methanol (about 24 hours at low concentrations of methanol).

Tests on Reliability of Extraction Procedure.—Three 10-ml. samples of kinetic solution containing 0.1015 *M* trityl chloride, 0.0984 *M* pyridine and 0.00884 *M* methanol were extracted with 10 ml. of water each. The first was extracted once, the second twice successively, and the third three times. The activities of the remaining organic phases were the same within 1.7%, with the highest activity in the third. This test demonstrates the sufficiency of only one extraction when equal volumes of water and sample are used. Single extractions of this same kinetic solution were made using 15-ml. samples with 10- and 5-ml. volumes of water, respectively. The activity of the aqueous phase of the second was twice that of the first within experimental error (less than 2%).

Methanol, at a concentration higher than any used kinetically, was shown not to increase the solubility of trityl methyl ether in water. Two samples from run 111 which had been left for 16 days and was calculated to contain 0.057 *M* trityl methyl ether were extracted with water alone and with water containing 0.08 *M* methanol. There was no difference in activity between the two aqueous phases: the first gave 15.7 counts per second and the second, 15.3 counts per second. The equivalent initial methanol activity for this run was 3780 counts per second.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Hydrolysis and Deuterium Exchange of Dibromofluoromethane and Fluorodiiodomethane[1]

BY JACK HINE, RICHARD BUTTERWORTH AND PAUL B. LANGFORD

RECEIVED AUGUST 26, 1957

Rate constants and heats and entropies of activation have been determined for the basic hydrolysis and the deuterium exchange of dibromofluoromethane and fluorodiiodomethane in aqueous solution. The hydrolysis of bromodichloromethane and dibromochloromethane also was studied. For all four haloforms the data support the hydrolysis mechanism in which trihalomethyl anions, formed reversibly from haloform and base, decompose to dihalomethylenes, reactive intermediates that react quickly, either with halide ions to regenerate haloform or with water and alkali to give carbon monoxide or formate ions. The effect of added salts on the rate of the hydrolysis of dibromofluoromethane is compared with their effect on bromodichloromethane and dibromochloromethane in order to learn how variations in the structure of dihalomethylenes affect the efficiency with which the dihalomethylenes may be captured by halide ions. The intermediates, dichloromethylene and bromochloromethylene, are captured with roughly equal efficiency, while bromofluoromethylene is captured with much less efficiency, if at all. While the rate of exchange of deuterodibromofluoromethane was about that expected from data on other haloforms, deuterofluorodiiodomethane exchanged more rapidly than anticipated.

In earlier articles[2] evidence was presented to show that the basic hydrolysis of several haloforms involves the intermediate formation first of a trihalomethyl anion and then a dihalomethylene. In order to investigate the generality of this reaction mechanism for haloforms as well as to learn more about the effect of structure on reactivity in trihalomethyl anion and dihalomethylene formation, we have studied the hydrolysis and deuterium exchange of dibromofluoromethane and fluorodiiodomethane. We also have studied briefly the effect of the structure of dihalomethylenes on their ease of capture by halide ions.

Results and Discussion

Hydrolysis.—Although the fluorodiiodomethane prepared by the reaction of iodoform with mercuric fluoride boiled higher than that reported by Ruff and co-workers[3] or by Haszeldine,[4] the agreement of the boiling point with that predicted from an empirical equation for correlating the boiling points of halomethanes[5] as well as the agreement of the molar refractivity and iodine analysis with the calculated values support the assignment of the $CHFI_2$ structure.

We have studied the hydrolysis of fluorodiiodomethane in aqueous solution at 0 and 20.85°. The rate constants were calculated from the equation used previously[2]

$$k = \frac{2.303}{t(a[3+f]-b)} \log \frac{b(a-x)}{a(b-[3+f]x)} \qquad (1)$$

where $a = [CHX_3]_0$, $b = [OH^-]_0$, $x = a - [CHCl_3]_t$, t = time, f = fraction of haloform that hydrolyzes to formate (the rest gives carbon monoxide), and k is expressed in liters/mole of haloform × seconds. In Table I are listed these data and heats and entropies of activation calculated from the absolute rate equation[6]

TABLE I

BASIC HYDROLYSIS OF DIBROMOFLUOROMETHANE AND FLUORODIIODOMETHANE IN AQUEOUS SOLUTION

	$CHBr_2F$	$CHFI_2$
10^3k at 0°	2.77 ± 0.03	0.153 ± 0.003
10^3k at 20.85°	70.8 ± 2.9[a]	6.15 ± .13
$\Delta H^{\ddagger}$, kcal./mole	25.7 ± 0.5	27.7 ± .3
$\Delta S^{\ddagger}$, e.u.	24.1 ± 2.0	25.6 ± 1.2

[a] At 19.6°.

$$k = \frac{\mathbf{k}T}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

Preliminary tests showed that dibromofluoromethane was the most reactive haloform that we have studied. The rate constants obtained in the first runs at 0° fell considerably as the reaction proceeded. This was found to be due to the temperature of the reaction solution being significantly above 0° for the first few minutes of the reaction.

