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

(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).

sodium acetate, was placed in a 250-ml. volumetric flask in a constant temperature bath at $94.8 \pm 0.1°$. 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 samples were withdrawn and titrated for chloride by the Mohr method.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 $\Delta[\mathrm{H}^+]/\Delta[\mathrm{Cl}^-]$ 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.

ATLANTA, GA.

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

BY JACK HINE AND DONALD C. DUFFEY

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 S_N2 attack of water on the chlorodifluoroacetate ion. An analogous S_N2 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

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

$$CX_3^- \longrightarrow CX_2 + X^-$$
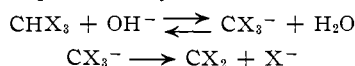
followed by rapid reactions of the intermediate dihalomethylene.[2] Subsequent work has shown that while bromodifluoromethane and chlorodifluoromethane also react through dihalomethylene intermediates,[3] their hydrolyses seem much too fast to involve the corresponding trihalomethyl anions.[4] Instead, 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.

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

$$CX_3^- \longrightarrow CHX_3$$
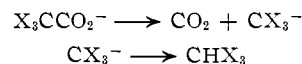
Later work supports this mechanism for dibromochloro-[8] and trifluoroacetic[9] acids. There is definitely a qualitative relationship between the reactivity of trihaloacetates in decarboxylation and of deuteriohaloforms in deuterium exchange, another

(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).

trihalomethyl-anion-forming reaction.[10] Since we have hypothesized that as the hydrogen is removed from chlorodifluoromethane the incipient carbanion largely decomposes to dihalomethylene, we should expect the same incipient carbanion arising during decarboxylation also to decompose as it is formed. That is, we should expect the rate-controlling step of the decarboxylation to be a single concerted process leading directly to carbon dioxide, chloride ion and difluoromethylene.

$$ClCF_2CO_2^- \longrightarrow \overset{-\delta}{Cl}\cdots\overset{-\delta}{CF_2}\cdots\overset{-\delta}{CO_2} \longrightarrow Cl^- + CF_2 + CO_2$$
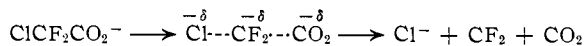
If this mechanism is correct, then unlike the typical trihaloacetic acids, chlorodifluoroacetic acid should not yield haloform upon decarboxylation, unless some is formed from the dihalomethylene produced. Auerbach, Verhoek and Henne reported that sodium chlorodifluoroacetate yielded fluoride and chloride ions and acid, but did not tell whether haloform was produced or not.[9] They concluded that hydrolysis of the acid was occurring faster than decarboxylation. Because of the possibility that the halide ions and acid are produced *by* the decarboxylation and the hydrolysis of the dihalomethylene produced, we decided to study the reaction in more retail.

Results and Discussion

Reaction Products.—Since the trihaloacetic acids are relatively strong they exist to a considerable extent as trihaloacetate ions in aqueous solution even when not neutralized. It was therefore convenient to study the decarboxylation in these acidic solutions where the hydrolysis of any haloform produced should be at a minimum. The infrared spectrum of the volatile products of such decarboxylation reactions showed the presence of carbon dioxide, carbon monoxide and formic acid and small amounts of chlorodifluoromethane and fluoroform. Since Haszeldine has reported that silver chlorodifluoroacetate decomposes in aqueous solution to give oxalic acid in good yield,[11] we tested for oxalate formation in our reaction mixtures. Upon finding a positive test we worked out a semi-quantitative method for analyzing for the oxalate in our reaction solutions, by initial precipitation as silver oxalate, transformation to dimethyl oxalate by the action of methyl iodide and infrared analysis. In runs carried out in the presence of large concentrations of fluoride ion, trifluoroacetic acid was also produced. This was established by a method based on the fact that the trifluoro- acid decarboxylates much more slowly than the chlorodifluoro- acid. The solution to be analyzed was first heated under conditions sufficient to decarboxylate essentially all of the chlorodifluoroacetic acid and then shown to give large amounts of fluoroform when heated to the temperatures at which trifluoroacetic acid is known to decarboxylate readily.

The yields of haloform from the decarboxylation reaction (that is, based on the carbon dioxide formed simultaneously) of 3.3 millimoles of chloro-

(10) J. Hine, N. W. Burske, M. Hine and P. B. Langford, THIS JOURNAL, **79**, 1406 (1957).

