of CF_3PBr_2. The low yield of PBr_3 again is to be ascribed to the condition of the stopcocks: with time there is an increase in the amount of grease squeezed out into the space available to the vapors, and a trace of bromine in the grease makes it especially effective for absorbing PBr_3.

The Bromine-transfer Reaction (6).—A 0.242 mmole sample of CF_3PBr_4 was made by mixing equimolar portions of CF_3PBr_2 and Br_2, which reacted completely within a few minutes at 0°. Then 0.311 mmole of PBr_3 (m.p. $-39.2°$; reported value, $-40.0°$) was added and the mixture was heated for 30 min. at 35°. Now it was possible to isolate 0.03 mmole of CF_3Br and 0.212 mmole of CF_3PBr_2 (volatility 22.8 mm. at 0°; known, 22.6 mm.). The remaining mixture weighed 118.2 mg.; calcd. as $PBr_3 + PBr_5$, 118.7 mg. The PBr_5 appeared as a lemon-yellow solid even at 45° and could be sublimed *in vacuo* at room temperature, along with the distilling PBr_3.

Tris-(trifluoromethyl)-phosphine with Bromine.—Equimolar samples of $(CF_3)_3P$ and Br_2 were brought together by condensation at $-196°$ and warmed to room temperature. The initially immiscible liquids reacted slowly to form a single colorless liquid, having the composition of the formula $(CF_3)_3PBr_2$. In the initial experiment this product was heated for 18 hr. at 80°, with results roughly summarized by the over-all empirical equation

$$8(CF_3)_3PBr_2 \longrightarrow 8CF_3Br + CF_3PBr_2 + 3(CF_3)_2PBr + 3(CF_3)_3P + PBr_3$$

This experiment was regarded as tentative because the fraction representing the $(CF_3)_2PBr$ and $(CF_3)_3P$ was not fully resolved; however, the weight of this fraction, taken with the accurately observed yields of CF_3Br and CF_3PBr_2, required this equation for a correct material balance.

A considerably more accurate experiment began with 1.008 mmole of $(CF_3)_3P$ and 1.005 mmole of Br_2. A 9-hr. heating at 90° yielded a mixture which was resolved, by high-vacuum fractional condensation, into the four fractions:

(a) CF_3Br, 150.0 mg. (1.007 mmoles); mol. wt. 148.8 (calcd., 148.9); 252.3 mm. at $-78.5°$ (calcd., 252.0 mm.).

(b) $CF_3PBr_2 + PBr_3$, 43.7 mg. (0.165 mmole by rough volume msmt.). This was hydrolyzed in 15% NaOH (30 hr. at 100°) to give 11.1 mg. of HCF_3 (0.159 mmole; mol. wt. 69.8 *vs.* calcd., 70.0); then a Volhard determination of bromide in acid solution showed 0.338 meq. Hence the fraction seemed to consist of 0.159 mmole of CF_3PBr_2 with 0.007 mmole of PBr_3.

(c) $(CF_3)_2PBr + (CF_3)_3P$, 180.5 mg. (0.749 mmole by volume). An analysis as in (b) gave 1.752 mmoles of HCF_3 and 0.320 meq. of Br^-; however, these results would imply only 0.371 mmole of $(CF_3)_3P$ and 0.320 mmole of $(CF_3)_2PBr$, falling short of the observed 0.749 mmole for the two together.

(d) PBr_3, 26.8 mg. (0.099 mmole by volume); mol. wt. 271 (calcd., 270.7); 2.7 mm. at 23.5° (calcd., 2.7).