---

[1] Part X in the series "Methylene Derivatives as Intermediates in Polar Reactions." For part IX, see ref. 21. This work was supported in part by the Office of Ordnance Research, U. S. Army.

[2] J. Hine, A. M. Dowell, Jr., and J. E. Singley, THIS JOURNAL, **78**, 479 (1956), and references cited therein.

[3] O. Ruff, O. Bretschneider, W. Luchsinger and G. Miltschitzky, *Ber.*, **69B**, 299 (1936).

[4] R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952).

[5] J. Hine and S. J Ehrenson, *J Org. Chem.*, **21**, 819 (1956).

[6] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

Although the pipets used to introduce the base that initiated the reaction were chilled before use, they and their contents warmed several degrees during the process of transferring the solutions. The necessity of shaking the reaction flask and the exothermic nature of the reaction added to this effect. In previous runs with less reactive compounds, it had been possible to ignore the first few minutes of reaction and calculate k's from data on the part of the reaction occurring after that time. In the present case, however, too much of the reaction took place during the first few minutes. We therefore calculated our rate constants by use of the following corrections.

The instantaneous rate constant at the higher temperatures occurring in our reaction (k_t) is related to the value at 0° (k) by the expression

$$k_t = k\, e^{E(T - 273)/273T}$$

where T is the absolute temperature of the reaction solution at the time t and E is the Arrhenius activation energy. Substitution into the differential form of eq. 1 and rearrangement gives

$$\frac{dx}{(a - x)(b - [3 + f]x)} = k\, e^{E(T - 273)/273T}\, dt$$

Since the integral of the left side of this equation is simply $k_{unc}\, t$ where k_{unc} is the uncorrected (falling) rate constant that we had calculated from eq. 1

$$k = \frac{k_{unc}}{t} \int_0^t e^{E(T - 273)/273T}\, dt \qquad (2)$$

a plot of T *vs.* t was made, and from this plot and a value of E the integral in eq. 2 could be evaluated for any t. As a check on the validity of the method it was found that the value of E that resulted in k's having the least average deviation from the mean in five different runs was 27.7 ± 1.5 kcal./mole, in reasonable agreement with the value determined experimentally (26.2). The experimental value was the one used in calculating the k's listed in Table I. The rate constants were determined at an ionic strength of about 0.10, but data on bromodichloromethane (Table II) and chloroform[7] show that haloform hydrolysis rates are not very sensitive to changes in ionic strength.

In addition to argument by analogy, there is much direct experimental evidence that diiodofluoromethane and dibromofluoromethane hydrolyze by the mechanism

$$CHX_3 + OH^- \rightleftharpoons CX_3^- + H_2O \qquad (I)$$
$$CX_3^- \longrightarrow CX_2 + X^-$$

followed by rapid reactions of the intermediate CX_2. Both compounds are reported herein to undergo base-catalyzed deuterium exchange more rapidly than they hydrolyze. Both are much more reactive than would be expected for the S_N2 mechanism.[8] The reactivity of each of the compounds fits satisfactorily into a quantitative correlation of haloform reactivities based on the proposed mechanism.[12]

Capture of Dihalomethylenes by Halide Ions.—From the observed relative reactivities of haloforms it appears that, relative to chlorine, fluorine stabilizes dihalomethylenes and bromine destabilizes them.[2,12] We thought it of interest to determine how the presence of the various halogens affects the ease of capture of dihalomethylenes by such nucleophilic reagents as halide ions. It has been reported earlier that the addition of chloride ion slows the basic hydrolysis of chloroform, due to reversal of the second step of the reaction (see mechanism I).[7] Bromide and iodide bring about even larger "apparent" decreases in reaction rate (they decrease the rate at which alkali disappears), by combining similarly with dichloromethylene to yield haloforms. *e.g.*

$$CCl_2 + I^- \longrightarrow CCl_2I^- \xrightarrow{H_2O} CHCl_2I$$

We therefore studied the effect of various sodium salts at concentrations around 0.08 M on the rate of the basic hydrolysis of dibromofluoromethane, dibromochloromethane and bromodichloromethane (as measured by the rate of disappearance of alkali). The rate constants obtained are shown in Table II.

