estimated to be about 3 kcal. Finally, E_4 is expected to be very small.[13] These estimates predict an apparent activation energy of 17 kcal, which is satisfactorily close to the experimental value of 19.8 kcal.[13a]

Explosion Limits. The thermal explosion theory of Semenov as described in detail by Khitrin[14] and Vulis[15] lends itself nicely to the interpretation of the experimentally observed explosion limits. In a reacting mixture in which Q is the heat of reaction, the rate of heat generation in volume V is given by $q_a = QWV$ where W is the reaction rate per unit volume, k_0c^m exp $(-E/RT)$. Thus

$$q_a = QVk_0c^me^{-(E/RT)} \qquad (14)$$

where c is the appropriate concentration term and m is the order of the reaction. The heat loss rate from the reacting mixture is given by

$$q_b = hA(T - T_w) \qquad (15)$$

where h is a heat transfer coefficient and T_w is the temperature of the container walls. The limiting condition for an explosion to occur is that the rate of heat generation equal the rate of heat loss and that their variations with temperature be equal; *i.e.*, $q_a = q_b$ and $dq_a/dT_w = dq_b/dT_w$. If these criterions are applied and the relation $c^m = [F_2][Cl_2]^{1/2}$ is used, application of the ideal gas law gives, neglecting higher order terms

$$\ln (p^{3/2}/T_w^{7/2}) = E/RT_w - \ln (QVk_0E/2.82hAR^{5/2}) \qquad (16)$$

Since the second term on the right-hand side of (16) is a constant, a plot of ln $(p^{3/2}/T_w^{7/2})$ *vs.* $1/RT_w$ for the limit should give a straight line with a slope of E. Such a plot is shown in Figure 8. The best least-squares estimate of the activation energy from the data points is 25 kcal. However, in view of the simplicity of the technique used for its determination and the many simplifying assumptions made in the formation of the theory and its application to the computation of activation energy, we would regard the value obtained from the rate studies as being more meaningful.

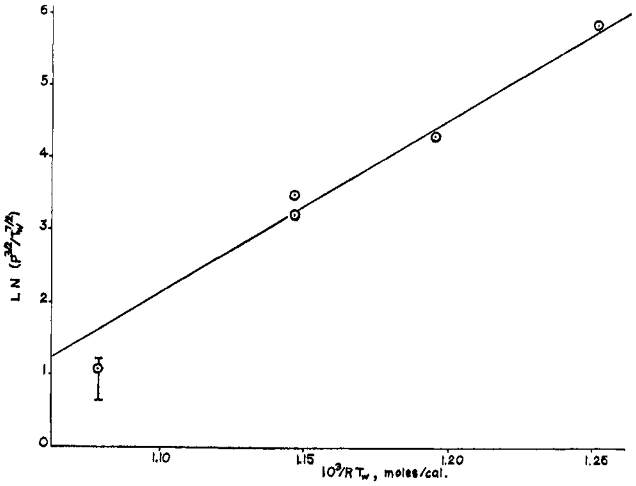

Figure 8. Plot of ln $(P^{2/3}/T_w^{7/2})$ *vs.* $10^3/RT_w$ for the experimentally observed spontaneous ignitions.

Discussion

The results of the present study suggest that the unusual behavior of Cl_2–F_2 flames is indeed due to an unexpected dependence of reaction rate on reactant concentrations. The kinetics are different from those predicted by Noyes[6] using an empirical method for selecting which mechanism will prevail in reactions between diatomic molecules and must thus be considered to be a portion of the "body of experimental evidence that does not yet exist" called for by that author. Evidently, for this small portion, the method has failed. It does suggest, however, that there are many new things to be learned about kinetics and combustion from studies of this interesting system.

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(12) D. J. Seery and D. Brillon, *J. Phys. Chem.*, 70, 4074 (1966).

(13) O. K. Rice, "Statistical Mechanics, Thermodynamics, and Kinetics," W. H. Freeman, & Co., San Francisco, Calif., 1967, Chapters 18 and 19.

(13a) NOTE ADDED IN PROOF. If a recently published value (W. Stricker, *Z. Naturforsch.*, **22a**, 1137 (1967)) of the dissociation energy of fluorine, 33.2 kcal, is taken for E_1, the apparent activation energy computed from eq 13 is 19.6 kcal. We are grateful to Professor M. L. Bernard of the University of Portiers for calling our attention to this paper.

(14) L. N. Khitrin, "Physics of Combustion and Explosion," translated for the National Science Foundation, Washington, D. C., by the Israel Program for Scientific Translations, Jerusalem, 1962.

(15) L. A. Vulis, "Thermal Regimes of Combustion," translated by M. D. Friedman, McGraw-Hill Book Co., Inc., New York, N. Y., 1961.