oxygen flame for 225 minutes at the rate of 775 ml./min. Thirty grams of sodium sulfite was added to the solution to reduce peroxides. Dilute sodium hydroxide was added to raise the *p*H to 7.0, and the solution was ether extracted continuously for 72 hours. From the ether extract there was obtained 3 g. of crude 2,2,5,5-tetramethyldihydropyrazine. After recrystallization from diethyl ether–petroleum ether mixtures, the crystals melted at 82–84°.

Anal. Calcd. for $C_8H_{14}N_2$: C, 69.6; H, 10.14; N, 20.23. Found: C, 69.57; H, 10.47; N, 20.17.

The aqueous layer was concentrated *in vacuo* to a volume of 200 ml. Solid potassium hydroxide (1.36 kg.) was added, and the solution was ether extracted batchwise with 1.36 kg. of ether. The ether extract was dried over solid potassium hydroxide and was distilled to yield a low boiling ether-*t*-butylamine azeotrope and 18 g. of higher boiling material, b.p. 80° (25 mm.) to 110° (5 mm.), and 5 g. of crude crystalline 2,2,5,5-tetramethyldihydropyrazine. Careful distillation of the higher boiling liquid fraction in a small spinning band column yielded the fractions shown in Table VI. Additional experimental details may be found in the patents listed below.[7]

TABLE VI

DISTILLATION OF HIGH BOILING AMINE FRACTION

Fraction	Ml.	B.p., °C., at 10 mm.	Analyses, % C	H	N	O^a	Neut. equiv.
1	2.7	72–73					
2^c	3.0	73–73.5	59.8	13.0	16.3	10.9	80.0
3^c	3.8	74–75.5	60.8	13.4	16.6	9.2	80.3
4	0.64	75.0–75.5					
5^b	2.0	76–78	64.6	13.8	17.8	3.8	75.5
6	1.1	80–107					
7	0.3	112.5–112.5					
8	1.5	118–135	62.4	12.1	17.2	8.3	84.0
9	0.3	135–133					

[a] By difference. [b] Fraction 5 is impure $\alpha,\alpha,\alpha',\alpha'$-tetramethyltetramethylenediamine. *Anal.* Calcd. for $C_8H_{20}N_2$: C, 66.2; H, 13.9; N, 19.5; neut. equiv., 72. [b,c] Fractions 2 and 3 appear to be very impure β-hydroxy-*t*-butylamine, probably contaminated by $\alpha,\alpha,\alpha',\alpha'$-tetramethyltetramethylenediamine. *Anal.* Calcd. for $C_4H_{11}NO$: C, 53.9; H, 12.4; N, 15.7; neut. equiv., 89. The other fractions have not been identified.

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[7] (a) C. S. Cleaver, U. S. Patent 2,782,219, issued February 19, 1957; (b) U. S. Patent 2,833,822, issued May 6, 1958.

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

Polar Effects on Rates and Equilibria[1]

BY JACK HINE

RECEIVED JULY 24, 1958

By assuming only the applicability of a linear free energy relationship like the Hammett equation, except that the *meta* and *para* reaction constants need not be identical, an equation is derived to show that the reaction constant for an equilibrium process divided by the difference between the substituent constants for the two groups being equilibrated yields a constant, τ_{meta} or τ_{para}, that is independent of the nature of the reaction, but which may vary with the solvent and temperature. From this relationship it is possible to calculate a reaction constant for any equilibrium for which the requisite substituent constants are available and, by application to rate processes, to calculate substituent constants for transition state groupings. By making the Hammett equation assumption that *meta* and *para* reaction constants are identical, equations are obtained that are clearly inconsistent with the substituent constants obtained from the defining reaction, the ionization of benzoic acids. It therefore follows that the Hammett equation could not possibly be *generally* applicable to equilibrium constants of *m*- and *p*-substituted benzene derivatives. Assuming, however, that the Hammett equation does hold, values of τ_m and τ_p are calculated from data on the acidity of benzenedicarboxylic acids, diols and diamines. The results show satisfactory internal consistency and each value is around 3.0.