This analysis is summarized by an empirical equation, with calculated and observed results (in mmoles) attached to the formulas, as follows:

$$\begin{array}{lllll} & 32(CF_3)_3PBr_2 \longrightarrow & 32CF_3Br + & 5CF_3PBr_2 + & 3PBr_3 \\ \text{calcd.} & 1.005 & 1.005 & 0.157 & 0.094 \\ \text{obsd.} & 1.005 & 1.007 & 0.159 & 0.106 \end{array}$$

$$\begin{array}{lr} & + 12(CF_3)_2PBr + 12(CF_3)_3P \\ \text{calcd.} & \underbrace{0.377 \qquad\qquad 0.377}_{} \\ \text{obsd.} & 0.749 \end{array}$$

Although much of this process may have gone according to equation (12), processes (11), (13) and (2) also would account for the equimolar yield of CF_3Br and seem necessary to explain the formation of $(CF_3)_3P$, CF_3PBr_2 and PBr_3. The alternative idea that these formed by disproportionation of $(CF_3)_2PBr$ seems to require that CF_3Br be reabsorbed by $(CF_3)_2PBr$ to form $(CF_3)_3PBr_2$. Such a step would contradict the whole trend of individually observed reactions favoring the more highly brominated phosphoranes.

Reactions Involving Mercury

Bis-(trifluoromethyl)-bromophosphine and Mercury.—Although $(CF_3)_2PBr$ seems to be quite inert toward mercury at room temperature, a 0.321 mmole sample, heated with mercury for 16 hr. at 100° (without shaking) was 80% converted to $P_2(CF_3)_4$ (0.128 mmole), with recovery of 0.067 mmole of the original $(CF_3)_2PBr$.

The Tribromophosphorane with Mercury.—The existence of $(CF_3)_2PBr_3$ made possible an experiment to determine whether the room-temperature inertness of $(CF_3)_2PBr$ toward mercury would persist even when this bromophosphine is being formed by a chemical reaction. A 144.3 mg. sample of $(CF_3)_2PBr_3$ (only slightly contaminated by the decomposition products CF_3PBr_4 and PBr_3) reacted rapidly with mercury in a sealed tube at room temperature. After some shaking, the mixture yielded 0.321 mmole of $(CF_3)_2PBr$ (calcd., 0.354 mmole; mol. wt. 248.6 *vs.* calcd., 248.9) as the only volatile product. Thus 91% of the expected $(CF_3)_2PBr$ withstood the action of mercury during formation.

Trifluoromethyl-dibromophosphine with Mercury.—Unlike $(CF_3)_2PBr$, the dibromophosphine CF_3PBr_2 reacts easily with mercury, to form CF_3P-polymers at room temperature. A 66.2 mg. sample of CF_3PBr_2 (0.255 mmole) was shaken briefly with excess mercury and the products separated. The main component was the equilibrium mixture of $(CF_3P)_4$ and $(CF_3P)_5$,[3] altogether amounting to 15.7 mg. and representing 70% of the CF_3PBr_2. The recovery of this dibromophosphine was 11.0 mg. (17%). The remaining CF_3P units (13%) presumably were aggregated as involatile higher polymers.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN 12, TEXAS]

The Effect of Fluorine Substitution on the Rate of Hydrolysis of Chloromethane[1]

BY JAMES E. BOGGS AND HELENE P. MOSHER

RECEIVED OCTOBER 24, 1959

Rate constants for the hydrolysis of CH_3Cl, CH_2FCl and CHF_2Cl in neutral aqueous solution are reported as a function of temperature. The activation energies decrease slightly with increasing temperature and range between 21 and 23 kcal./mole for all three substances. The rate constants decrease regularly with increasing fluorination.

There is much qualitative evidence available to indicate that the reactivity of a halogen atom in an aliphatic compound is markedly reduced by the presence of one or more fluorine atoms attached to the same carbon atom. There have been, however, relatively few quantitative investigations from which the extent of the reduction might be judged.

The problem is of special interest in connection with the relationships between bond length, bond dissociation energy and force constants in the carbon–halogen bonds involved. For carbon–carbon bonds, a shortened bond length is associated with

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[1] The authors wish to express their appreciation to the Research Corporation for financial support of the work described.

