The correlation of data by use of equations involving separate ρ's for *m*- and *p*-compounds is to be the subject of a subsequent article in this series.

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ATLANTA, GA.

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

Methylene Derivatives as Intermediates in Polar Reactions. XV. The Decomposition of Dichlorofluoroacetic Acid[1]

BY JACK HINE AND DONALD C. DUFFEY

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The kinetics of the decomposition of dichlorofluoroacetic acid have been studied in aqueous solution. All of the observations are consistent with a reaction mechanism involving a first-order decomposition of the dichlorofluoroacetate ion to carbon dioxide and a dichlorofluoromethide ion that is usually protonated to give dichlorofluoromethane but that often (up to 30% of the time) loses a chloride ion to give the intermediate chlorofluoromethylene which is then hydrolyzed to a mixture of carbon monoxide and formic acid.

Introduction

The decarboxylation of a number of trihaloacetic acids has been shown to be a first-order reaction of the anion that involves the initial formation of carbon dioxide and a trihalomethyl anion that is subsequently protonated to give a haloform.[2-4] A correlation between the rates of carbanion formation by decarboxylation and the rates of carbanion formation from deuteriohaloforms and alkali has been established.[5] In connection with this correlation and a study of the decarboxylation of the chlorodifluoroacetate ion, which appears to be a concerted decomposition to difluoromethylene not involving a carbanion intermediate,[6] we have studied the decarboxylation of dichlorofluoroacetic acid. The reaction has already been investigated briefly by Auerbach, Verhoek and Henne, who reported that solutions of the sodium salt in ethylene glycol at 178° rapidly became acidic with the liberation of fluoride and chloride ions and that below 100° some decarboxylation occurred but that only about 23% of the expected base was produced.[4] These authors then concluded that the acid hydrolyzed more rapidly than it decarboxylated. It seems plausible to us that the reaction is initiated by the carbanion formation characteristic of other trihaloacetic acids, but that a considerable fraction of the intermediate carbanions, unlike those of the acids studied previously (except bromochlorofluoroacetic, which gave poorly reproducible results[3]), decompose to a dihalomethylene instead of being protonated to haloform molecules. Another explanation is that the haloform that is produced may subsequently hydrolyze. It may be noted in this regard that the hydrolytic reactivity of dichlorofluoromethane compared to the decarboxylation rate of the acid from which it is formed is the largest of any acid studied except perhaps bromochlorofluoroacetic. Thus, of course, the subsequent hydrolysis of initially produced haloform becomes more probable in this case.

Results and Discussion

The decomposition of dichlorofluoroacetic acid in aqueous solutions at 70–100° was studied both in the presence and absence of an acetate buffer. Infrared measurements on the gaseous products showed that large amounts of carbon dioxide and dichlorofluoromethane and smaller amounts of carbon monoxide were formed. Tests on the reaction solution for oxalate, by the method described elsewhere,[6] were negative, showing that no significant amount of the material had undergone hydrolysis. We thus concluded that the following reaction scheme operates

$$Cl_2CFCO_2^- \longrightarrow Cl_2CF^- + CO_2$$

$$Cl_2CF^- \xrightarrow[H_2O]{H^+} CHCl_2F \qquad (1)$$

$$Cl_2CF^- \longrightarrow Cl^- + CClF$$

$$CClF \xrightarrow{H_2O} HCl,\ HF,\ CO \text{ and } HCO_2H$$

the observed products being formed according to the stoichiometry

$$Cl_2CFCO_2H \longrightarrow CO_2 + CHCl_2F$$

$$Cl_2CFCO_2H + H_2O \longrightarrow 2HCl + HF + CO_2 + CO$$

$$Cl_2CFCO_2H + 2H_2O \longrightarrow 2HCl + HF + CO_2 + HCO_2H$$

Dichlorofluoromethane that is hydrolyzed gives the same stoichiometry as that which decomposes as the carbanion without ever reaching the haloform stage. From the equations above it may be seen that the concentration of chloride ion formed is equal to the following function of the concentration of dichlorofluoroacetic acid that has reacted and the dichlorofluoromethane that has been formed

$$[Cl^-] = 2(\Delta[Cl_2CFCO_2H] - [CHCl_2F]) \qquad (2)$$

Similarly, the change in total acid concentration may be expressed

$$\Delta[H^+] = (2 + f)(\Delta[Cl_2CFCO_2H] - [CHCl_2F]) - [CHCl_2F] \qquad (3)$$

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[1] For part XIV see J. Hine and P. B. Langford, THIS JOURNAL, **80**, 6010 (1958).