(11) R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952).

difluoroacetic acid in 25 ml. of water at gentle reflux for 11 to 24 hours are shown in Table I.

TABLE I

YIELDS OF HALOFORMS IN THE DECARBOXYLATION OF CHLORODIFLUOROACETIC ACID IN AQUEOUS SOLUTION

Added salt	Haloform yield, % $CHClF_2$	CHF_3
None	1	3
1.2 M NaF	0.1	23
2.6 M NaCl	8	0.1

Just as these quantitative experiments showed that sodium fluoride increased the fluoroform yield and sodium chloride increased the chlorodifluoromethane yield, qualitative experiments showed that the addition of lithium bromide and of sodium iodide brought about the formation of bromodifluoromethane and difluoroiodomethane, respectively.

In acetate-buffered (pH 4–5) solutions the yield of oxalate was 22 ± 4% while in the more acidic (pH ~1) unbuffered solutions it was about 43%.

Reaction Kinetics.—Believing that the decarboxylation of chlorodifluoroacetic acid would prove to be a first-order reaction of the anion, like that of other trihaloacetic acids has been found to be,[6-9] we studied the reaction kinetics in a solution containing a sodium acetate–acetic acid buffer. In a strongly acidic solution the kinetics might have been complicated by the presence of considerable amounts of chlorodifluoroacetic acid in its un-ionized form, while in a basic solution any chlorodifluoromethane that was produced might be lost by subsequent hydrolysis. One chloride ion is liberated for every chlorodifluoroacetate ion that reacts by any of the paths except the one that leads to chlorodifluoromethane. Since very little of this haloform is produced, particularly in the dilute solutions on which we made kinetic studies, the over-all rate of decomposition of chlorodifluoroacetate may be followed satisfactorily by titration of the chloride ions liberated. The reaction may also be followed acidimetrically. Except in those runs where sodium or potassium fluoride was added with the result of a large amount of attack on the walls of the glass reaction vessel, the ratio of the change in acidity to the concentration of chloride ions formed remained essentially constant throughout the reaction. This is expected since the concentrations of halide ions liberated in the dilute solutions used are not sufficient to bring about any major change in the fractions of reaction proceeding by the various paths. Thus kinetic runs were made by acidimetric measurements on each point, coupled with enough chloride determinations to give the ratio accurately. The ratio was found to be little affected by the pH over the range studied (1 to 5). In the runs made in the presence of large concentrations of sodium chloride and bromide the ratio could not be determined at all accurately and was therefore assumed to be the same as in similar runs without added salt. A correction for the amount of additional haloform probably produced in these cases would raise the rate constants by no more than 8%.

Despite the presence of the buffer the hydrogen ion concentration changed by several-fold in most of our kinetic runs. Therefore the constancy of the rate constants obtained within the various runs is good evidence that the present process is a first-order reaction of the carboxylate anion.

The rate constants obtained under the various conditions used are summarized in Table II. Infrared measurements showed that in the presence of the acetate buffer about 3% of a mixture of chlorodifluoromethane and fluoroform was produced, much as had been observed (Table I) with the unbuffered solution. From a plot of log k − log $(\mathbf{k}T/h)$ vs. $1/T$ based on Table II, a heat of activation of 32 ± 2 kcal./mole and an entropy of activation of $+3 \pm 3$ e.u. may be calculated for the decomposition reaction as a whole. If the fraction of the reaction that involves hydrolysis to give oxalate is independent of the temperature, the activation parameters for the decarboxylation

Table II

RATE CONSTANTS FOR THE DECOMPOSITION OF CHLORODI-FLUOROACETIC ACID IN AQUEOUS SOLUTION[a]