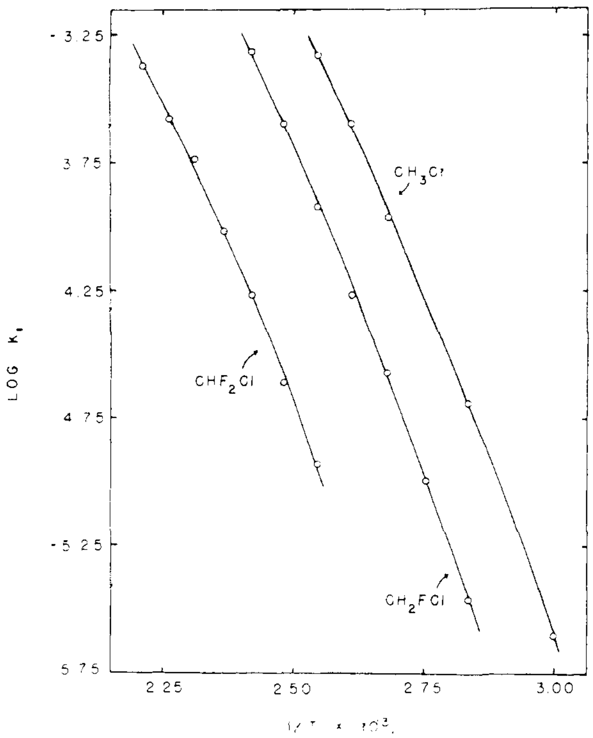

Fig. 1.—Arrhenius plot of the rate constant for the hydrolysis of CH_3Cl, CH_2FCl and CHF_2Cl in neutral aqueous solution.

an increased bond dissociation energy. It has been shown[2] that the carbon–chlorine bond length in CF_3Cl is approximately 0.03 Å. shorter than that in CH_3Cl. On the other hand the carbon–chlorine bond dissociation energy in CF_3Cl is actually about 4 kcal. lower than that of CH_3Cl.[3] A similar relationship has been found for CF_3Br and CH_3Br.[4] In spite of this difference in bond dissociation energy, it is known that in many reactions the chlorine atom in CH_3Cl is more reactive than that in CF_3Cl.

The purpose of the present work was to measure the rates and activation energies for hydrolysis in neutral aqueous solution of CH_3Cl, CH_2FCl, CHF_2Cl and CF_3Cl. It was found that the water solubility of the last compound was too low for hydrolysis kinetics measurements to be made, but results are reported for the other three.

In the course of his extensive investigations of the solution kinetics of compounds of the general type CHX_3, Hine has studied the alkaline hydrolysis of CHF_2Cl[5] and the reactions of CHF_2Cl with sodium methoxide and with sodium thiophenoxide.[6] The neutral hydrolysis of CH_3Cl has been carefully studied,[7] but no such work has been done with CH_2FCl or CHF_2Cl.

Experimental

Solutions of approximately 0.001 to 0.01 molar concentration were made by dissolving the respective gases in boiled, distilled water. Samples of 25 ml. volume were sealed in 50 ml. Pyrex tubes and submerged in a thermostatted oil bath for various periods of time. Samples were removed at intervals, the tubes were opened and the solutions were titrated with 0.01 *M* NaOH to determine the amount of hydrochloric acid formed by hydrolysis. Qualitative tests for fluoride ion were negative, indicating that all of the acid in the solution was formed by hydrolysis of the chlorine. A blank titration was run on each set of samples. Titration of a solution of 0.01 *M* HCl heated in similar tubes indicated that there was no loss of acid during the period of reaction.

The authors wish to express their appreciation to Dr. W. B. McCormack of E. I. du Pont de Nemours and Co. for furnishing a sample of CH_2FCl.