Introduction

If the Hammett equation[2,3] is applicable to the reaction series

$$\mathrm{ArX_1} \rightleftharpoons \mathrm{ArX_2} \qquad (1)$$

where ArX_1 is the reactant and ArX_2 represents the product in an equilibrium process or the transition state in a rate process, then for the rate or equilibrium constants obtained one may write

$$\log \frac{K^x}{K^x_0} = \rho_x \sigma \qquad (2)$$

where K^x_0 is the rate or equilibrium constant for the unsubstituted compound, K^x is the value for a *m*- or *p*- substituted derivative under the same conditions, σ is a constant that depends on the nature of the substituent, and ρ_x is a constant that depends only on the nature of the reaction, solvent and temperature. The electron-donating or -withdrawing ability of the substituent is measured by σ, and ρ is a measure of the sensitivity of the reaction to changes in the polar character of substituents. A number of workers have pointed out that the sign and magnitude of ρ give valuable information about the difference in polar character between the groups X_1 and X_2. No quantitative relationships between ρ's and other parameters of linear free energy relationships appear to have been reported, however, and in fact, for the related Taft equation it has been stated "The quantitative prediction of ρ^* from theory has not been considered and remains an endeavor for the future."[4a] It is now shown that if the groups X_1 and X_2 in the general reaction 1 can, as substituent groups, be fitted to the Hammett equation (even if the σ's for them hold only for the conditions under which the K^x's are determined), ρ_x will be proportional to the difference between the σ constants of the two groups. The proportionality constants, measures of the effectiveness with which the influence of the substituents is *transmitted* to the reaction center, will be denoted τ. While a τ will have a definite value under a given set of conditions its value may vary with temperature, solvent and ionic strength.

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[1] Presented before the Philadelphia Organic Chemist's Club, May 1, 1958.

[2] L. P. Hammett, *Chem. Revs.*, **17**, 125 (1935); THIS JOURNAL, **59**, 96 (1937); "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapt. VII.

[3] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[4] R. W. Taft in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956; (a) p. 612, (b) Chapt. 13.

Equations will also be derived to point out some of the limitations on the generality of applicability of the Hammett equation.

Discussion

Definitions of τ's.—We shall start our derivation with the assumption that the data may be fit by use of two reaction constants, a ρ^p and a ρ^m. Any results we may get will, of course, be applicable to the Hammett equation which is simply a special case in which ρ^p and ρ^m are equal. From an equation of the type of 2 it is seen that the K^x values for the compounds p-$Y_1C_6H_4X_1$ and p-$Y_2C_6H_4X_1$ will fit the relationship

$$\log \frac{K^{x}{}_{p-X_1}}{K^{x}{}_{p-X_2}} = \rho^{p}{}_{x}\,(\sigma_{p-Y_1} - \sigma_{p-Y_2}) \qquad (3)$$

For the second reaction series, under the *same* set of reaction conditions

$$ArY_1 \rightleftarrows ArY_2 \qquad (4)$$

the relation is also assumed to hold and therefore for the reactants[5] p-$X_1C_6H_4Y_1$ and p-$X_2C_6H_4Y_1$ the relation

$$\log \frac{K^{y}{}_{p-X_1}}{K^{y}{}_{p-X_2}} = \rho^{p}{}_{y}\,(\sigma_{p-X_1} - \sigma_{p-X_2}) \qquad (5)$$

follows. Since $K^{x}{}_{p-Y_1}/K^{x}{}_{p-Y_2}$ is identical with $K^{y}{}_{p-X_1}/K^{y}{}_{p-X_2}$ eqs. 3 and 5 may be combined to give

$$\rho^{p}{}_{x}(\sigma_{p-Y_1} - \sigma_{p-Y_2}) = \rho^{p}{}_{y}(\sigma_{p-X_1} - \sigma_{p-X_2}) \qquad (6)$$