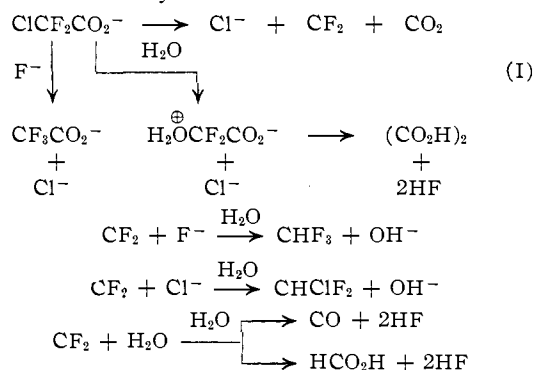| Temp., °C.	Added salt	$10^6 k$, sec.$^{-1}$
97.2	None	2.0 ± 0.2
97.1	None	$1.84 \pm .02$
71.6	None	$0.129 \pm .003$
97.2	$1.2\,M$ NaF	$4.4 \pm .1$
97.3	$0.95\,M$ NaF	$3.5 \pm .5$
94.9	$2.3\,M$ KF	9.4 ± 1.1
97.3	$0.8\,M$ NaBr	2.2 ± 0.1
97.2	$1.64\,M$ NaCl	1.94 ± 0.08

[a] An acetate buffer was also present in each case to keep the pH between 4 and 5.5.

reaction are essentially the same. The change in the ratio of acid to chloride formed in the experiments at lower temperatures suggested that the oxalate yield was increasing, but direct determinations showed a small decrease.

Reaction Mechanism.—The data of Table I, on the yields of the volatile products in the presence and absence of added salts, provide good evidence that the decarboxylation of chlorodifluoroacetate is a concerted process, yielding difluoromethylene directly without the intervention of a trihalomethyl carbanion. The relative absence of chlorodifluoromethane from the reaction products was not due to hydrolysis of this haloform after it was produced. Separate experiments showed that the hydrolysis of this compound in aqueous solution is so slow that little of it would have been destroyed under the reaction conditions. The fluoroform observed could not have been formed from trifluoroacetic acid present as an impurity or formed during the reaction because separate experiments showed that trifluoroacetic acid decarboxylates too slowly to yield an observable amount of fluoroform under our reaction conditions. Nor is it possible that the fluoroform is produced by the reaction of chlorodifluoromethane with fluoride ions. Independent experiments showed that this process would never be more than a minor reaction under the conditions used.
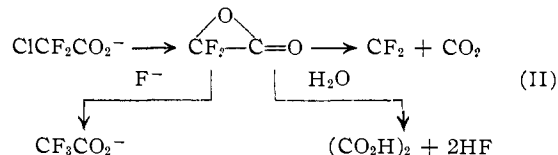
It appears that even that small amount of chlorodifluoromethane that is formed arises, at least

largely, from difluoromethylene molecules and chloride ions produced in the decarboxylation reaction. Most of the intermediate CF_2 molecules are hydrolyzed to yield fluoride ions that combine with some of the CF_2 to produce the fluoroform observed. This explanation for the formation of fluoroform is supported by the sharp increase in fluoroform yield that occurs in the presence of added fluorides and by the independent observation that in the presence of fluoride ions the reaction of chlorodifluoromethane with alkali, another process in which difluoromethylene is formed, yields fluoroform. We believe that our data are accommodated by the reaction scheme

$$
\begin{array}{c}
\text{ClCF}_2\text{CO}_2^- \longrightarrow \text{Cl}^- + \text{CF}_2 + \text{CO}_2 \\[4pt]
\text{F}^- \downarrow \quad \text{H}_2\text{O} \\[4pt]
\end{array}
\tag{I}
$$

$$
\begin{array}{ccc}
\text{CF}_3\text{CO}_2^- & \overset{\oplus}{\text{H}_2\text{OCF}_2\text{CO}_2^-} \longrightarrow & (\text{CO}_2\text{H})_2 \\
+ & + & + \\
\text{Cl}^- & \text{Cl}^- & 2\text{HF}
\end{array}
$$

$$\text{CF}_2 + \text{F}^- \xrightarrow{\text{H}_2\text{O}} \text{CHF}_3 + \text{OH}^-$$

$$\text{CF}_2 + \text{Cl}^- \xrightarrow{\text{H}_2\text{O}} \text{CHClF}_2 + \text{OH}^-$$

$$\text{CF}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{O}} \begin{cases} \text{CO} + 2\text{HF} \\ \text{HCO}_2\text{H} + 2\text{HF} \end{cases}$$

Except in those runs made in the presence of large concentrations of fluoride ions, the principal reaction path is a concerted decarboxylation to difluoromethylene, which reacts subsequently as shown. The second reaction path shown is simply a solvolysis reaction in which the nucleophilic solvent water displaces a chloride ion by what seems best classified as an SN2 reaction.[12] The intermediate thus formed then undergoes a number of rapid reactions to yield oxalic and hydrofluoric acids. The chlorodifluoroacetate ion is also susceptible to nucleophilic attack by fluoride ion, and the third primary reaction path, which becomes important only in the presence of considerable concentrations of fluoride ion, consists of this reaction, leading to the trifluoroacetate ion.