TABLE II

EFFECT OF SALTS ON HALOFORM HYDROLYSIS IN AQUEOUS SOLUTION[a]

Haloform	Salt	10^5k, l. mole^{-1} sec.$^{-1}$
$CHBr_2F$	0.080 M NaF	276 ± 8[b]
$CHBr_2F$	.080 M $NaClO_4$	277 ± 3[b]
$CHBr_2F$	.080 M NaBr	276 ± 3[b]
$CHBr_2F$	.080 M NaI	266 ± 2[b]
$CHBrCl_2$	None	1.49 ± 0.02[b]
$CHBrCl_2$	0.083 M NaF	1.47 ± .02[b]
$CHBrCl_2$	.083 M NaBr	1.20 ± .02[b]
$CHBrCl_2$	.083 M NaI	0.95[b,d]
$CHBrCl_2$	.089 M NaF	1025 ± 20[c]
$CHBrCl_2$	.089 M NaBr	783 ± 15[c]
$CHBrCl_2$	.089 M NaI	590[c,d]
$CHBr_2Cl$	.089 M NaF	562 ± 21[c]
$CHBr_2Cl$	.089 M $NaNO_3$	570 ± 30[c]
$CHBr_2Cl$	.089 M $NaClO_4$	551 ± 10[c]
$CHBr_2Cl$	.089 M NaBr	428 ± 5[c]
$CHBr_2Cl$	.089 M NaI	340[c,d]

[a] $[OH^-]_0$ ~0.036 M for $CHBr_2F$ and ~0.020 M for other haloforms. [b] At 0°. [c] At 40°. [d] Falling rate constants extrapolated to zero time.

It was found earlier with chloroform that with such salts as sodium fluoride, nitrate and perchlorate, which would not be expected to be effective at capturing dihalomethylene intermediates, the reaction rate is essentially independent of the exact nature of the anion at concentrations below 0.16 M.[7] This observation, which was substantiated by measurements on dibromofluoromethane and dibromochloromethane, shows that the specific salt

---

(7) J. Hine and A. M. Dowell, Jr., THIS JOURNAL, **76**, 2688 (1954).

(8) The compounds are the α-fluoro derivatives of methylene bromide and methylene iodide, respectively. The α-fluoro substituent appears to decrease the S_N2 reactivity in the cases that have been studied.[9,10] The reactivity of alkyl halides toward sodium hydroxide in water appears to be about the same as toward sodium methoxide in methanol.[11] Dibromofluoromethane is therefore about a million times as reactive as methylene bromide and diiodofluoromethane about fifty thousand times as reactive as methylene iodide.

(9) J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955).

(10) J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *ibid.*, **78**, 2282 (1956).

(11) Compare the data on methyl bromide and iodide in methanol from ref. 8 with that in water obtained by E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A196**, 540 (1949).

(12) J. Hine and S. J. Ehrenson, THIS JOURNAL, **80**, 824 (1958).

effects produced by bromides and iodides are very probably not due to such factors as ionic size, degree of solvation and ion-pair formation. Therefore the sharp decreases in the rate of hydrolysis of bromodichloromethane brought about by these two salts and their negligible effect on dibromofluoromethane show that dichloromethylene is much more effectively captured by bromide and iodide ions than is bromofluoromethylene. This interpretation is supported by the fact that the rate constants obtained in the presence of bromide ion showed no drift, since capture of dichloromethylene by bromide leads to re-formation of the starting haloform, while those obtained in the presence of iodide ion drifted downward during the reaction, since the less reactive haloform, dichloroiodomethane, was being formed. While the rate constants obtained with dibromofluoromethane and sodium iodide showed no appreciable drift, this may just mean that iodide ion did not capture bromofluoromethylene to any significant extent.

In order to learn whether the difference in behavior of dichloromethylene and bromofluoromethylene was due to the bromine or to the fluorine, we studied the intermediate, bromochloromethylene. This was done by measurements on dibromochloromethane, which, being somewhat less reactive, was studied at 40° rather than 0°. The results and analogous data on bromodichloromethane at 40° are listed in Table II and show that bromochloromethylene is captured approximately as effectively as dichloromethylene. This is shown more clearly in Table III where there are listed values for the competition factors k_x/k_w

$$CY_2 + X^- \xrightarrow{k_x} CY_2X^-$$

$$CY_2 + H_2O \xrightarrow{k_w} H_2\overset{\oplus}{O}\text{–}\overset{\ominus}{C}Y_2$$

calculated from the following equation, which was developed previously[7]

$$\frac{k_x}{k_w} = \frac{\left([H_2O] + \frac{k_h}{k_w}[OH^-]\right)\left(\frac{k}{k'} - 1\right)}{[X^-]}$$

where k' is the rate constant in the presence of NaX, k that obtained with the same concentration of an inert salt, and k_h/k_w is the competition factor for hydroxide ion, *assumed* as before, to be equal to 229. The data on bromodichloromethane at the two temperatures show that the values of k_x/k_w are not *highly* temperature dependent. The values, particularly those of k_{Br}/k_w, having been determined from fairly small differences between two numbers each of which may be in error by several per cent., are not very precisely known, but the increase with temperature of k_I/k_w, at least, is probably meaningful. The values for bromodichloromethane are seen to be within the experimental error of those obtained previously for chloroform, as expected since both give the same intermediate, dichloromethylene.