The terms in this equation can be separated into a function of the X's and an analogous and equal function of the Y's. Therefore, since the only limitations placed on reactions 1 and 4 were that they and the σ constants for X_1, X_2, Y_1 and Y_2 could be fit to the linear free energy relationship involving ρ^m's and ρ^p's, the value of such functions must be independent of the nature of the reactions involved

$$\frac{\rho^{p}{}_{x}}{\sigma_{p-X_1} - \sigma_{p-X_2}} = \frac{\rho^{p}{}_{y}}{\sigma_{p-Y_1} - \sigma_{p-Y_2}} = \tau_p \qquad (7)$$

τ_p being a constant whose value depends only on the conditions under which the two reactions were studied. In a like manner, the constant τ_m is defined

$$\frac{\rho^{m}{}_{x}}{\sigma_{m-X_1} - \sigma_{m-X_2}} = \frac{\rho^{m}{}_{y}}{\sigma_{m-Y_1} - \sigma_{m-Y_2}} = \tau_m \qquad (8)$$

Limitations on the Applicability of the Hammett Equation and Related Linear Free Energy Relationships.—If the Hammett equation is applicable, that is, if, in general, $\rho^{m}{}_{x}$ and $\rho^{p}{}_{x}$ are equal, eq. 8 may be divided by eq. 7 to give

$$\frac{\sigma_{p-X_1} - \sigma_{p-X_2}}{\sigma_{m-X_1} - \sigma_{m-X_2}} = \frac{\sigma_{p-Y_1} - \sigma_{p-Y_2}}{\sigma_{m-Y_1} - \sigma_{m-Y_2}} = \frac{\tau_m}{\tau_p} \qquad (9)$$

However, σ-constants derived from the standard reaction, the ionization of benzoic acids in aqueous solution at 25°, reveal that the constancy of σ-difference ratios required by eq. 9 is not actually found. The actual ratios[6] include, for example

$$\frac{\sigma_{p-NO_2} - \sigma_{p-MeO}}{\sigma_{m-NO_2} - \sigma_{m-MeO}} = \frac{1.046}{0.595} = \frac{\tau_m}{\tau_p}$$

and

$$\frac{\sigma_{p-F} - \sigma_{p-Me}}{\sigma_{m-F} - \sigma_{m-Me}} = \frac{0.232}{0.406} = \frac{\tau_m}{\tau_p}$$

In one case, the difference between *para* σ's is 0.451 larger than the difference between *meta* σ's while in the other case it is 0.172 smaller. Therefore the Hammett equation could not apply to both of the reaction series

$$ArNO_2 \rightleftarrows ArOMe, \text{ and}$$
$$ArF \rightleftarrows ArMe$$

at the same time, and, in fact, would not apply to either one unless its σ-difference ratio was the same as for the standard reaction, $(\sigma_{p-CO_2H} - \sigma_{p-CO_2^-})/(\sigma_{m-CO_2H} - \sigma_{m-CO_2^-})$.[7] Thus the presently known σ-values show that *the unmodified Hammett equation*[7a] *could not possibly fit the equilibrium constants of m- and p-substituted benzene derivatives in general.* That is, there could be no set of data on the other possible ArX_1–ArX_2 equilibria consistent with the Hammett equation and the benzoic-acid-derived σ's. This dilemma was brought on by the restriction that $\rho^{p}{}_{x}$ and $\rho^{m}{}_{x}$ had to be equal and may be solved by removing this restriction. The use of separate *meta* and *para* ρ constants has been suggested and practiced a number of times before. In a recent case, Gutowsky and co-workers found that nuclear magnetic resonance data on substituted fluorobenzenes seemed to require a ρ^p different from the ρ^m.[8] These data have been explained alternatively by Taft on the basis of an equation involving the same ρ for inductive effects for m- as for p-derivatives.[9] However, explanations of this type, those involving the use of dual σ-values,[2,3] and such equations as

$$\log \frac{k}{k_0} = \rho\sigma + \rho_R\sigma_R$$

cannot explain all of the data that seem to demand separate ρ^m- and ρ^p-values. Most of these equations reduce to expressions the type of the simple Hammett equation in the case of a substituent, like the trimethylammonio cation group, whose effect is entirely inductive. The fact that σ_m for this group is larger than σ_p[10,11] shows that such equations could not explain its powerful m-orienting influence in electrophilic aromatic substitution reactions. This fact could be explained by a dual-ρ equation, however, if ρ^p were sufficiently larger than ρ^m. Furthermore, ρ^p would be expected to be considerably larger than ρ^m since, from eqs. 7 and 8

$$\rho^{p}{}_{x} = \tau_p(\sigma_{p-X_1} - \sigma_{p-X_2})$$
and
$$\rho^{m}{}_{x} = \tau_m(\sigma_{m-X_1} - \sigma_{m-X_2}) \qquad (10)$$

