

Experimental

A cell with hanging cadmium amalgam drop⁹ was utilized. The drop falling from a dropping amalgam electrode was collected in a small glass spoon and then, by rotation of the spoon, suspended on a gold-plated platinum tip. This method of collecting drops was found much easier to apply than the one in which drops are collected in a spoon attached to the capillary dropping amalgam electrode as recommended by Gerischer. A large pool of cadmium amalgam served as reference electrode. The amalgam was prepared by dissolution of fine cadmium turnings in mercury in a nitrogen atmosphere. The same amalgam was used for the pool and the hanging drop electrode.

The cell was connected to two resistances R_1 and R_2 in series. The calibrated and adjustable resistance R_1 was

(9) H. Gerischer, *Z. physik. Chem.*, **202**, 302 (1953); see also ref. 4.

connected to a Tektronix cathode-ray oscilloscope model 531 with 53D preamplifier. Resistance R_2 (a few ohms; not critical) across which the voltage increment of 2–5 mv. was set up was connected to a 1.5 volt battery with a suitable resistance in series. Resistance R_2 was normally short-circuited by a *good* switch, which upon opening thus caused the voltage applied to the cell to vary by a few mv. Toggle switches were not adequate because vibrations in the switch caused transients, whereas switches with blades did not have this defect.

The preparation of solution, the deaeration by nitrogen, and the recording of current-time curves followed conventional practice.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY]

The Kinetics of the Reaction of Fluorine with Iodine Pentafluoride to Form Iodine Heptafluoride¹

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The kinetics of the vapor phase reaction of fluorine with iodine pentafluoride to form iodine heptafluoride has been studied from 55.6 to 95°. The rate of the reaction was found to be second order with respect to the reactant pressures. The rate constants showed an Arrhenius temperature dependence, with an activation energy of 14 kcal. per mole. The reaction was homogeneous, suggesting that the rate-determining step is a bimolecular collision.

The preparation of iodine pentafluoride^{2a} and iodine heptafluoride^{2b} had been described by Ruff. The authors suggested that the reaction of iodine pentafluoride and fluorine, in the temperature region of 100 to 270°, resulted in an equilibrium mixture of the pentafluoride and the heptafluoride. Experimental limitations prevented them from observing whether complete conversion of the pentafluoride was possible.

This investigation was undertaken to establish the stoichiometry and kinetics of the reaction, and to obtain some insight of the mechanism involved.

Experimental

Materials.—Iodine pentafluoride was prepared by the direct combination of fluorine and reagent grade resublimed iodine in a reaction vessel at 0°, at which temperature very little iodine heptafluoride was formed. The reaction vessel was cooled to the temperature of liquid nitrogen and the excess fluorine was distilled off at a pressure less than 10 μ . After the vessel had been warmed to 0°, traces of iodine heptafluoride and fluorine were removed by a partial distillation of the iodine pentafluoride from the reaction vessel. The purity of the iodine pentafluoride was indicated by a constant vapor pressure (269.8 \pm 0.8 mm.) at 75° before and after distillation of half its volume from the reaction vessel. As indicated in the experimental data, the apparent molecular weight given by gas density measurements was close to the formula weight. The vapor pressure of the iodine pentafluoride was found to be 116.4 mm. at 55°, which is in substantial agreement with the value of 119.9 and 120.0 mm. reported by Ruff^{2a} and Rogers,³ respectively.

Commercial high-purity fluorine gas was used after it had been assayed for purity by the method of Aoyama and Kanda.⁴ This method, which employs the quantitative reaction of fluorine with mercury, indicated a purity in ex-

cess of 99% by volume. It was also shown to contain less than 0.5% of impurities by its quantitative reaction with bromine.⁵

Apparatus.—The apparatus consisted of a manifold made from welded 3/4-inch nickel tubing, a cylindrical 575.8-ml. nickel reaction vessel, and a similar 573-ml. storage and metering vessel. The vessels were attached to the manifold by 3/4-inch flare connectors, which were sealed with Teflon gaskets. A 25-ml. Fluorothene (polychlorotrifluoroethylene) tube, which contained the iodine pentafluoride, was similarly joined to the manifold. The components were separated by Hoke No. 1197 bellows-type valves, which are made of Monel with Teflon seats.

Pressure transmitters, which are described later, were attached directly to the reaction and metering vessels. The apparatus was contained in a forced-air thermostated box, and joined to an external nickel manifold which was equipped with liquid nitrogen cold traps, a high vacuum pump, and gas supplies of fluorine and helium.