TABLE III

COMPETITION FACTORS TOWARD THE DIHALOMETHYLENES FORMED FROM VARIOUS HALOFORMS

Haloform	Ion	Temp., °C.	k'/k	k_x/k_w
$CHBr_2F$	Bromide	0	~1	<50
$CHBr_2F$	Iodide	0	~1	<70
$CHBrCl_2$	Bromide	0	0.816	159
$CHBrCl_2$	Bromide	40	.764	203
$CHBrCl_2$	Iodide	0	.646	386
$CHBrCl_2$	Iodide	40	.556	485
$CHBr_2Cl$	Bromide	40	.762[a]	204
$CHBr_2Cl$	Iodide	40	.606[a]	427

[a] Based on the average value, $k = 561 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$.

It might have been expected that the fluorine-containing dihalomethylenes, being more stable, would have been able to discriminate better between the solvent water and the more nucleophilic halide ions.[13] We are not sure why they actually have less tendency to combine with halide ions. It is true that combination would lead to somewhat less stable trihalomethyl carbanions,[14] but if this were the sole explanation bromochloromethylene would show larger k_x/k_w values than dichloromethylene. Any complete explanation should take into account the effect of structure on k_w as well as k_{Br}. We know very little about the combination of water with dihalomethylenes, but if in some cases a proton donation to carbon is important the possibly more basic fluoromethylenes might be more reactive.

Deuterium Exchange.—The rates of carbanion formation of the haloforms were studied, as previously, by measuring the rate of the base-catalyzed hydrogen exchange of the deuteriohaloforms in "light" water solution. Preliminary measurements on diiodofluoromethane showed that the exchange reaction proceeded more than one hundred times as fast as the hydrolysis. Because of this and the fact that we used a buffer solution as the basic catalyst, the change in base concentration during a run was negligible. Therefore the following first-order rate equation derived previously was used in the calculation of rate constants.[15]

$$k[OH^-] + k'[CH_3NH_2] = \frac{2.303}{t}\log\left(\frac{D_0}{D_0 + H_0}\right)\left(1 + \frac{H}{D}\right) \quad (3)$$

$D = [CDFI_2]$, $H = [CHFI_2]$, t = time (sec.). The ratio H/D was determined by extraction of the reaction solution with isoöctane and infrared measurements. The hydroxide and methylamine concentrations at the ionic strength used were calculated from the data of Everett and Wynne-Jones.[16] Values of k and k' determined from runs at two different buffer concentrations but with the same buffer ratio are listed in Table IV as are heats and entropies of activation.[6]

In the case of dibromofluoromethane hydrolysis of the haloform is so extensive that the concentration of catalyzing base changes appreciably, even in the presence of a buffer, if the exchange re-

---

(13) Compare the increases in mass-law constants that accompany increasing stability of carbonium ions; L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, **979** (1940); C. G. Swain, C. B. Scott and K. H. Lohmann, THIS JOURNAL, **75**, 136 (1953).

(14) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957).

(15) J. Hine, R. C. Peek, Jr., and B. D. Oakes, *ibid.*, **76**, 827 (1954).

(16) D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A177**, 499 (1941).

TABLE IV

KINETIC DATA ON THE DEUTERIUM EXCHANGE OF DIIODOFLUOROMETHANE AND DIBROMOFLUOROMETHANE[a]

Haloform	$CDFI_2$	$CDBr_2F$
10^3k at 0°	50.7 ± 1.4	20.7 ± 0.5
$10^3k'$ at 0°	0.027 ± 0.01	0.013 ± 0.005
10^3k at 20°	823 ± 30	730 ± 20[b]
$10^3k'$ at 20°	0.67 ± 0.3	
$\Delta H^{\ddagger}$, kcal./mole[c]	21.6 ± 0.5	22.5 ± 0.4
$\Delta S^{\ddagger}$, e.u.[c]	14.8 ± 2.0	16.1 ± 1.5

[a] All rate constants in l. $mole^{-1}$ $sec.^{-1}$. [b] At 25.05°. [c] For the hydroxide ion catalyzed reaction (k).

action is allowed to proceed to as much as half of completion. We have therefore followed the acidity of the reaction solution as well as the deuterium content of the haloform as the reaction proceeded. From acidimetric titrations we learned the change in the ionic strength and in the concentration of methylamine and for each point calculated the hydroxide ion concentration from data on the ionization of methylamine.[16] Plots of the hydroxide ion concentration *versus* the concentration of deuteriohaloform gave a smooth curve which could be fit well by an equation of the type

$$[OH^-] = [OH^-]_0(1 - mz - nz^2) \qquad (4)$$

where z is equal to $D_0 - D$ and m and n are constants whose optimum values are determined by the method of least squares. The simple rate equation

$$dz/dt = k(D_0 - z)[OH^-]$$

may therefore be combined with eq. 4 and integrated to give

$$k = \frac{2.303}{2(1 - mD_0 - nD_0^2)[OH^-]_0t}\left[2 \log \frac{D_0}{D_0 - z} + \log (1 - mz\text{-}nz^2) - \frac{2nD_0 + m}{\sqrt{m^2 + 4n}} \log \frac{2 + z(\sqrt{m^2 + 4n} - m)}{2 - z(\sqrt{m^2 + 4n} + m)}\right] \qquad (5)$$

Rate constants calculated from this equation are in error, because we have neglected catalysis by methylamine. However, the observation that the values of k obtained increase by less than 4% when the buffer concentration is more than doubled at constant buffer ratio and constant ionic strength shows that the methylamine catalysis and hence the error is not very large. By extrapolation of the rate constants from two such runs to zero buffer concentration the error may be removed and a value of k', the catalysis constant for methylamine, determined. The data obtained are listed in Table IV.

