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The Kinetics of the Base-catalyzed Deuterium Exchange of Dichlorofluoromethane in Aqueous Solution^{1,2}

BY JACK HINE AND NORBERT W. BURSKE

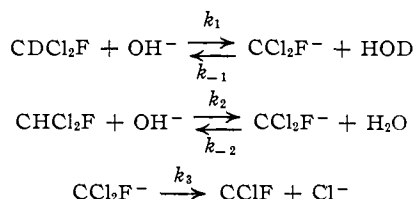
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The alkaline hydrolysis and the base-catalyzed deuterium exchange of dichlorofluoromethane have been studied in aqueous solution at 0 and 20°. Kinetic equations are derived to take into account the complication of the deuterium exchange reaction by concomitant hydrolysis. The deuterium exchange is slower than that of chloroform, in agreement with other evidence that α -chlorine stabilizes carbanions better than α -fluorine does. Hydroxide ions remove protons from dichlorofluoromethane only about 50–75% faster than they remove deuterons.

In order to rationalize previously reported data on the relative reactivities of haloforms toward basic hydrolysis³ as well as to add to our general knowledge of the effect of structure on reactivity in carbanion formation, we have been investigating the effect of various halogen atoms on the ease of removal by bases of hydrogen atoms attached to the same carbon atom. We here report the investigation of dichlorofluoromethane and hope, by comparison with earlier data on chloroform,⁴ to learn something about the effect of α -fluorine (compared to α -chlorine) on the ease of carbanion formation.

Results

Preliminary experiments showed that the deuterium exchange of dichlorofluoromethane, unlike that of chloroform, is complicated by the hydrolysis reaction whose rate is comparable. Therefore the kinetic treatment is considerably more complicated than that used previously. While dichlorofluoromethane has not been studied as carefully as has chloroform, the data that have been obtained (*e.g.*, it undergoes deuterium exchange, it reacts with alkali much faster than methylene chloride) support the α -elimination or carbon dihalide mechanism for this compound, too. Therefore, our results will be discussed in terms of the reaction mechanism



Application of the steady-state approximation to the hydrolysis of pure CHCl_2F gives the kinetic equation

$$-\frac{dH}{dt} = \frac{k_2 k_3}{k_{-2} + k_3} \text{BH} \quad (1)$$

where $H = [\text{CHCl}_2\text{F}]$, $B = [\text{OH}^-]$ and $t = \text{time}$. With the definitions $x = H_0 - H$, $f = \text{fraction of formate in product}$ and $k_h = k_2 k_3 / (k_{-2} + k_3)$, eq. 1 may be expressed in the integrated form⁵

(1) This study was supported in part by the U. S. Atomic Energy Commission.

(2) Paper V in the Series "Carbon Dihalides as Intermediates in the Basic Hydrolysis of Haloforms." For paper IV see reference 3.

(3) J. Hine, A. M. Dowell, Jr., and J. B. Singley, Jr., *THIS JOURNAL*, **78**, 479 (1956).

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

(5) This equation has been expressed in terms of somewhat different symbols in previous papers of this series.

$$k_h = \frac{2.303}{t[(3+f)H_0 - B_0]} \log \frac{B_0(H_0 - x)}{H_0[B_0 - (3+f)x]} \quad (2)$$

Data for a hydrolysis run at 0° are given in Table I. Rate constants at 20.2° and the heat and entropy of activation are included in Table III.

TABLE I

ALKALINE HYDROLYSIS OF DICHLOROFUOROMETHANE IN AQUEOUS SOLUTION AT 0°

t , sec.	$[\text{CHCl}_2\text{F}]_0$	$[\text{OH}^-]_t$	$10^4 k_h$
271,890	0.03573	0.02034	1.216
301,337	.03147	.02037	1.248
307,910	.03412	.01951	1.244
347,730	.03520	.01830	1.230
428,240	.03093	.01755	1.233
Av.			1.234 ± 0.010

In considering our deuterium exchange studies in aqueous solution, since there were about 10^4 times as many protons in the water as there were deuterons in the haloform, the reaction governed by k_{-1} may be neglected. Defining $D = [\text{CDCl}_2\text{F}]$ and treating k_{-2} as a first-order rate constant, it may be seen that

$$-dD/dt = k_1 B D$$

and

$$-\frac{dH}{dt} = k_2 B H - \frac{k_{-2} B (k_1 D + k_2 H)}{k_{-2} + k_3}$$

Combining these two equations

$$\frac{dH}{dD} = \frac{k_2 H}{k_1 D} - \frac{k_{-2}(k_1 D + k_2 H)}{k_1(k_3 + k_{-2})D}$$