The pressures in the system were measured with well-type mercury manometers, employing Booth-Cromer pressure transmitters⁶ with self-balancing relays. Thin nickel diaphragms, which serve as sensing elements in this instrument, separated the vapor in the system from the mercury manometer balancing system, which contained only nitrogen. Very low pressures were measured with a thermocouple gage tube attached to the manifold in the constant temperature box.

The temperatures of the vapor in the apparatus were obtained from copper-constantan thermocouples inserted so as to be in contact with the bottom of nickel thermocouple wells in the reaction and metering vessels. A Rubicon Type B potentiometer was used, and the thermocouples were calibrated to 0.01° with a standard platinum resistance thermometer, employing a Leeds and Northrup G-2 Mueller bridge.

The time was measured with an electric timer which could be read to 0.01 minute.

Procedure.—The rate of the reaction was obtained from the change in total pressure, with time, after known partial pressures of the reactants were mixed in the reaction vessel.

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) O. Ruff and A. Braid, *Z. anorg. allgem. Chem.*, **220**, 43 (1934); (b) O. Ruff and R. Keim, *ibid.*, **193**, 176 (1930).

(3) M. Rogers, *et al.*, *THIS JOURNAL*, **76**, 4843 (1954).

(4) S. Aoyama and E. Kanda, *Bull. Chem. Soc. Japan*, **12**, 409 (1937).

(5) J. Fischer, R. C. Vogel and J. Bingle, *THIS JOURNAL*, **78**, 902 (1956).

(6) S. Cromer, "The Electronic Pressure Transmitter and Self-Balancing Relay," SAM Laboratories, Columbia University, MDDC-803, 1947.

Iodine pentafluoride vapor was added to the vessel first, and its pressure was obtained. Fluorine was then added from the metering vessel and its partial pressure in the reaction vessel was calculated from the pressure decrease in the metering vessel. The volume factors between the vessels were measured, using both helium and fluorine individually.

Since the measurements were all based on pressure data, it was necessary to show that the concentrations were related to the pressures by the ideal gas law. Vapor densities of iodine pentafluoride and iodine heptafluoride were determined by measuring the pressure of weighed amounts of the materials added to a vessel of known volume at a fixed temperature. Iodine pentafluoride at temperatures around 80° and pressures of 200 to 250 mm. gave an average value of 224.3 ± 1.5 g./G.M.V. (formula weight, 221.9 g./mole). The heptafluoride at 28° and over a pressure range of 129 to 258 mm. gave a value of 260.9 ± 2.0 g./G.M.V. (formula weight, 259.9 g./mole). The same cylinder of fluorine had been shown previously⁷ to exhibit ideal behavior (gas density, 38.00 ± 0.15 g./G.M.V.; formula weight, 38.00 g./mole). Thus, all three gases were considered ideal within the over-all accuracy of the measurements.

Before meaningful rate determinations could be made, the stoichiometry of the reaction had to be demonstrated. The data in Table I indicate that the reaction $\text{IF}_5 + \text{F}_2 \rightarrow \text{IF}_7$ occurs quantitatively within the temperature range of these experiments. Physical separations or chemical analyses of the reactants and products in this system are difficult. In order to confirm the quantitative nature of the reaction, an additional experiment was performed. At the conclusion of the second experiment in Table I, the mixture in the reaction vessel was cooled with liquid nitrogen, and the system was evacuated to remove the residual fluorine. When the system was warmed to 75.3°, an observed total pressure of 103.6 mm. was in good agreement with the theoretical yield of 101.2 mm. of iodine heptafluoride.

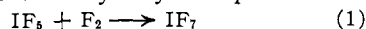
TABLE I
STOICHIOMETRIC BEHAVIOR OF THE REACTION $\text{IF}_5 + \text{F}_2 \rightarrow \text{IF}_7$

Temp., °C.	Initial pressures, mm. F ₂	Initial pressures, mm. IF ₅	Final pressure, mm.	Elapsed time, min.
55.7	562.1	99.4	563.6	1402
75.0	575.2	101.2	574.2	197
85.7	560.2	102.4	561.5	1098

Therefore, it was possible to calculate the partial pressures of the reactants at any time during the reaction from the difference in the total initial pressure and the total pressure at that time.