While the reactivity of dibromofluoromethane fits satisfactorily into a quantitative correlation of the relative reactivities of haloforms (in carbanion formation),[17,18] it seems anomalous that fluorodiiodomethane should be more than twice as reactive in view of the fact that the replacement of the bromine atoms of bromoform or bromodichloromethane by iodine has virtually no effect on the carbanion formation rate. None of our explanations for this irregularity seem probable enough to warrant discussion here.

Experimental

Reagents.—The bromodichloromethane,[2] dibromochloromethane,[2] sodium salts,[7] sodium hydroxide solutions[7] and "oxygen-free" water[7] have been described previously. Dibromofluoromethane was prepared from bromoform and mercuric fluoride by the method of Thomas.[19] The properties of the material (b.p. 63° at 739 mm., m.p. below −78°, $d^{27.7}_4$ 2.2533, $n^{27.7}_D$ 1.4628; molar refractivity calcd. 22.25, found 22.37) compared satisfactorily with those listed in the literature[20] (b.p. 64.9° at 757 mm., $d^{18.5}$ 2.4256). Deuteriodibromofluoromethane was prepared analogously from deuterated bromoform, the method having been described in detail in connection with the by-product deuterobromodifluoromethane.[21]

Fluorodiiodomethane.—Fluorodiiodomethane was prepared by a method based on that of Thomas.[19] Under a nitrogen atmosphere, 363 g. (0.92 mole) of iodoform was heated with stirring until it began to melt, when the heating was discontinued and 90 g. (0.377 mole) of anhydrous mercuric fluoride added slowly through an apparatus of the type described by Fieser.[22] After the addition was complete the temperature was held around 120° for about 15 minutes and the material was then distilled using a water aspirator vacuum. Between 60 and 105° (largely at 65–75°) 122 g. (56%) of purple liquid was obtained. This was washed with sodium thiosulfate solution, added to 50 g. of material from a run on 40% the scale, and fractionally distilled. The amber liquid boiling at 59.8–60.2° (50 mm.) weighed 97 g., m.p. −35 to −31° (mostly −32 to −31°), $d^{26.3}_4$ 3.1596, $n^{26.3}_D$ 1.6496; molar refractivity calcd. 32.15, found 32.98. Ruff and co-workers[3] report m.p. −34.5° and $d^{14.4}_4$ 3.2206 and $d^{21.5}_4$ 3.1969, from which may be extrapolated $d^{26.3}_4$ 3.1809. They also report the vapor pressure at several temperatures between 26° (30.2 mm.) and 59.5° (113.3 mm.) and an equation relating the vapor pressure to temperature. They state that for this equation they calculate a b.p. of 100.3°, but our calculations using their equation show that a vapor pressure of 760 mm. would be expected at 122°. Haszeldine[4] reported a b.p. at 50 mm. of 50°, a temperature 12° higher than that for which Ruff's equation predicts a vapor pressure of 50 mm. An empirical equation from which may be calculated the boiling points of all of the measured halides of methane with an average deviation of less than three degrees predicts a boiling point of 142.6° for fluorodiiodomethane.[5,23] From a Trouton's rule constant of 21, b.p.'s of 133 and 145° (760 mm.) may be estimated from Haszeldine's and our data, respectively.

The infrared spectrum of the material is also reasonable for the assignment of the fluorodiiodomethane structure. In addition to the carbon–hydrogen stretching band at about 2950 $cm.^{-1}$ there is the rather strong absorption in the range 1000–1100 $cm.^{-1}$ said to be typical of monofluorides.[24] One of the bands in this latter range is, no doubt, analogous to the band (probably carbon–hydrogen deformation) that we have found between 1060 and 1220 $cm.^{-1}$ in all of the fourteen haloforms for which we have spectra. Furthermore, as for all the twelve haloforms we have observed, a new band appears in the range 740–820 $cm.^{-1}$ (at wave lengths differing by a factor of about $\sqrt{2}$ from 1060–1220 $cm.^{-1}$) for the deuterium compound.

Anal. Calcd. for $CHFI_2$: I, 88.80. Found (by reaction with excess alkali and titration by the Fajans method): I, 88.81, 88.85.

Deuteriofluorodiiodomethane was prepared similarly from deuterated iodoform[3] on a smaller scale. The product obtained after the final fractional distillation still had a

---

(17) See ref. 4, Fig. 2, where the rate constant used for deuteriodibromofluoromethane was a preliminary value, 13% smaller than the one now reported.

(18) Use of the present value would still give a satisfactory correlation.