An alternate reaction scheme in which the initial step of the reaction is the formation of an α-lactone (or as Ingold prefers to consider it, a carbonium ion whose configuration is maintained by interaction with the carboxylate anion group[13]) which then reacts further with the available nucleophilic reagents, or decomposes to CF_2 and CO_2, would also explain the reaction products that we have observed.

$$
\text{ClCF}_2\text{CO}_2^- \longrightarrow \overset{\displaystyle O}{\underset{}{\text{CF}_2\!\!-\!\!\text{C}}}\!\!=\!\!\text{O} \longrightarrow \text{CF}_2 + \text{CO}_2
\tag{II}
$$

$$
\begin{array}{cc}
\text{F}^- \downarrow & \text{H}_2\text{O} \downarrow \\
\text{CF}_3\text{CO}_2^- & (\text{CO}_2\text{H})_2 + 2\text{HF}
\end{array}
$$

However this reaction mechanism seems to be rendered implausible by our kinetic results. Thus, according to this reaction mechanism, fluoride

(12) For a discussion of the SN2 and SN1 mechanisms see J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1956, pp. 93–113.

(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 383–384.

ion may intercept an intermediate to produce trifluoroacetate but it cannot change the total rate of disappearance of chlorodifluoroacetate, except by a salt effect. The increases in decomposition rate brought about by the addition of sodium and potassium fluorides (Table II) seem altogether too large to be merely "salt effects." These increases are quite reasonably interpreted in terms of an SN2 attack of fluoride ion on the chlorodifluoroacetate molecule (scheme I). It is known that as α-substituents fluorine atoms decrease SN2 reactivity less than any other halogen.[14] This fact coupled with its relatively low decomposition rate makes the chlorodifluoroacetate ion more likely to undergo significant SN2 attack than any other trihaloacetate ion that has been studied. It may also be noted from Table II that the increase in the decomposition rate is more than proportional to the concentration of added fluoride. This is exactly the result that would be expected if the increase is due to a reaction between two like-charged ions, such as fluoride and chloridifluoroacetate. The rate constant for such reactions increases with increasing ionic strength and the increase continues as a qualitative phenomenon into concentrated salt solutions[15] far beyond the concentration range where the Brönsted–Bjerrum equation[16] holds. Furthermore, if the trifluoroacetate is formed by the combination of α-lactone with fluoride ions then we might expect that the lactone would also combine with chloride ions and slow the reaction rate by a "mass-law effect" like that established by Grunwald and Winstein in the solvolysis of the α-bromopropionate anion.[17] That no mass-law effect was found is added evidence that fluoride ions attack chlorodifluoroacetate ions by an SN2 mechanism.

Since the bromide ion is usually more nucleophilic than the fluoride ion[18] we would expect it to attack the chlorodifluoroacetate ion much faster, with the formation of the bromodifluoroacetate ion. Since this ion should then decompose much more rapidly than the chlorodifluoroacetate ion, the addition of bromide ion should catalyze the reaction. Yet the data in Table II show that any such catalytic action is minor, at best. Apparently, for some reason the fluoride ion is more nucleophilic than bromide toward the chlorodifluoroacetate ion.

The data on the effect of added halide ions thus seem best explained without the hypothesis of an intermediate α-lactone. We prefer mechanism I for the formation of difluoromethylene, both for this reason and because of the fact that mechanism I is much more analogous to the process by which difluoromethylene is formed from chlorodifluoromethane and alkali. This argument is particularly relevant because of the fact that the decarboxylation rate, when plotted against the rate of proton removal from chlorodifluoromethane, gives a reason-

able fit to the relationship[10] obtained from data on other trihaloacetic acids and haloforms.

