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Abstract

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Elementary Reactions of Molecular Fluorine

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Molecular fluorine differs from the other halogens in its enormous reactivity. This is connected with the great affinity of fluorine for hydrogen, carbon, and metals. The bond energies C—F, H—F, Me—F exceed 100 kcal/mole, whereas the energy of the F—F bond in the molecule F_2 is only about 40 kcal/mole. This leads to a number of peculiarities in the reactions of molecular fluorine. Thus, reactions of F_2 with formation of atoms and radicals of the type

$$F_2 + RH \rightarrow F\cdot + HF + R\cdot, \tag{1}$$

$$F_2 + C = C \rightarrow F\cdot + F - C - C\cdot \tag{2}$$

do not require an expenditure of heat, or are even exothermic, and the activation energy of these reactions must be small (*1*). The possibility of such reactions was confirmed in Miller' s work (*2*).

The chain-propagation reactions:

$$R\cdot + F_2 \rightarrow RF + F\cdot, \qquad F + RH \rightarrow HF + R\cdot$$

are extremely exothermic and proceed practically without activation energy (*3*). The enormous release of energy in these reactions may lead to branching in the chain reactions of molecular fluorine (*4*) and, consequently, to an explosive character of the reactions. Finally, rapid processes with large heat evolution may be the cause of a thermal explosion.

In the present work we give the principal results of a series of investigations on the kinetics and mechanism of elementary reactions of types (1) and (2).

As we have already reported (*5*), at liquid-nitrogen temperatures gaseous fluorine forms free radicals upon interaction with frozen olefins, evidently in reactions of type (2).

The temperature at which these reactions occur indicates their low activation energy. This was confirmed by direct kinetic measurements. The reaction rate, determined from the decrease in fluorine pressure over frozen olefins with a thermocouple vacuum gauge, proved too high to measure in the case of ethylene and divinyl.

For chlorine-substituted ethylenes the reaction rate decreases; moreover, according to the rates of interaction with F_2, the olefins are arranged in the following series (Fig. 1):

$$C_2H_4 > C_2H_3Cl > C_2H_2Cl_2 > C_2HCl_3 > C_2Cl_4.$$

The most detailed kinetic study was carried out for trichloroethylene, to which addition of F_2 proceeds at a measurable rate.

Special measurements of the surface area of the frozen olefin by the BET method before the reaction showed that the number of F_2 molecules absorbed by the olefin at $-196°$ is almost exactly equal to the number of olefin molecules located on the surface. Thus, at this temperature there occurs

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Fig. 2

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Fig. 2. **A** –photographic recording of the propagation of the flame front in acetylene at $P = 3.5$ atm (flame motion from right to bottom to left); **B** – oscillogram of the ionization current.

only a surface reaction occurs. As the temperature is raised, deeper layers also begin to react.

Measurement of the temperature dependence of the reaction rate of C_2HCl_3 in the interval from -196 to $-163°$ showed that the activation energy of this reaction is only about 0.5 kcal/mole. This means that for olefins with a smaller number of Cl atoms in the molecule, in particular for ethylene, the activation energy should be close to zero.

At the same time, measurements were made of the rates of reaction of molecular fluorine with gaseous ethylene by the diffusion-flame method. Kistiakowsky' s method (6) was used, based on measuring the temperature in the zone of a diffusion flame, formed in our case when small amounts of fluorine are admitted into a stream of olefin. In this case one might expect the formation of chains according to the scheme:

$$F_2 + C_2H_4 \to FCH_2{-}CH_2\bullet + F\bullet, \qquad (I)$$

$$F\bullet + C_2H_4 \to F{-}CH_2{-}CH_2\bullet^*, \qquad (II)$$

Fig. 1

Figure 1: Fig. 1

$$FC_2H_4\bullet + F_2 \rightarrow C_2H_4F_2 + F\bullet, \qquad \text{(III)}$$

$$2C_2H_4F\bullet \rightarrow C_4H_8F_2. \qquad \text{(IV)}$$

The activation energy of reactions (II) and (III) is probably negligible, but if reaction (I) also proceeds with a low activation energy, then the main consumption of F_2 will take place in reaction (I), and then the chain will degenerate into a radical process (reactions (I), (II), and (IV)) at a rate determined by reaction (I). An approximate calculation shows that, with a large excess of ethylene, reaction (III) can be neglected even if reaction (I) proceeds with an activation energy of several kilocalories (up to 7-9 kcal/mole). This considerably broadens the possibilities of the diffusion-flame method.

Fig. 1

The results of experiments with ethylene showed that at jet pressures of 10–20 mm and ratios $F_2/C_2H_4 \sim\sim 1/100$ the reaction is first order with respect to F_2 and C_2H_4, and the rate constant changes hardly at all when oxygen is added to the stream. These data indicate the radical (and not chain) character of the reaction.