Rearrangement and substitution yields

$$\frac{dH}{dD} = \frac{k_h H}{k_1 D} + \frac{k_h}{k_2} - 1$$

which may be integrated between the limits H_0 and H , and D_0 and D to give⁶

$$\left(\frac{D_0}{D}\right)^{1-(k_h/k_1)} = \frac{[1 - (k_h/k_1)](H/D) - (k_h/k_2) + 1}{[1 - (k_h/k_1)](H_0/D_0) - (k_h/k_2) + 1} \quad (3)$$

Measurement of the extent of haloform hydrolysis and the deuterium content of the haloform at a given time would, under conditions where k_h is known, leave k_1 and k_2 as the only unknowns in eq. 3. In theory then k_1 and k_2 could be determined by

(6) For the derivation of this equation we are indebted to Mr. Stanton J. Ehrenson.

making a number of such measurements and ascertaining values of k_1 and k_2 that give the least deviation from the experimental observations. In practice, however, there is a considerable range of values for these k 's that do not differ greatly in their agreement with the experimental data. Therefore, we preferred to use a different method to determine k_2/k_1 , the kinetic isotope effect for carbanion formation from the haloform, and by substitution of this value into eq. 3 arrive at an equation with only one unknown.

Values of k_2/k_1 were determined as follows: The hydrolysis of deuterated dichlorofluoromethane should follow the equation

$$\frac{dy}{dt} = \frac{k_2(k_1D + k_2H)(3+f)(B_0 - y)}{k_{-2} + k_3}$$

or

$$\frac{dy}{dt} = \left(\frac{k_1}{k_2} k_h D + k_h H \right) (3+f)(B_0 - y) \quad (4)$$

where $y = B_0 - B$. As a first approximation we substituted the constant s for the term $[(k_1/k_2)k_h D + k_h H](3+f)$. This is permissible because over the range of reaction we followed, H increased while D decreased, and although D decreased faster than H increased, this was largely compensated by the fact that k_2 is larger than k_1 . In fact, later calculations showed that s never varied by so much as 4% from its average value in any kinetic run. With this approximation eq. 4 may be integrated readily to give an equation from which values of k_1/k_2 may be calculated. From the preliminary value of

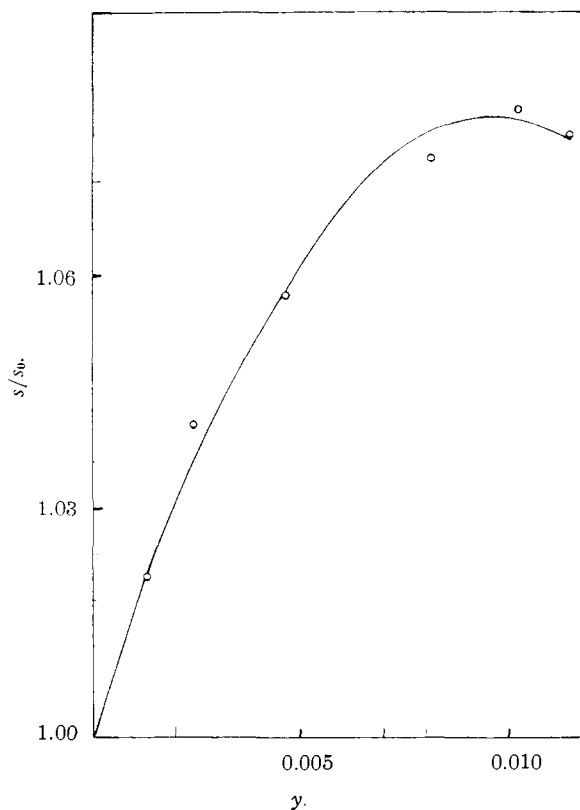


Fig. 1.—Plot of y ($\Delta[\text{OH}^-]$) vs. s/s_0 for the run described in Table II.

k_1/k_2 thus obtained and the experimental data, it is possible to calculate the value of s/s_0 for each point. A plot of s/s_0 vs. y for the data obtained at 0° is given in Fig. 1.

As a second approximation we have expressed s in terms of s_0 and y by the equation

$$s = s_0(1 + my - ny^2) \quad (5)$$

choosing the optimum values of m and n by the method of least squares. The line in Fig. 1 is a plot of such an equation. The substitution of eq. 5 into 4 gives

$$dy/dt = s_0(1 + my - ny^2)(B_0 - y)$$

which may be integrated to

$$s_0 t = C_2 \ln \frac{B_0 \sqrt{1 + my - ny^2}}{B_0 - y} + \frac{[(m/2) - nB_0]C_2}{C_1} \ln \frac{(m - 2ny - C_1)(m + C_1)}{(m - 2ny + C_1)(m - C_1)} \quad (6)$$

where

$$C_1 = \sqrt{m^2 + 4n} \text{ and } C_2 = \frac{1}{1 + mB_0 - nB_0^2}$$

From eq. 6 and the data on any point a value for s_0 may be calculated, and since

$$s_0 = k_h(3+f)[(k_1/k_2)D_0 + H_0]$$

this permits the calculation of a value of k_1/k_2 . If the value obtained differed too much from the preliminary value used, the second approximation procedure was repeated. The final values of k_1/k_2 obtained at 0° are listed in Table II.