Since none of our observations appear to require the α-lactone mechanism, while the SN2 mechanism for the reaction of chlorodifluoroacetate with fluoride ion seems established, we also prefer the SN2 mechanism to explain the hydrolysis reaction to give oxalate. The increase in yield of oxalate in acidic solution is presumably due to the fact that chlorodifluoroacetic *acid* can undergo SN2 attack by water but it cannot react by the decarboxylation path.

It should be noted that if the concerted mechanism is considered established for the hydrolysis[4] of CHBrF₂ and CHClF₂, then the formation of these haloforms from CF₂ and the corresponding halide ion in aqueous solution must, according to the principle of microscopic reversibility, not proceed through an intermediate trihalomethyl anion. It must instead be a concerted reaction, in which the carbon atom of CF₂ accepts a proton from some acid at the same time that it combines with a halide ion. The combination of CF₂ with a proton and fluoride ion is probably not a concerted process, though. The fact that fluoroform is produced in essentially quantitative yield in the decarboxylation of trifluoroacetate ion in boric acid-buffered ethylene glycol solution[9] shows that this decarboxylation probably gives a trifluoromethyl anion as a true intermediate. If this is so, then it is very likely that the hydrolysis of fluoroform proceeds by the carbanion rather than the concerted mechanism and therefore the formation of fluoroform from CF₂ and fluoride ion is also a two-stage process.

$$CF_2 + F^- \longrightarrow CF_3^-$$
$$CF_3^- + H_3O^+ \longrightarrow CHF_3 + H_2O$$
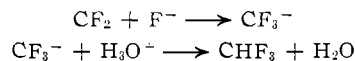
The occurrence of the two-step mechanism for the hydrolysis of fluoroform is probably a result of the great difficulty with which fluoride ions are ejected from organic molecules.

The fact that fluoride ions are more effective than chloride ions at combining with the intermediate *difluoro*methylene, as shown by the fact that higher yields of fluoroform could be obtained than of chlorodifluoromethane, was rather surprising in view of the fact that the reactivities of the halide ions toward *dichloro*methylene[19] stand in the same order as do their average nucleophilicities in other reactions, I > Br > Cl > F.[20] Our data are not adequate to show the relative reactivities of bromide and iodide ions toward CF₂, and in any event a quantitative comparison of the relative reactivities of the four halide ions toward CF₂ might be difficult to interpret, since it appears that fluoride reacts by a mechanism different from that of the other halide ions. This difference in mechanism does not, in itself, however, explain the greater reactivity of fluoride, since it is the other halogens for which there is, between haloform and difluoro-

(14) J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955); J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *ibid.*, **78**, 2282 (1956).

(15) A. v. Kiss and P. Vass, *Z. anorg. allgem. Chem.*, **209**, 236 (1932); **217**, 305 (1934); *Z. physik. Chem.*, **160**, 290 (1932); A. N. Kappanna, *J. Indian Chem. Soc.*, **6**, 419 (1929); **8**, 541 (1931).

(16) Reference 12, p. 84.

(17) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 841 (1948).

(18) Reference 12, sec. 6-2.

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

(20) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953). The nucleophilicity constant of 2.0 for fluoride ion[21] was taken from the talk given by C. G. Swain before the 13th National Organic Chemistry Symposium of the American Chemical Society, June 17, 1953, Ann Arbor, Mich.

(21) Reference 12, p. 140.

methylene, a path of *lower* energy than the intermediate carbanion would have. The unexpectedly high nucleophilicity of fluoride ions toward difluoromethylene has already been observed in the reaction of potassium isopropoxide with chlorodifluoromethane where about 5% fluoroform was observed[22] despite the fact that the fluoride ion concentration remains quite small (because of the limited solubility of potassium fluoride in isopropyl alcohol). It seems probable that this nucleophilicity is related to the presence of fluorine atoms on the carbon undergoing nucleophilic attack since we have already mentioned the similar unexpected high rate of attack of fluoride ions on the chlorodifluoroacetate ion. The tendency of even one fluorine substituent to increase the reactivity toward nucleophilic atoms that stand higher in the periodic table relative to nucleophilic atoms of higher atomic weight may also be found in the data on the reactivity of methylene halides. Thus while sodium iodide in acetone and sodium thiophenolate in methanol are respectively 330 and 1450 times as reactive as sodium methoxide in methanol toward methylene bromide, they are only 9 and 23 times as reactive toward fluorobromomethane.[14] This is an added example of the type of phenomena recently discussed by Bunnett.[23]