Results and Discussion

Since the solubility of the halomethanes in water is limited, the reactant was distributed between the gas and liquid phases of the reaction tube. If reaction occurs only in the liquid phase and it is assumed that the reaction rate is slow compared with the rate of solution, a first order reaction rate can be written as

$$\frac{d(n_T/v_L)}{dt} = -k_1c_L$$

where n is number of moles of halomethane, v is volume, c is molar concentration and the subscripts L, G, and T refer to liquid phase, gas phase and total, respectively. The phase distribution of the halomethane is given by

$$\frac{c_G}{c_L} = k_2$$

From this it can be shown that

$$c_L = \frac{(n_T/v_L)}{k_2(v_G/v_L) + 1}$$

For our experiments, $v_G = v_L$. The reaction rate constant, then, is given by

$$k_1 = -\frac{k_2 + 1}{t}\ln\frac{(n_T/v_L)_t}{(n_T/v_L)_0}$$

Since $(n_T/v_L)_t/(n_T/v_L)_0 = (c_L)_t/(c_L)_0$, this is equivalent to

$$k_1 = -\frac{k_2 + 1}{t}\ln\frac{(c_L)_t}{(c_L)_0}$$

where c_L is the concentration measured directly by the titration, the initial concentration $(c_L)_0$ being calculated from the titration after the reaction is essentially completed.

The water solubility of CH_3Cl, CH_2FCl and CHF_2Cl has been measured by Boggs and Buck[8] at temperatures up to the lower ones of the present experiments. These data were extrapolated, using the linear ΔH^0 *vs.* T curves, to give solubilities at the higher temperatures we have used.

The solubility constants, k_2, and the hydrolysis rate constants, k_1, are shown in Table I. Each of the rate constants shown is the average of the rate constants determined from separate samples after different times of reaction, an average of 16 samples being used for each point. The data are shown in an Arrhenius plot in Fig. 1. It will be noted that the activation energy falls off with increasing temperature, as has been found to be true generally for the hydrolysis of methyl halides.[9] For each of the curves, the activation energy falls from approxi-

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TABLE I

HYDROLYSIS RATE CONSTANTS

T, °C.	CH_3Cl		CH_2FCl		CHF_2Cl	
	k_2	$k_1 \times 10^5$	k_2	$k_1 \times 10^5$	k_2	$k_1 \times 10^5$
60	0.817	0.25	..	...	..	...
80	1.04	2.08	0.71	0.35	..	...
90	..	...	.79	1.01	..	...
100	1.26	10.9	.87	2.67	..	...
110	1.38	25.9	.94	5.36	..	...
120	1.49	46.5	1.02	12.0	4.89	1.16
130	...	...	1.10	25.2	5.27	2.40
140	...	...	1.18	49.0	5.65	5.55
150	...	...	..	...	6.04	9.5
160	...	...	..	...	6.42	18.5
170	...	...	..	...	6.80	26.6
180	...	...	..	...	7.18	42.2

mately 21 kcal./mole at the higher temperatures to about 23 kcal./mole at the lower.

A careful study of the hydrolysis of CH_3Cl by Moelwyn-Hughes[7] has given a rate constant of 1.08×10^{-4} and an activation energy of 22.7 kcal./mole, both at 100°, compared with the present values of 1.09×10^{-4} and 21.5 kcal./mole.

There is a steady decrease in the rate of hydrolysis of the chlorine atom in the compounds we have studied as the number of fluorine atoms attached to the same carbon increases. The energy of activation, however, is approximately the same for all of the substances, so that the difference is in the pre-exponential factor in the rate equation. In this connection, it is of interest to note that Glew and Moelwyn-Hughes[9] found that the hydrolysis rates of CH_3F and CH_3Br at 100° differed by a factor of 3,400, although their energies of activation were 21,163 and 21,424, respectively.

The solubility of a methyl halide gas is at least partially a measure of the forces of interaction between the methyl halide molecules and water molecules. The water solubility of the series CH_3F, CH_3Cl and CH_3Br rises[10] in a manner roughly parallel to the increase in rate of hydrolysis.[9] No such parallelism is noted in the series CH_3Cl, CH_2FCl and CHF_2Cl, however. In the temperature range we have used, CH_2FCl is more soluble than either of the other gases, but its hydrolysis rate is intermediate between the other two.