TABLE II

DEUTERIUM EXCHANGE OF DICHLOROFUOROMETHANE IN AQUEOUS SOLUTION AT 0°

$[\text{OH}^-]_0 = 0.01700$, $m = 16.7$, $n = 870$, $D_0/(H_0 + D_0) = 0.6310$

t, sec.	$H_0 + D_0$	$\Delta[\text{OH}^-]$	$D/(H + D)$	k_1/k_2	$10^4 k_1$
77,060	0.03157	0.00134	0.5728	0.5728	8.516
170,325	.03039	.00249	.5177	.4523 ^a	9.114
258,830	.03458	.00455	.4591	.5796	9.271
521,660	.03555	.00816	.3737	.5724	8.962
838,160	.03127	.01021	.3038	.5564	8.936
947,715	.03345	.01142	.3003	.5566	8.802
				Av. 0.5676	8.934

^a Not averaged.

Using the average value of k_1/k_2 obtained at a given temperature, a value of k_1 was calculated for each point by use of eq. 3. The values obtained at 0° are shown in Table II and the average values of k_1/k_2 and k_1 at 20° are listed in Table III.

TABLE III

SUMMARY OF KINETIC DATA

	0°	20.2°	$\Delta H \pm \text{kcal.}$	$\Delta S \pm \text{e.u.}$
$10^4 k_h$	1.234 ± 0.010	39.5 ± 0.4	26.8 ± 0.2	17.1 ± 0.5
$10^4 k_1$	$8.93 \pm .18$	255 ± 16	$25.9 \pm .6$	17.7 ± 2.3
$10^4 k_2$	$15.7 \pm .3$	388 ± 24	$24.7 \pm .6$	14.6 ± 2.3
k_1/k_2	$0.568 \pm .009$	0.657 ± 0.040		

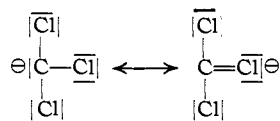
Also listed are heats and entropies of activation calculated from the absolute rate equation⁷

$$k = \frac{kT}{h} e^{-\Delta H \pm / RT} e^{\Delta S \pm / R}$$

(7) 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.

Discussion

Comparison of the present results with those obtained previously⁴ shows that the replacement of a chlorine atom in chloroform by fluorine decreases the rate constant for carbanion formation at 0° by about fifty-fold. There are several other cases known where the α -chlorine substituent excels α -fluorine at facilitating carbanion formation. The decarboxylation of trihaloacetic acids, for example, is a first-order reaction of the acid anion leading directly to carbon dioxide and the trihalomethyl anion.⁸ It is therefore relevant that the trifluoroacetate anion decarboxylates much more slowly than the trichloroacetate anion.⁹ This may be due to stabilization of the carbanion-like transition state by the contribution of structures with ten electrons in the outer shell of chlorine, *i.e.*, *d*-orbital resonance.¹⁰ Fluorine could expand its outer shell



only with much greater difficulty, of course. On the other hand, the chlorine atoms may absorb the negative charge of the carbanion better than fluorine atoms do because of their greater polarizability. Reactivity in the carbanion formation of haloforms will be discussed in more detail in connection with data on more compounds subsequently.

The magnitude of the kinetic isotope effect in this reaction is of interest. The value of k_1/k_2 increases with increasing temperature as would be expected from theoretical considerations.¹¹ The isotope effect for chloroform may be estimated from our earlier data if it is assumed that the reactivity of deuterium ions in heavy water relative to that of hydroxide ions in light water is in the same range (1.36–1.42) as it is for reaction with nitroethane and 2-nitropropane,¹² the only carbanion formation reactions for which there appear to be data. The resultant estimate of k_1/k_2 for chloroform is 0.675 ± 0.015 at 20°, very near the value for dichlorofluoromethane at this temperature. These data suggest that the hydrogen ion being transferred in the reaction is held rather tightly in the transition state.¹¹

Experimental

Reagents.—Matheson Chemical Co. dichlorofluoromethane (Freon 21) was used without further purification. Sodium hydroxide solutions used were carbonate-free. Deuterodichlorofluoromethane was prepared from the protium compound by deuterium exchange. In a typical experiment 30 ml. of dichlorofluoromethane and a solution made from 17 ml. of 99.8% deuterium oxide¹³ and 1.9 g. of metallic

sodium were placed in a 125-ml. erlenmeyer flask equipped with a magnetic stirrer and a Dry Ice cooled condenser. The solution was stirred and allowed to reflux (at about 10°) for 12 hr., and then the haloform was distilled into a Dry Ice trap. This process was then repeated several times, the deuterium oxide solution being replaced by fresh material each time.