Another argument for the concerted nature of the decarboxylation of the chlorodifluoroacetate ion may be based on the reaction rate. Since the rates of carbanion formation from haloforms and alkali change smoothly as the nature of the halogen atoms is changed and since there is a semi-quantitative relation between these rates and the rates of decarboxylation of trihaloacetate ions[10] we might expect decarboxylation rates also to change smoothly with the structure of the trihaloacetate ion. The only available data that are relevant to this point are represented in Fig. 1. Here the rate constants for decarboxylation in water at $70^{06-10,24}$ (extrapolated from the nearest possible temperature, if necessary) are plotted *vs.* the number of the chlorine atoms of trichloroacetate that have been replaced by other halogens. For the replacement of chlorine by bromine the points fall near a straight line. For the replacement of chlorine by fluorine three points fall near a straight line but chlorodifluoroacetate, it may be seen, reacts about 40 times as fast as would be expected from the carbanion mechanism. Apparently this carboxylate anion does not have to form a chlorodifluoromethide ion. It has available an alternate lower energy path in which carbon dioxide, chloride ion and difluoromethylene are formed in a single concerted step. This argument is analogous to the previous one based on the rates of haloform hydrolysis and deuterium exchange[4] except that in the present case the rate "expected" for chlorodifluoromethide ion formation was estimated by interpolation rather than by extrapolation. The 40-fold augmentation of rate above that expected leaves open the possibility that 2.5% of the reaction may proceed by the carbanion mechanism.

This investigation leaves several questions un-

(22) J. Hine and K. Tanabe, THIS JOURNAL, **80**, 3002 (1958).

(23) J. F. Bunnett, *ibid.*, **79**, 5969 (1957).

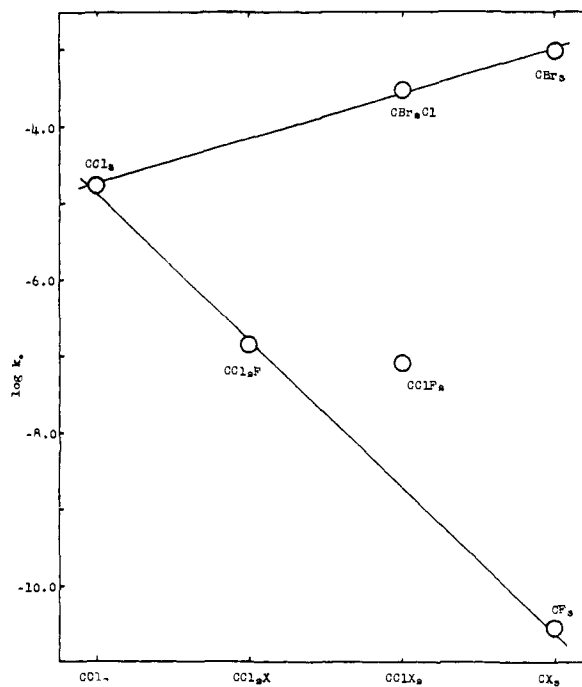(24) J. Hine and D. C. Duffey, *ibid.*, **81**, 1129 (1959).

Fig. 1.—Decarboxylation rates of trihaloacetic acids in water at 70°.

answered, of course. One is why the addition of 2.6 *M* sodium chloride causes the fluoroform yield to drop so sharply although the chloride ions are only reacting with 8% of the available difluoromethylene molecules. Another relates to the fact that the products we studied accounted for only about 80% of the reacted starting material.

Experimental

Reagents.—The chlorodifluoromethane used has been described previously. The chlorodifluoroacetic acid (Columbia Organic Chemicals Co.) used, m.p. 25°, was fractionated (b.p. 114–116° at 740 mm.) before use.