(19) C. H. Thomas, Ph.D. Thesis, Georgia Institute of Technology, 1953, p. 18.

(20) F. Swarts, *Bull. acad. roy. Belg.*, 113 (1910); *C. A.*, **5**, 1086[9] (1911).

(21) J. Hine and P. B. Langford, THIS JOURNAL, **79**, 5497 (1957).

(22) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., New York, N. Y., 1955, p. 265.

(23) The extrapolation of Haszeldine's b.p. to 122° cited in ref. 5 was done from a vapor pressure chart that has since been found to be considerably in error.

(24) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, p. 270.

strong purple color, but titration with sodium thiosulfate showed that this was due to only 0.8% of iodine.

Kinetics of Hydrolysis.—The hydrolysis of dibromofluoromethane by aqueous sodium hydroxide at 0° was carried out in the following way. Into each of a number of 100-ml. volumetric flasks containing 80 ml. of 0.100 *M* salt solution was put 0.2500 ± 0.0008 ml. of dibromofluoromethane (at a known temperature) by use of a "tuberculin" syringe. The haloform was dissolved by vigorous shaking and the flask was returned to the 0° bath. When the material had reached thermal equilibrium 20 ml. of standard sodium hydroxide was introduced from a flask cooled in the same bath, by use of a pre-chilled pipet. To take a point the contents of a reaction flask (and two rinsings) were poured into a known volume (excess) of standard perchloric acid; the excess acid was then titrated to the phenolphthalein end-point with standard alkali. In several of the later points of several runs the concentration of bromide ion was determined by the Fajans method when the acidimetric titration was complete. From these data, values of *f* for eq. 1 could be calculated. The average value obtained was 0.536. In the run at 19.6° the 80 ml. of haloform solution that went into every reaction flask was pipeted from a large flask in which 0.250 ml. of dibromofluoromethane had been dissolved in one liter of 0.1 *M* sodium perchlorate. The solution at 0° was forced from this reaction flask into the 80-ml. pipets by nitrogen pressure, rather than being sucked, so as to avoid loss of the rather volatile haloform. An *f*-value of 0.536 was used at this temperature also since the data on fluorodiiodomethane as well as that on other haloforms[12,25] show that *f* is only slightly dependent on the temperature (and *k* is only slightly dependent on *f*).

The temperature of the reaction mixture in several runs at 0° that were not followed titrimetrically was measured by use of a thermocouple at intervals of a few seconds during the first part of the reaction and longer intervals later. The reaction run at 19.6° did not rise appreciably above this temperature, probably because the reactants were more dilute, the constant temperature bath was stirred and the room temperature was nearer the reaction temperature.

The hydrolysis of dibromochloromethane and bromodichloromethane at 40° was studied by a technique like that used for dibromofluoromethane at 19.6°, except that four to six times as much haloform was used. For these haloforms the first point was taken within a minute or two after the reaction was started. This was used as a "zero" point, corrections being applied to the data on the other points for the amount of reaction that occurred prior to the time of this point. In the runs on bromodichloromethane at 0°, the "one-flask-per-point" method was replaced by a technique in which the reaction flask contained several hundred milliliters of solution and points were taken by removing samples by pipet at various times. The value of *f* used for bromodichloromethane was 0.15 (since the intermediate formed in this case is the same as with chloroform) and that found for dibromochloromethane was 0.164 (the difference between these two values is well within the experimental error).

The hydrolysis of fluorodiiodomethane at both temperatures used was studied by the method just described for bromodichloromethane at 0°. A value of *f* of 0.362 was found at 0° and the value 0.34 at 20.85°. Carbon monoxide was shown to be a reaction product by infrared analysis of the gas above the reaction mixture at the end of one run.

Kinetics of Deuterium Exchange.—For the exchange of deuteriofluorodiiodomethane the following run is typical. To a solution of 0.16 ml. of deuteriohaloform in 400 ml. of oxygen-free distilled water containing 0.05 ml. of 0.08 *M* perchloric acid, to prevent exchange, was added 0.4 ml. of 0.1 *M* sodium thiosulfate to remove the iodine color. When this solution in a 500-ml. volumetric flask had equilibrated at 0°, 100 ml. of 0.4824 *M* methylammonium perchlorate-0.5606 *M* methylamine, also at 0°, was added. At measured times, 50-ml. samples were pipeted into excess acid and the D/H ratio determined by extraction with isoöctane and infrared measurement.