Results and Discussion

The reaction under study may be expressed as



If the product results from the homogeneous bimolecular interaction of iodine pentafluoride and fluorine molecules, the rate of the reaction will be second order with respect to the partial pressures of the reactants. It may then be expressed as

$$\frac{d[\text{F}_2]}{dt} = k[\text{IF}_5][\text{F}_2] \quad (2)$$

or as

$$\frac{dx}{dt} = k(a-x)(b-x) \quad (3)$$

a and b = initial reactant concn. in mm.

x = decrease in reactant concn. at time t

k = second-order rate constant

The integrated expression is

$$t = \frac{2.303}{k(a-b)} \log \frac{b}{a} + \frac{2.303}{k(a-b)} \log \frac{a-x}{b-x} \quad (4)$$

A plot of t against $\log (a-x)/(b-x)$ would be linear. When $a = b$, the integrated equation becomes

$$t = \frac{1}{k(a-x)} - \frac{1}{ka} \quad (5)$$

and a plot of t against $1/(a-x)$ is linear. When a and b are approximately equal, and d is the mean initial concentration of the reactants

$$\frac{1}{d-x} - \frac{1}{d} = kt \quad (6)$$

In this case, a plot of $1/(d-x)$ against t would be linear. Graphical methods were employed to ob-

TABLE II
SECOND-ORDER RATE CONSTANTS FOR THE REACTION $\text{IF}_5 + \text{F}_2 \rightarrow \text{IF}_7$

Expt.	Temp., °C.	Initial pressures, mm. F ₂	Initial pressures, mm. IF ₅	Rate constant, $k \times 10^3$ (mm. ⁻¹ hr. ⁻¹)
1	55.6	99.5	98.8	2.02
2	55.6	106.0	99.4	2.02
3	55.6	99.8	99.6	2.01
4	55.7	562.1	99.4	2.01
5	55.7	560.8	99.5	2.07
6	65.0	100.8	100.1	3.86
7	65.0	99.7	100.0	3.97
8	65.0	299.0	99.6	3.75
9	65.0	299.5	99.5	3.77
10	65.0	569.0	100.0	3.63
11	65.0	568.7	99.6	3.65
12	69.8	100.2	100.0	5.03
13	75.3	99.6	99.8	6.94
14	75.3	100.8	100.2	6.79
15	75.3	298.3	99.5	6.93
16	75.3	575.0	101.0	7.09
17	80.3	99.8	99.8	8.57
18	85.1	100.5	100.4	10.5
19	85.1	99.7	99.8	11.9
20	85.1	100.1	99.7	12.1
21	85.1	299.8	99.4	10.6
22	95.0	100.6	101.1	18.9

tain the rate constant as a function of the parameter of the appropriate eq. 4, 5 and 6.

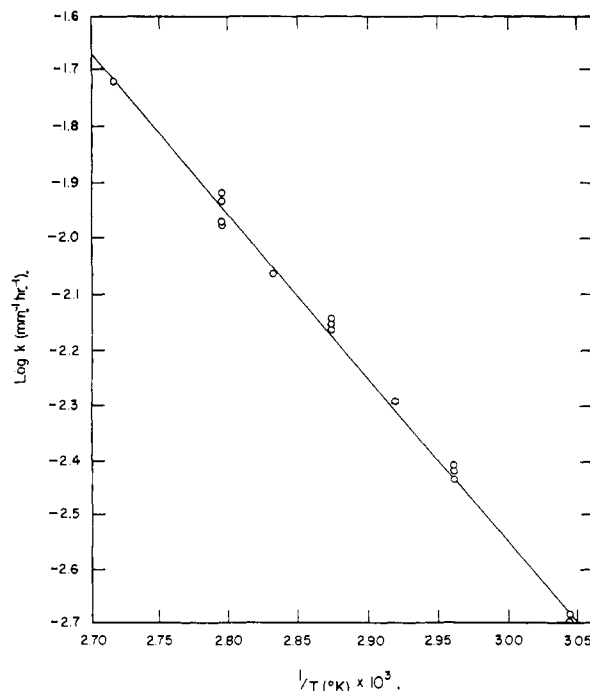


Fig. 1.—Determination of the activation energy.

(7) R. K. Steunenberg and R. C. Vogel, THIS JOURNAL, 78, 90 (1956).

The rate data obtained from the experiments are given in Table II. The initial partial pressures of the reactants are given to show the variations in the initial pressures used. The pressures were assumed to be reliable to ± 0.2 mm. and the temperatures to $\pm 0.05^\circ$. The rate constants, in dimensions of $(\text{mm.}^{-1})(\text{hr.}^{-1})$, were computed from the slopes of lines drawn through the plotted data.