Measurements in the temperature interval from +20 to +200°C gave for the rate constant of the reaction of F_2 with ethylene (reaction (I)) the value

$$7 \cdot 10^{-13} e^{-6000/RT} \text{ cm}^3/\text{sec}.$$

Noteworthy is the fact that the activation energy, although small enough for a chain process not to develop, is nevertheless appreciably greater than the activation energy of the reaction of F_2 with olefins on a surface. This is possibly explained by the fact that in the latter case the radical formed proves to be more firmly bound to the surface than the initial molecule, which leads to an additional energy gain.

To investigate the kinetics of a reaction of the type $F_2 + HR \rightarrow F\bullet + HF + R\bullet$, we chose the interaction of F_2 with hydrogen iodide, the first stage of which, if it proceeds by the mechanism $F_2 + HJ \rightarrow F\bullet + HF + J\bullet$, is exo-

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* In reaction (II), 55 kcal/mole is liberated. This may lead to ejection of an H atom from the radical $C_2H_4F^*$: $C_2H_4F^* \rightarrow C_2H_3F + H - 38$ kcal. Then, in

an excess of ethylene, the H atom forms the ethyl radical $H + C_2H_4 \to C_2H_5\bullet$. Subsequent reactions of C_2H_5 will be analogous to the reactions of $C_2H_4F\bullet$.

thermal by 27 kcal/mol. The reaction of F_2 with HJ is accompanied by a bright glow. A study of the spectrum of this glow showed that it coincides completely with the known emission spectrum of excited FJ* molecules ([7]). The stable products of the reaction of F_2 with excess HJ are molecular iodine and hydrogen fluoride.

The formation of the glow made it possible to use it to measure the reaction rate by means of a modification of the diffusion-flame method ([8]), in which the rate constants are determined from the positions of equal blackening on photographs of flames taken with different exposure times. Fig. 2 shows the photographs from which the constants were determined. In these experiments fluorine was fed through a nozzle into a stream of hydrogen iodide. The HJ pressure in the stream was 10 mm. The ratio $F_2/HJ = 0.05$.

At the same time the kinetics was measured from heating in a diffusion flame under other stream conditions ($P_{HJ} = 6$ mm; $F_2/HJ = 0.003$).

The rate constants measured at room temperature by the first and second methods proved to be $2 \cdot 10^{-16}$ and $1 \cdot 10^{-16}$ cm^3/sec. The good agreement of the constants obtained by different methods under different stream conditions shows that the rates of luminescence and of heat evolution are limited by one and the same process. We believe that this process is the reaction $HJ + F_2 \to F\cdot + HF + J\cdot$, followed by the reactions:

$$F \cdot + HJ \to HF + J\cdot, \qquad F \cdot + F + M \to FJ^* + M, \qquad J \cdot + J \cdot + M \to J_2 + M.$$

Measurement of the rate constant in the range 295–513° K led to the following value of the constant:

$$K = 5 \cdot 10^{-14} e^{-3500/RT} \text{ cm}^3/\text{sec}.$$

Investigation by the diffusion-flame method of the reactions F_2 with CH_4 and F_2 with HCl showed that these reactions, under similar conditions, are not registered at all, i.e., the elementary processes

$$F_2 + HCl \to F \cdot + HF + Cl \cdot \quad CH_4 + F_2 \to F \cdot + HF + CH_3\cdot$$

require considerable activation energies.

The reactions with HCl and CH_4 are practically thermoneutral, which distinguishes them from the strongly exothermic reactions of fluorine with olefins and HJ. These data once again indicate the existence of a relation between activation energy and heat effect, evidently similar to Polanyi' s rule for radical reactions.

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CITED LITERATURE

1. N. N. Semenov, *On Certain Problems of Chemical Kinetics and Reactivity*, Moscow, 1958.
2. W. T. Miller, A. L. Dittman, *J. Am. Chem. Soc.*, **78**, 2793 (1956); W. T. Miller, S. D. Koch, T. W. McZafferty, *J. Am. Chem. Soc.*, **78**, 4992 (1956); W. T. Miller, S. D. Koch, *J. Am. Chem. Soc.*, **79**, 3084 (1957).
3. G. C. Fettis, J. H. Knox, A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 1064.
4. V. I. Vedeneyev, A. M. Chaikin, A. E. Shilov, *Kinetics and Catalysis*, **4**, No. 2 (1963).
5. G. A. Kapralova, A. E. Shilov, *Kinetics and Catalysis*, **2**, No. 3, 362 (1961).
6. D. Garvin, V. P. Guinn, G. B. Kistiakowsky, *Disc. Farad. Soc.*, No. 17, 32 (1954).
7. R. A. Durie, *Proc. Roy. Soc.*, **207**, 388 (1951).
8. D. Rapp, G. S. Jonston, *J. Chem. Phys.*, **33**, 695 (1960).

Note: Figure translations are in progress. See original paper for figures.