The exchange of deuteriodibromofluoromethane at 0° was carried out as follows. By use of a "tuberculin" syringe 1.00 ± 0.01 ml. (2.34 g.) of deuterated dibromofluoromethane was dissolved in 400 ml. of "oxygen-free" water in each of two 500-ml. volumetric flasks. After the flasks had reached thermal equilibrium in a 0° bath, 100 ml. of 0.0800 *M* methylamine-0.1005 *M* methylammonium perchlorate-0.150 *M* sodium perchlorate was added to flask no. 1 and 100 ml. of 0.2000 *M* methylamine-0.2513 *M* methylammonium perchlorate added to no. 2 (both buffers also at 0°). After about ten minutes (to be sure that the temperature was 0° again), a "zero point" was taken by withdrawing a 75-ml. sample from no. 1 and a 25-ml. sample from no. 2, each into a known volume (excess) of standard perchloric acid. The excess acid was titrated to the brom cresol purple end-point with standard sodium hydroxide and then 4 ml. of 1.2 *M* perchloric acid was added to ensure the transformation of all methylamine to its conjugate acid. The solutions were then extracted with isoöctane and infrared measurements carried out to determine the isotopic content of the haloform. Subsequent points were taken similarly and some later points were titrated for the bromide ion content by the method of Fajans, in order to permit the calculation of *f*. In calculating the hydroxide ion concentration at various points it was assumed that all of the methylamine used up was transformed to methylammonium ion, that is, that the reaction followed only the equations

$$CHBr_2F + 4CH_3NH_2 + 2H_2O \longrightarrow 4CH_3NH_3^+ + 2Br^- + F^- + HCO_2^-$$

and

$$CHBr_2F + 3CH_3NH_2 + H_2O \longrightarrow 3CH_3NH_3^+ + 2Br^- + F^- + CO$$

It is plausible that N-methylformamide and methyl isocyanide also may have been formed, but our observation that 3.44 moles of base reacted per mole of haloform showed that no more than 13% (100 × 0.44/3.44) of the methylamine that reacted could have given these products. Details of the data from run 2 are given in Table V. The calculated rate constants seem to climb slightly as the reaction proceeds. The possible error concerning the assumption involving *f* mentioned above could have caused as much as a 1% climb. The neglect of general base catalysis in the derivation of eq. 5 could not only cause the average value of *k* to be too high (this is corrected for, in extrapolating to zero buffer concentration) but could also cause a climb of about 0.2% in *k*.

TABLE V

KINETICS OF THE HYDROGEN EXCHANGE OF DEUTERIODIBROMOFLUOROMETHANE IN AN AQUEOUS METHYLAMINE BUFFER

$[CH_3NH_2]_0$ = 0.03993, $[CH_3NH_3ClO_4]_0$ = 0.05022, $[CDBr_2F]_0$ = 0.02143, $[CHBr_2F]_0$ = 0.00295, m = 13.74, n = 839.47

Time, sec.	Δml., 0.0487 *N* NaOH	Optical density 11.226 μ	Optical density 14.204 μ	$\frac{D}{H+D}$	[CD-Br₂F]	100*k*, l. mole⁻¹ sec.⁻¹
58,140	2.29	0.218	0.315	0.5602	0.01293	2.143
69,060	2.90	.264	.449	.5195	.01181	2.169
77,880	3.15	.212	.411	.4869	.01100	2.187
88,080	3.50	.237	.513	.4594	.01029	2.160
106,680	4.19[a]	.253	.195[b]	.4489	.00988	1.899[a]
150,420	5.69	.171	.226[b]	.3169	.00669	2.220
154,020	5.75	.191	.203[c]	.3020	.00638	2.280
					Av.	2.193 ± 0.032

[a] The titration on this point was clearly out of line with those on the other points, and the infrared analysis led to a *k* deviating from the mean by about six times the average deviation. The data on the point was therefore neglected. [b] The isoöctane solution for this determination was diluted to one-third the strength of that measured at 11.226 μ. [c] One-fourth as strong as at 11.226 μ.

Since practically all of the reaction was due to hydroxide ion and only a minor part to methylamine, at 25.05° data was taken at only one initial buffer concentration. A value of 0.350 was determined for *f* under these conditions. From the values for dibromofluoromethane at 0° and fluorodiiodomethane and other haloforms at several temperatures[14,15] the value 7.4 × 10^{-4} was estimated for *k'* at 25°. By use of this value the average value of *k* (78.7 ± 1) × 10^{-2} ob-

---

(25) Unpublished observations from this Laboratory.

tained from eq. 5 was corrected to give the value shown in Table IV.

The apparatus and methods of infrared analysis and of calculation of the extent of deuteration of deuterated haloforms have been described previously.[12] The following extinction coefficients were used in the present work. For $CHFI_2$, $\epsilon_{9.173}$ 428.4 ± 0.6, $\epsilon_{9.475}$ 171 ± 0.4, $\epsilon_{9.622}$ 70.4 ± 0.8, $\epsilon_{9.752}$ 272.9 ± 1.6, $\epsilon_{12.154}$ 0.00 ± 0.2; $CDFI_2$, $\epsilon_{9.173}$ 200.2 ± 0.4, $\epsilon_{9.475}$ 110.8 ± 2.5, $\epsilon_{9.622}$ 260 ± 3.1, $\epsilon_{9.752}$ 157 ± 1.2, $\epsilon_{12.154}$ 308.4 ± 3.1; $CHBr_2F$, $\epsilon_{11.226}$ 324.5 ± 2.5, $\epsilon_{14.204}$ 0.00 ± 0.2; $CDBr_2F$, $\epsilon_{11.226}$ 0.00 ± 0.2, $\epsilon_{14.204}$ = 597 ± 8.