In experiment 7, the surface area of the reaction vessel was increased by a factor of about five by placing nickel wire mesh in it. The volume change was negligible. In experiments 3, 5 and 9, another reaction vessel of approximately twice the original volume was used. The fact that variations in the surface and volume had no effect on the rate in-

dicates homogeneous behavior of the reaction.

The activation energy for the reaction was determined by plotting the logarithm of the rate constant against the reciprocal absolute temperature as shown in Fig. 1. The activation energy calculated from the slope of the line is 14 kcal. per mole. This activation energy is a reasonable value for a homogeneous bimolecular reaction. The linear nature of this plot is in accord with a reaction of this type.

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

The Photolysis of Ketene at 3650 Å. in the Presence of Oxygen¹

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The photolysis of ketene at 3650 Å. was investigated in the presence of oxygen. Even at low concentrations, oxygen virtually eliminates the dissociation of ketene into carbon monoxide and methylene radicals at room temperature. There is a direct reaction of oxygen with excited ketene molecules which leads to carbon monoxide and carbon dioxide among the products, but which gives very little ethylene. Within experimental error, the quantum yield of formation of carbon monoxide is equal to that of oxygen consumption. All quantum yields are small and the principal reaction of oxygen is deactivation of excited ketene molecules. At low oxygen concentrations, the quantum yields, with the exception of that of ethylene, show maxima at about 5×10^{-6} mole of oxygen/liter (about 0.1 mm. pressure). At 160°, there is an intensity dependent chain reaction with oxygen.

The photochemistry and photooxidation of ketene have been studied extensively at wave lengths near 2700 Å.^{3,4} At these wave lengths, dissociation into methylene radicals and carbon monoxide occurs with a quantum yield of unity. At 3650 Å., near the long wave length limit of absorption, the quantum yields are small and are functions of pressure. This effect has been interpreted to mean that electronically excited ketene molecules are formed. The excited ketene molecules may in turn dissociate, internally convert or suffer collisional deactivations.^{3,5,6}

In the presence of oxygen at 2700 Å., the products include carbon monoxide, carbon dioxide, formaldehyde and ethylene.^{3,4} The ethylene quantum yield is reduced somewhat by the addition of oxygen, but does not fall below 0.67.

At about 1 mm. of oxygen, the products are formed in different ratios at 3650 Å. compared with those formed at 2700 Å.³ Since the photolysis of ketene at 3650 Å. almost certainly involves the formation of electronically excited molecules, the

difference in the ratios of products at these two wave lengths may be interpreted as reaction of oxygen with excited molecules at the longer wave length, rather than with radicals as at the shorter wave length.⁷

The photooxidation at 3650 Å. has now been studied in some detail. Only two other examples of oxygen-excited molecule reaction have appeared in the literature.^{8,9} One of these⁸ is somewhat ambiguous. This study may aid in interpretation of the photochemical decomposition of pure ketene and of the various electronic states that are formed.

Experimental

The experimental procedure and apparatus have been described.^{3,4} The 3650 Å. lines from a British Thomson-Houston Hg lamp ME/D 250 watt were isolated on the short wave length side by a Corning filter #7380 and on the long wave length side by the rapid decrease in absorption coefficient of ketene. A cylindrical quartz cell with a volume of 78 ml. was enclosed in an electrically heated brass block and was connected to a magnetically driven centrifugal stirrer to circulate the gases in the cell. In the work at low oxygen concentrations, a 1-liter bulb was included in the cell-stirrer system and oxygen was dosed into the cell at frequent intervals to avoid serious oxygen depletion.

The dosing technique is somewhat different than that previously employed^{3,4} in that a sample of oxygen was measured into the Toepler-McLeod gage,³ then part of this was pumped into the cell. This amount and the amount of further additions during a run were determined by measuring the remaining oxygen in the Toepler-McLeod gage. Thus the oxygen concentration during a run could be calculated after the rate of oxygen consumption had been measured. The rate of addition of oxygen was determined by trial and error.

(1) This work was supported in part by contract with the Office of Naval Research, United States Navy, and the Chemistry Division, Air Force Office of Scientific Research, United States Air Force. The material in this article may be reproduced or used in any way by the United States Government.

(2) Postdoctoral fellow 1954-1956 under a grant from the Shell Fellowship Committee. Department of Chemistry, University of British Columbia, Vancouver, Canada.

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