Decarboxylation of Chlorodifluoroacetic Acid.—The reaction vessel for this study was a 50-ml. flask into which had been sealed a gas inlet tube fitted with a stopcock. This flask was fitted through a 15-cm. (over-all) reflux condenser to the 100-ml. gas buret of an Orsat gas analysis apparatus. Five runs were made in which 3.3 mmoles of chlorodifluoroacetic acid was used in 25 ml. of aqueous solution. In one run no salt was added, in the second 33 mmoles of sodium fluoride (not all of which dissolved) and in the other three, 66 mmoles of sodium chloride, lithium bromide and sodium iodide, respectively. The reaction flask containing successively the five solutions described was heated with an oil-bath so that its contents refluxed slowly. After a time between 11 and 24 hours, the reaction was discontinued and nitrogen gas was allowed to sweep through the gas inlet tube. The nitrogen and gaseous reaction products, which were collected over mercury in the gas buret, were then admitted to a 10-cm. infrared cell and analyzed as described previously.[24] The presence of bromodifluoromethane and of difluoroiodomethane in the runs with bromide and iodide ions was shown clearly by the spectra, but no quantitative estimates of the yields were attempted. Titrations showed that after 300 hours at 100°, chloride ion was formed from chlorodifluoroacetic acid in 98% yield. In one run, using improved analytical techniques,[24] 67 ± 2% carbon dioxide, 34 ± 3% oxalate, 10 ± 1% carbon monoxide, 24 ± 1% formate, 1 ± 0.2% chlorodifluoromethane, 1 ± 0.2% fluoroform and 68 ± 5% fluoride ion were obtained. Thus the fate of the carboxyl carbon atom was accounted for quantitatively but not that of the α-carbon atom nor of the fluorine. The gas infrared spectra showed no bands except for the compounds reported. It thus seems possible that

part of the decomposition reaction may be following a path of an unknown nature.

The Hydrolysis of Chlorodifluoromethane in Acidic Aqueous Solution.—Twenty-five ml. of a solution 0.0752 N in both acetic acid and sodium perchlorate and 0.1248 N in sodium acetate (to inhibit the action of hydrofluoric acid on the container) was pipetted into an ampoule. The vapor space above the liquid was evacuated and filled with chlorodifluoromethane twice and then the liquid was cooled to 0° and shaken to saturate it with gas. At least 0.5 mmole dissolved. The ampoule was then sealed and placed in a bath at 97.2° for 72 hours. It was then found to be 0.0035 M in chloride ion. Therefore less than 20% of the haloform had hydrolyzed. Manometric measurements on a similar container showed that about half of the haloform that dissolved at 0° was still in solution in the sealed tube at 100°. With so small an amount of hydrolysis occurring in 72 hours in a solution in equilibrium with a high pressure of chlorodifluoromethane, it seems very unlikely that there should be any significant amount of hydrolysis in less than 24 hours in a solution in contact almost entirely with water vapor and from which the haloform is continually being swept by the refluxing action and the evolution of other gases.

The Reaction of Chlorodifluoromethane with Fluoride Ions.—A 1.6 M solution of sodium hydroxide in water was saturated with sodium fluoride and then with chlorodifluoromethane at 0°. After this solution was heated in a sealed tube for 30 minutes at 100° the dissolved gas was found to be 10% fluoroform and 90% chlorodifluoromethane.

When an aqueous solution 10 M in potassium fluoride and 0.0043 M in perchloric acid was saturated with chlorodifluoromethane at 0° and then heated in a sealed tube at 100° for 48 hours, a 19% conversion of chlorodifluoromethane to fluoroform was observed. Titration of the resultant solution, however, using phenolphthalein, showed that it had become basic to an extent greater than 0.026 M. The condition of the walls of the reaction vessel suggested that fluoride ions had been hydrolyzed to hydrogen fluoride which was then destroyed by reaction with the glass. In any case, since the fluoroform formation is obviously base-catalyzed it seems likely that most of the observed 19% of fluoroform was produced after the reaction solution became basic.

Kinetic runs were carried out by withdrawing samples of the reaction solutions contained in volumetric flasks immersed in a constant temperature bath. These samples were titrated with standard carbonate-free sodium hydroxide to the phenolphthalein end-point, made slightly acidic with perchloric acid and in some cases then titrated with silver nitrate by Mohr's method. The ratio of the change in acid concentration to the change in chloride concentration did not vary significantly during a run and for this reason the more accurate acidimetric titrations were used in calculating the rate constants. From these titrations and the average value of the ratio $\Delta[H^+]/\Delta[Cl^-]$ the value of Δ [ClCF$_2$CO$_2^-$] was determined, since essentially one chloride ion is formed for every chlorodifluoroacetate ion that reacts. The rate constant was then calculated as shown in Table III, where the data obtained in one run is summarized.