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(5) Such reactants will be experimentally accessible only when the K^x's are equilibrium constants. When they are rate constants, X_2, the reaction center with its transition state configuration and energy, will be too unstable to be a part of an isolable compound. Analogously the K^y's must be equilibrium constants if p-$Y_2C_6H_4X_1$ is to represent a true chemical compound.

(6) Sigma constants from D. H. McDaniel and H. C. Brown's compilation (*J. Org. Chem.*, **23**, 420 (1958)) based on the ionization of benzoic acids.

(7) The general success of the Hammett equation shows that for the reactions that have received the most study, the σ-difference ratio has usually been reasonably near that for the standard reaction.

(7a) The term *Hammett equation* in this paragraph refers to the simple relation in which each substituent has a unique σ. By the use of a sufficiently large number of σ's for each group the equation may be made to fit any obtainable data, of course.

(8) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952); L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

(9) R. W. Taft, Jr., THIS JOURNAL, **79**, 1045 (1957).

(10) J. D. Roberts, R. A. Clement and J. J. Drysdale, *ibid.*, **73**, 2181 (1951).

(11) F. G. Bordwell and P. J. Boutan, *ibid.*, **78**, 87 (1956).

The τ-constants have around the same value,[12] σ_{p-X_1} and σ_{m-X_1} are zero since X_1 is hydrogen, and X_2 is of such a nature[13] that σ_{p-X_2} should be much larger than σ_{m-X_2}. This argument may be seen to be closely related to the explanation of Pfeiffer and Wizinger[14] as modernized by Roberts, Clement and Drysdale.[10]

The Evaluation of τ's for the Hammett Equation.—While it is thus shown that the known ionization constants of benzoic acids are inconsistent with the possibility that the Hammett equation is completely general, the Hammett equation is certainly useful enough and accurate enough to make the evaluation of τ's for it well worth while. This evaluation is hampered by the dearth of measurements on equilibria for which ρ and the two required σ's are known. Of the 39 equilibria listed by Jaffé,[3] for example, 33 involve electrically charged groups, and for none of the other σ's are both σ_{X_1} and σ_{X_2} known. Since equilibria involving species of differing electrical charge type are known to respond to solvent changes in different ways, the Hammett equation with constant values of σ for charged groups would not be expected to be applicable over a wide range of solvents. Roberts, Clement and Drysdale have found variations in the σ obtained for the trimethylammonio cation group in different solvents.[10] As an example of the variations in the reported values of such σ's, Jaffé lists values of -0.519 for the *p*-oxy anion and 0.132 for the *p*-carboxylate anion group, while Berliner and Monack[15] point out that values of -1.07 and -0.33, respectively, may also be calculated for these groups. To avoid errors due to such variations in σ's with solvent changes and the errors caused by use of σ's and a ρ obtained from different reactions, we have devised a method for evaluating τ's by use of measurements on symmetrical difunctional acids and bases. Since the compounds to be considered do not in any state of protonation contain a group capable of electron-withdrawal by a resonance effect in conjugation with one capable of resonance-electron-donation, deviations due to resonance interaction between substituent groups[2] should also be minimized. The substituent constant for the *p*-AH group may be expressed

$$\sigma_{p-\text{AH}} = \frac{\log\,(K_1{}^{p-\text{AH}}/2K_0)}{\rho_{\text{AH}}} \qquad (11)$$

where ρ_{AH} is the reaction constant for the acidity of ArAH's, K_0 is the acidity constant of C_6H_5AH, $K_1{}^{p-\text{AH}}$ is the first acidity constant of *p*-HAC_6H_4-AH, and the factor "2" corrects for the *two*-AH groups in the molecule. Likewise