[2] F. H. Verhoek, *ibid.*, **56**, 571 (1934); R. A. Fairclough, *J. Chem. Soc.*, 1186 (1938).

[3] L. H. Sutherland and J. G. Aston, THIS JOURNAL, **61**, 241 (1939).

[4] I. Auerbach, F. H. Verhoek and A. L. Henne, *ibid.*, **72**, 299 (1950).

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

[6] J. Hine and D. C. Duffey, *ibid.*, **81**, 1131 (1959).

where f is the fraction of the haloform hydrolysis that yields formate; that is

$$f = [HCO_2H]/([CO] + [HCO_2H])$$

From eqs. 2 and 3 the following equation may be obtained for the yield of dichlorofluoromethane

$$\frac{[CHCl_2F]}{\Delta[Cl_2CFCO_2H]} = 1 - \frac{1}{3 + f - 2(\Delta[H^+]/[Cl^-])} \quad (4)$$

Analyses for the formate and carbon monoxide produced gave f-values ranging from 0.44 to 0.66. We have used an intermediate value of 0.50 in our calculations. A 20% error in this value will change the calculated dichlorofluoromethane yield by less than 1% in the range of our observations. The calculated yields of haloform (69 ± 6%) are reasonably near that found by direct analysis in one experiment (72%). To calculate the change in dichlorofluoroacetic acid concentration eqs. 2 and 4 were combined to give

$$\Delta[Cl_2CFCO_2H] = \frac{(3 + f)}{2}[Cl^-] - \Delta[H^+] \quad (5)$$

The kinetics of the decomposition of dichlorofluoroacetic acid were studied by heating an aqueous solution of the acid and an acetate buffer in a constant temperature bath and following the changes in acidity and/or chloride ion concentration. Rate constants calculated from eq. 5 and the integrated form of the first-order rate equation remained reasonably constant within a run as shown by a typical example in Table I.

TABLE I

DECARBOXYLATION OF DICHLOROFLUOROACETIC ACID IN AQUEOUS SOLUTION AT 94.8°[a]

Time, sec.	Ml. 0.1356 M $AgNO_3$[b]	10^6k, sec.$^{-1}$
0	0.23	
49,700	2.78	6.47
66,270	3.53	6.63
134,600	5.63	6.48
158,100	6.22	6.56
181,100	6.65	6.50
231,200	7.36	6.33
232,300	7.48	6.54
	Av.	6.50 ± 0.07

[a] $[Cl_2CFCO_2H]_0 = 0.1619$ M, $[NaOAc]_0 = 0.336$ M, $\Delta[H^+]/[Cl^-] = -0.18$. [b] Per 15-ml. sample.

From the summary of rate constants obtained under various conditions given in Table II there appears to be no very large salt effect, below concentrations of 1.0 M at least, nor any significant effect produced by changing the initial hydrogen ion concentration by more than 100-fold.

Using the absolute rate equation[7]

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

a plot of log k − log($\mathbf{k}T/h$) *versus* $1/T$ was made. From the best straight line through these points a heat of activation of 38.3 ± 2 kcal./mole and an entropy of activation of 21 ± 6 e.u. were calculated.

These observations support reaction mechanism 1, which like that of most trihaloacetic acids involves a rate-controlling decomposition of the carboxylate anion to carbon dioxide and a trihalomethyl carbanion. The question of whether the halide ions observed in the reaction arose directly from dichlorofluoromethyl carbanions formed in the decarboxylation reaction or whether some of them are formed by the subsequent hydrolysis of the dichlorofluoromethane is not definitely settled by our experiments. However, since it was found that dichlorofluoromethyl carbanions decompose about 7.8% of the time they are formed at 0° and 9.4% at 20°,[8] it seems possible that 30% decompose at 100° so that it is not *necessary* to postulate the subsequent hydrolysis of the haloform.