Analysis for Oxalate.—Since the fluoride, chloride, formate, acetate or trihaloacetate present seemed to interfere with some of the standard methods for the determination of oxalate, the following new method was devised. A 100% excess of silver nitrate solution was added to the reaction solution and the resultant precipitate of silver chloride, oxalate and perhaps formate was collected on a filter and dried for about 45 minutes at 110°. The dry powder was refluxed with about 20 ml. of methyl iodide for at least an hour and the unreacted methyl iodide was almost entirely removed by fractional distillation. The residue was refluxed with a known volume of carbon disulfide to dissolve the dimethyl oxalate. Some of the clear supernatant carbond disulfide solution was then removed by use of a syringe

TABLE III

DECOMPOSITION OF SODIUM CHLORODIFLUOROACETATE IN AQUEOUS SOLUTION AT 97.1°

[ClCF$_2$CO$_2$H]$_0$ = 0.0477; [NaOAc]$_0$ = 0.1355; $\Delta[H^+]/\Delta[Cl^-]$ = 2.377

Time, sec.	Ml. NaOH 0.04807 N[a]	Δ[ClCF$_2$CO$_2^-$]	$10^6 k$, sec.$^{-1}$
0	4.98	0.00000	
21,600	5.43	.00189	1.87
83,400	6.61	.00685	1.87
128,400	7.34	.00992	1.81
173,400	8.04	.01286	1.82
262,200	9.37	.01844	1.86
433,800	11.20	.02612	1.83
527,400	12.02	.02958	1.84

Av. 1.84 ± 0.02

[a] Per 5-ml. sample.

and the concentration of oxalate therein determined by quantitative measurements on the 5.64 and 5.72 μ carbonyl bands. Determination of the full spectra showed that the compound being measured was indeed dimethyl oxalate. Blank experiments using reagent sodium oxalate showed that there is some loss of material in the procedure described, but that the yields were 85 ± 10%. Blank experiments were also used to show that neither sodium fluoride, chloride, formate, acetate nor chlorodifluoroacetate interferes with the determination. Oxalate was shown to be stable to even the most acidic conditions employed by a blank experiment in which sodium oxalate was refluxed with 0.03 M trifluoroacetic acid for 13 days.

Trifluoroacetate from Chlorodifluoroacetate and Fluoride.—A solution of 14.9 mmoles of chlorodifluoroacetic acid and 21.9 mmoles of sodium acetate in 250 ml. of 2.3 M aqueous potassium fluoride was maintained at 94.9° for 92 hours, at which time the titration of an aliquot showed that 89% of the chlorine present had been liberated as chloride ions. A 25-ml. aliquot was neutralized, evaporated to dryness under reduced pressure, dissolved in 25 ml. of ethylene glycol and heated to about 165°. Only carbon dioxide and fluoroform were found in the evolved gases. During the first 2.25 hours 0.3 mmole of fluoroform was evolved, and at the end of this time the rate of gas evolution had not decreased sensibly. The two facts show that the fluoroform must have been coming from trifluoroacetate since the maximum amount of chlorodifluoroacetate present was 0.16 mmole, too small to account for the amount of fluoroform liberated, and the half-life of chlorodifluoroacetate at 165° is only a few minutes, so that any gas evolution from it should quickly stop. The half-life of trifluoroacetate at the temperature, however, is some 20 hours.[9]

The Decarboxylation of Trifluoroacetic Acid.—To a solution of 5.0 g. of sodium acetate in 100 ml. of water, 10.4 mmoles of trifluoroacetic acid was added. At various times, 10-ml. samples were withdrawn and titrated with 0.0482 N sodium hydroxide solution to the phenolphthalein end-point. At 97.2°, after 122.3 hours, a change in titer of 0.33 ml. had occurred. This corresponds to less than 2% reaction. The presence of 0.65 M lithium bromide was found to have no effect on the reaction rate.

ATLANTA, GA.