Hydrolysis Kinetics.—Reaction mixtures were kept at 0° by use of a water-ice slurry in a one-gallon Dewar flask kept in a refrigerator. At the higher temperature a bath at $20.2 \pm 0.1^\circ$ was used. In a typical run 90 ml. of oxygen-free distilled water was pipetted into each of several 100 ml. volumetric flasks under nitrogen. About 0.3 g. of haloform was weighed into each of the flasks which were shaken until the haloform dissolved. Each flask was then allowed to stand in the 0° bath for several hours and examined for the formation of the crystalline haloform hydrate¹⁴ that forms if the solutions are too concentrated and are allowed to stand too long. At a recorded time 10 ml. of 0.3096 *N* sodium hydroxide solution at 0° was added by pipet to each flask which was then shaken. At a subsequent time each flask was transferred quantitatively to a vessel containing 4 ml. of 1.1900 *N* perchloric acid to stop the reaction. The excess perchloric acid was titrated with 0.3096 *N* sodium hydroxide solution to the phenolphthalein end-point. Lower concentrations of haloform and base were used in the runs at 20°.

The value of *f* (the fraction of the haloform that reacts to give formate) was determined at 0° by use of reaction mixtures of the type described above except that two and one-half times as much of each reagent was used. When the reaction had proceeded until all of the base was used up, the concentration of chloride ion was determined by a Volhard titration.

$$f = [\text{OH}^-]_0 / 2[\text{Cl}^-]$$

Seven determinations at 0° gave $f = 0.72 \pm 0.01$.

Deuterium Exchange Kinetics.—These runs were started in the same way as were the hydrolysis runs except that 63.1% deuterated dichlorofluoromethane and 0.1700 *N* sodium hydroxide solution were used. The reactions were stopped with 20 ml. of 0.1090 *N* hydrochloric acid at 0°, and the excess hydrochloric acid back-titrated, also at 0°, care being taken to avoid the loss of the volatile haloform. The solution was then extracted with carbon disulfide which was subsequently dried over a minimal amount of indicating silica gel and analyzed for CHCl_2F and CDCl_2F .

Isotopic Analysis.—The deuterated dichlorofluoromethane was analyzed by infrared measurements using a Perkin-Elmer model 21 instrument. The maxima for the protium compound at 9.415 and 12.635 μ and those for the deuterium compound at 10.637 and 13.290 μ were used, the measurements being made in carbon disulfide solution. By assuming that the deuterium compound has no absorption at 12.635 μ , it may be calculated that the deuterium content of the material used in the runs reported in this paper was 63.1%. If this assumption is not valid, the deuterium content is higher. The values of the rate constants obtained are relatively insensitive to the truth of the above assumptions.¹⁵ However, if the actual deuterium content had been too much higher than 63.1%, we should have obtained drifting rate constants.

The Beer-Lambert law was shown to hold in all cases and the following molecular extinction coefficients (and average deviations), determined at a resolution of 965, were used: for CHCl_2F , 393 ± 2 , 1.5 ± 0.2 , 516 ± 2 and 26 ± 2 at 9.415, 10.637, 12.635 and 13.290 μ , respectively; for CDCl_2F , 220 ± 2 , 420 ± 3 , -0.05 ± 0.01 and 392 ± 5 , in the same order. The optical density at 12.635 was used to calculate $[\text{CHCl}_2\text{F}]$ while the $[\text{CDCl}_2\text{F}]$ value used was the average of those calculated from $D_{10.637}$ and $D_{13.290}$. $D_{9.415}$ was used as a check on both figures.

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(14) W. P. Banks, B. O. Heston and F. F. Blankenship, *J. Phys. Chem.*, **58**, 962 (1954).

(15) In the limiting case where k_h is negligible in comparison to k_1 , the values of the rate constants obtained are completely independent of the truth of an assumption of this sort.

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(11) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(12) S. H. Maron and V. K. La Mer, *THIS JOURNAL*, **60**, 2588 (1938).

(13) Obtained from the D. A. Stuart Oxygen Co. on allocation from the U. S. Atomic Energy Commission.