TABLE II

DECOMPOSITION OF DICHLOROFLUOROACETIC ACID IN AQUEOUS SOLUTION

Temp., °C.	Initial ionic strength	pH	10^6k, sec.$^{-1}$
71.3	0.77	5.02	0.18 ± 0.05
81.0	0.08	4.70	0.78 ± .01
90.5	0.17	5.02	3.39 ± .19
90.5	0.77	5.02	3.34 ± .17
90.5	1.37	5.02	3.25 ± .14
90.5	1.97	5.02	2.72 ± .06
94.8	0.11	4.77	7.02 ± .25
94.8	.34	4.77	6.50 ± .06
94.8	.89	6.25	6.97 ± .56

In connection with the results obtained when chlorodifluoroacetic acid decomposes in the presence of fluoride ions,[6] the effect of added sodium fluoride on the decomposition of dichlorofluoroacetic acid was studied. Even in the presence of saturated sodium fluoride (about 1.0 M) less than 1% of dichlorofluoromethane and fluoroform was produced. It seems unlikely that the fluoride ions were displacing chloride ions from the starting material to form chlorodifluoroacetate to any major extent since the latter decomposes (about as fast as dichlorofluoroacetate) to give around 23% oxalate while we observed less than 0.3% oxalate in the dichlorofluoroacetate decomposition carried out in the presence of sodium fluoride.

Experimental

Reagents.—Dichlorofluoroacetic acid from the Columbia Organic Chemicals Co., Inc., was found to have a neutral equivalent of 147.1 ± 0.8, n^{24}_D 1.4181, d^{24}_4 1.565 and was used without further purification. Other reagents have been described previously.[1,6,8]

Analysis of Gaseous Products.—In some of the studies a 40-ml. reaction vessel equipped with a gas inlet tube was connected through a short condenser to a gas buret in which mercury was used as the confining liquid. At intervals the gas was flushed with nitrogen from the inlet tube into the buret and then transferred to a 10-cm. infrared gas cell. The gas was then analyzed by infrared measurements at 4.33 μ for carbon dioxide, 4.64 μ for carbon monoxide, 8.72 μ for fluoroform, 8.97 μ for chlorodifluoromethane and 9.23 and 9.33 μ for dichlorofluoromethane. Measurements using pure materials showed this analytical method to be reliable within 15% for all of the gaseous products except carbon dioxide (perhaps because of interference by atmospheric carbon dioxide), for which errors up to 40% are possible. In some cases the carbon dioxide was determined by Orsat analysis using 35% KOH solution as the absorbant, prior to the infrared analysis. The KOH solution absorbed some of the dichlorofluoromethane, but this amount could be determined by comparison with an example in which the carbon dioxide was not absorbed before infrared analysis.

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(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.

(8) J. Hine and N. W. Burske, THIS JOURNAL, **78**, 3337 (1956).

In one run 4.02 mmoles of dichlorofluoroacetic acid and 8.4 mmoles of sodium acetate in 21 ml. of water was refluxed gently for 62 hours. The gas analysis revealed the presence of 4.0 ± 0.1 mmoles of carbon dioxide, 2.9 ± 0.1 mmoles of dichlorofluoromethane and 0.61 ± 0.05 mmoles of carbon monoxide. Titration of the aqueous solution showed the presence of 1.05 mmoles of chloride, 2.30 mmoles of fluoride[9] and 0.47 mmole of formate.[10] The reacting material is thus accounted for essentially quantitatively.

Kinetic Runs.—In a typical run, 250 ml. of aqueous solution, 0.1619 *M* in dichlorofluoroacetic acid and 0.336 *M* in sodium acetate, was placed in a 250-ml. volumetric flask in a constant temperature bath at 94.8 ± 0.1°. At intervals, 15-ml. samples were withdrawn and titrated for chloride by the Mohr method. Acidimetric titrations carried out at the end of the run showed that the fraction $\Delta[H^+]/\Delta[Cl^-]$ was -0.18. In other runs in which acidimetric titrations were made at every point it had been found that this ratio remains essentially constant throughout the reaction. The data obtained in this run are given in Table I.

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[9] By the method of I. M. Kolthoff and E. B. Sandell, "Quantitative Inorganic Analysis," 3rd ed., The Macmillan Co., New York, N. Y., 1952, p. 721.

[10] By the method of J. W. Hopton, *Anal. Chim. Acta*, **8**, 429 (1953).