Acknowledgment.—The authors wish to thank Dr. Stanton J. Ehrenson for checking many of the calculations and derivations carried out during this investigation.

ATLANTA, GEORGIA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Effect of Structure on the Relative Stability of Dihalomethylenes[1]

BY JACK HINE AND STANTON J. EHRENSON

RECEIVED AUGUST 26, 1957

The relative reactivities of ten haloforms toward hydrolysis in aqueous solution are correlated in terms of an equation based on the dihalomethylene reaction mechanism. This equation uses the known carbanion formation rate constants and contains parameters for (1) the relative abilities of the various halogens to stabilize dihalomethylenes, (2) the relative ease with which halogens are separated as anions from the intermediate trihalomethyl anion, and (3) the carbanion character of the transition state for dihalomethylene formation. From the values of these parameters, halogens appear to facilitate dihalomethylene formation in the order F ≫ Cl > Br > I. Since the dihalomethylenes appear to be non-radicals rather than diradicals, this order is attributed to the relative abilities of the halogens to supply electrons to the carbon atom by tautomeric effects. The relative electrophilic and nucleophilic characters of several methylenes are discussed in terms of these parameters. The parameters for the differences between the abilities of halogens to separate as anions (Br > I > Cl) are smaller and probably less significant. The transition state for dihalomethylene formation appears to have considerable carbanion character. For the basic decomposition reactions in methanol and aqueous dioxane, where carbanion formation rates are not known, equations are developed for correlating the data on smaller groups of haloforms. When an inhibitor is used to prevent the free radical reactions that occur with certain haloforms in these solvents, the rate constants obtained fit the equations satisfactorily.

Introduction

In earlier articles of this series evidence was presented that at least some haloforms undergo alkaline hydrolysis by the mechanism

$$CHX_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CX_3^- + H_2O \qquad (1)$$

$$CX_3^- \xrightarrow{k_2} CX_2 + X^-$$

followed by rapid reactions of CX_2. Some of the first evidence that haloforms hydrolyze by this mechanism was the fact that their reactivities are so much greater than would be expected from the SN2 mechanism.[2] Since mechanism I explains the great reactivity of haloforms in general, toward basic hydrolysis, we hoped to be able to use this mechanism in correlating the relative reactivities of different haloforms, thus learning more about the ease of formation and hence perhaps the relative stabilities of various dihalomethylenes. We obtained data on the relative reactivities of six haloforms in 66²/₃% dioxane–water solution,[3] which would have sufficed for a *qualitative* discussion of the effect of structure on reactivity, but by this time it was beginning to appear that the relative reactivities might be correlated *quantitatively* if values of k_1, the rate constant for the initial carbanion formation, were available. Unfortunately, these values were not available and, in fact, would be rather difficult to determine in such a solvent.[4] However, the kinetics of carbanion formation from haloforms may be studied by deuterium exchange experiments in purely aqueous solution, and data on a number of haloforms have been obtained in this solvent.[5-8] We therefore have determined rate constants for the basic hydrolysis of a number of haloforms in aqueous solution and correlated these rate constants in terms of the values of k_1 and of certain additional parameters by use of an equation based on mechanism I.

Discussion and Results

The Correlation Equation.—In terms of the rate constants for the individual steps of the reaction, the over-all rate constant for hydrolysis may be expressed

$$k_h = \frac{k_1(k_2/k_{-1})}{1 + (k_2/k_{-1})}$$

Since the values of k_1 are known (or may be closely approximated by estimating the kinetic isotope effect), a correlation of the values of k_2/k_{-1} is equivalent to a correlation of k_h values. The fraction k_2/k_{-1} is simply the rate constant by which the trihalomethyl anion yields dihalomethylene divided by the rate constant for its abstraction of a proton from water to re-form haloform.

The generality of applicability of the Brönsted catalysis law shows that the acids that donate pro-

---

[1] Part XI in the series "Methylene Derivatives as Intermediates in Polar Reactions." For part X see preceding paper. This work was supported in part by the Office of Ordnance Research, U. S. Army, and was presented in preliminary form at the Sixth Biannual Conference on Reaction Mechanisms, Swarthmore, Pa., Sept. 13, 1956.

[2] J. Hine, THIS JOURNAL, **72**, 2438 (1950).

[3] J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *ibid.*, **78**, 479 (1956).

[4] The dioxane would be extracted, with the haloform, in the first step of the isotopic analysis in the required deuterium exchange experiments.

[5] J. Hine, R. C. Peek, Jr., and B. D. Oakes, THIS JOURNAL, **76**, 827 (1954).

[6] J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956).

[7] J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957).

[8] J. Hine, R. Butterworth and P. B. Langford, *ibid.*, **80**, 819 (1958).