A few experiments on the rate of the reaction of CH_3Cl, CH_2FCl and CHF_2Cl with thiosulfate ion in dioxane–water solution show behavior very similar to that observed in the neutral hydrolysis reaction.[11] At 50.3°, the rate of the reaction between thiosulfate ion and CH_2FCl is slower than the reaction with CH_3Cl by a factor of about 15. CHF_2Cl reacts still more slowly than does CH_2FCl.

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(11) The experiments on the thiosulfate ion were performed by Mrs. Janice Goodwin Lonadier to whom the authors are indebted.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY, SCHENECTADY, NEW YORK]

Radiation Chemistry of Polydimethylsiloxane.[1] I. Crosslinking and Gas Yields

BY A. A. MILLER

RECEIVED NOVEMBER 30, 1959

The electron-irradiation of a linear polydimethylsiloxane oil, $[-Si(CH_3)_2O-]_n$, with a molecular weight of 85,000, was studied in the glass state at −180° and in the fluid state from −40 to +150°. At 25° and a radiation intensity of 13.8×10^6 r./min., the crosslinking yield, derived from gel and gas measurements, is $G(\text{c.l.}) = 3.0$. In the fluid state the crosslink and gas yields are both temperature- and intensity-dependent. The transition from the fluid to the glass state produces some apparent anomalies in the over-all radiation chemical effects.

Introduction

A review of the earlier literature on the effects of ionizing radiation in silicone polymers has been compiled by Bovey.[2] Thus far, no systematic study of the radiation chemistry of the linear polydimethylsiloxane $[-Si(CH_3)_2O-]_n$ structure has been reported. Kantor has reported work on the cyclic tetramer[3] and Dewhurst and St. Pierre have studied the irradiation of hexamethyldisiloxane.[4]

The polydimethylsiloxane structure has certain radiation chemical features which are quite different from other crosslinking-type polymers, such as polyethylene $(-CH_2CH_2-)_n$. Thus, the irradiation of dimethylsilicones causes both $\equiv Si-CH_3$ and $\equiv SiCH_2-H$ scissions with the evolution of H_2, CH_4, and C_2H_6 as the gaseous products. Recombinations of the two types of polymer radicals $\equiv Si\cdot$ and $\equiv SiCH_2\cdot$ can lead to three types of crosslinks. In linear polyethylene, the gaseous product is H_2 and only carbon–carbon crosslinks can be formed. Also, the polyethylene structure permits the formation of H_2 and *trans*-vinylene unsaturation without crosslinking,[5] while the dimethylsiloxane structure precludes the formation of unsaturation and consequently an exact correspondence between gas and cross-linking yields should be expected.

In the first paper of this series, measurements of crosslinking and evolved gas will be described for a polydimethylsiloxane oil in the glass state at liquid nitrogen temperature and in the fluid state between −40° and +150°. The effects of additives are reported in the second paper. On the basis of these

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(1) Presented, in part, at a Symposium on Chemical Effects of High Energy Radiation, A. A. A. S. Meeting, Washington, D. C., Dec. 26–31, 1958.

(2) F. A. Bovey, "Effects of Ionizing Radiation on Natural and Synthetic High Polymers," Interscience Publishers, Inc., New York, N. Y., 1958, p. 178.

(3) S. W. Kantor, Abstracts, 140th A. C. S. Meeting, Atlantic City, September, 1956, Div. of Org. Chem., Paper No. 94.

(4) H. A. Dewhurst and L. E. St. Pierre, Abstracts, 136th A. C. S. Meeting, Atlantic City, September, 1959, Div. of Polymer Chem. Papers No. 51 and 52.

(5) A. A. Miller, E. J. Lawton and J. S. Balwit, *J. Phys. Chem.*, **60**, 599 (1956); also E. J. Lawton, J. S. Balwit and R. S. Powell, *J. Polymer Sci.*, **32**, 257 (1958).