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

Methylene Derivatives as Intermediates in Polar Reactions. XVI. The Decomposition of Chlorodifluoroacetic Acid[1]

BY JACK HINE AND DONALD C. DUFFEY

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The decarboxylation of chlorodifluoroacetate ion (unlike most trihaloacetate ions, which lose carbon dioxide to give a trihalomethyl anion) appears to be a concerted decomposition to carbon dioxide, chloride ion and difluoromethylene. This is shown by the fact that very little chlorodifluoromethane is formed, even in acidic solution, and even this small amount appears to come from difluoromethylene rather than from a trihalomethyl anion. Fluoroform is also produced and its yield may be greatly increased if fluoride ion is added to the decarboxylation reaction solution. The addition of chloride ion increases the yield of chlorodifluoromethane, and bromide and iodide ions bring about the formation of bromodifluoromethane and difluoroiodomethane, respectively. Further evidence for the concerted character of the decarboxylation is provided by the rate constant for the reaction which is about forty times as large as would be expected for a decomposition to the chlorodifluoromethide ion. The decarboxylation reaction is accompanied by the formation of oxalic acid by a process that appears to be initiated by the SN2 attack of water on the chlorodifluoroacetate ion. An analogous SN2 attack by fluoride ion to give trifluoroacetate becomes another important side reaction in the presence of 1 *M* or stronger fluoride ion.

Introduction

Evidence presented in earlier articles in this series shows that the basic hydrolysis of a number of haloforms proceeds by the mechanism

$$CHX_3 + OH^- \rightleftharpoons CX_3^- + H_2O$$

$$CX_3^- \longrightarrow CX_2 + X^-$$

followed by rapid reactions of the intermediate dihalomethylene.[2] Subsequent work has shown that while bromodifluoromethane and chlorodifluoromethane also react through dihalomethylene intermediates,[3] their hydrolyses seem much too fast to involve the corresponding trihalomethyl anions.[4] Instead, it appears that the relatively unstable carbanions are by-passed in a concerted α-elimination that leads *directly* to difluoromethylene, the most stable of the dihalomethylenes.[5] The concerted mechanism is further supported by the observation that the basic hydrolysis of deuteriobromodifluoromethane, unlike that of the nine other deuterohaloforms studied, is *not* accompanied by deuterium exchange.[4] This observation is permissive but not compelling evidence for the concerted mechanism. The two-stage mechanism could always be supported by the argument that the carbanion is indeed a true reaction intermediate but that under the basic conditions employed for hydrolysis it is reprotonated much more slowly than it undergoes loss of a halide ion. This objection may, of course, be made to the use of deuterium exchange as a test for carbanion intermediacy in any base-catalyzed reaction. However in the present case we have at least partially met this objection by attempting to generate the intermediate carbanion, if indeed there is one, in acidic solution. This was accomplished by studying the decarboxylation of chlorodifluoroacetic acid.

Verhoek[6] and also Fairclough[7] have described evidence that the decarboxylation of trichloroacetic and tribromoacetic acids is a unimolecular decomposition of the carboxylate anion to give a trihalomethyl anion that is subsequently protonated.

$$X_3CCO_2^- \longrightarrow CO_2 + CX_3^-$$

$$CX_3^- \longrightarrow CHX_3$$

Later work supports this mechanism for dibromochloro-[8] and trifluoroacetic[9] acids. There is definitely a qualitative relationship between the reactivity of trihaloacetates in decarboxylation and of deuteriohaloforms in deuterium exchange, another

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[1] For part XV see ref. 24. This work was preliminarily described at the Sixth Biennial Conference on Reaction Mechanisms, Swarthmore, Penna., September 13, 1956.

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

[3] J. Hine and J. J. Porter, *ibid.*, **79**, 5493 (1957).

[4] J. Hine and P. B. Langford, *ibid.*, **79**, 5497 (1957).

[5] J. Hine and S. J. Ehrenson, *ibid.*, **80**, 824 (1958).

[6] F. H. Verhoek, *ibid.*, **56**, 571 (1934).

[7] R. A. Fairclough, *J. Chem. Soc.*, 1186 (1938).

[8] L. H. Sutherland and J. G. Aston, THIS JOURNAL, **61**, 241 (1939).

[9] I. Auerbach, F. H. Verhoek and A. L. Henne, *ibid.*, **72**, 299 (1950).