$$\sigma_{p-\text{A}^-} = \frac{\log\,(2K_2{}^{p-\text{AH}}/K_0)}{\rho_{\text{AH}}} \qquad (12)$$

where $K_2{}^{p-\text{AH}}$ is the second ionization constant and "2" corrects for the two $-A^-$ groups in *p*-$C_6H_4(A^-)_2$. From eqs. 7, 11 and 12 it is seen that

$$\tau_{\text{p}} = \frac{(\rho_{\text{AH}})^2}{\log\,(K_1{}^{p-\text{AH}}/4K_2{}^{p-\text{AH}})} \qquad (13)$$

An analogous expression may be derived for τ_{m}.

The use of values of K_1/K_2 for terephthalic and isophthalic acids in dilute aqueous solution near 25° to calculate τ's is of particular interest since there is no possibility of error in the appropriate ρ_{AH}, which is defined as unity under these conditions. From the values of K_1/K_2 for terephthalic[16] and isophthalic acids[16] may be calculated values for τ_{p} and τ_{m} as shown in Table I, along with values calculated from K_1/K_2's for hydroquinone,[21] resorcinol[21] and *m*- and *p*-phenylenediamines,[25] and the ρ's (2.113[3] and 2.767[3]) for the acidity of phenols and anilinium ions.

TABLE I

VALUES OF τ_{m} AND τ_{p}

Source	τ_{m}	τ_{p}
$C_6H_4(CO_2H)_2$[16]	2.66	3.05
$C_6H_4(OH)_2$[21]	2.84	2.91
$C_6H_4(NH_2)_2$[25]	3.53	2.87
Av.	3.01 ± 0.35	2.94 ± 0.07

The agreement of the three τ_m-values is well within the experimental uncertainty as is that for the τ_{p}-values. It is further seen that τ_m and τ_p do not differ significantly from each other.

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(12) See Table I.

(13) In a rate process, X_2 is the group(s) attached to the ring at the reaction center in the transition state.

(14) P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 132 (1928).

(15) E. Berliner and L. C. Monack, THIS JOURNAL, **74**, 1574 (1952).

(16) The only careful modern determination of K_1/K_2 in water for terephthalic acid appears to be that of Thamer and Voigt[17] who studied the ultraviolet spectra of the acid at various degrees of neutralization and used the Debye–Hückel equation to obtain a value of 8.5 ± 3.5 at infinite dilution (at 25°). For isophthalic acid these workers obtained a K_1/K_2 value of 9.5 ± 2.0 at infinite dilution. This value is well within the combined experimental errors of those reported earlier by Maxwell and Partington (10),(12)[18] Kuhn and Wassermann (12),(14)[19] and Chandler (12),(14).[20]

(17) B. J. Thamer and A. F. Voigt, *J. Phys. Chem.*, **56**, 225 (1952).

(18) W. R. Maxwell and J. R. Partington, *Trans. Faraday Soc.*, **31**, 922 (1935); **33**, 670 (1937).

(19) R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, **11**, 3 (1928).

(20) E. E. Chandler, THIS JOURNAL, **30**, 694 (1908).

(21) Ionization constants reported for hydroquinone and resorcinol vary by as much as 30-fold. We have chosen the data of Abichandani and Jatkar,[22] the most recent determination in which measurements were made in dilute solution and extrapolated to infinite dilution (by use of the Debye–Hückel equation). These workers report a K_1 of 1.22×10^{-10}, a K_2 of 9.18×10^{-13} and thus a K_1/K_2 of 133 for hydroquinone and values of 7.11×10^{-10}, 4.78×10^{-12} and 149, respectively, for resorcinol. By colorimetric indicator measurements, Kolthoff obtained considerably different results for resorcinol,[23] but his results may have been affected by the colors that phenolic solutions acquire in the presence of air and alkali. The careful measurements of Baxendale and Hardy were, unfortunately, made at an ionic strength of 0.65.[24]

(22) C. T. Abichandani and S. K. K. Jatkar, *Proc. Ind. Inst. Sci.*, **21A**, 417 (1938); *C. A.*, **33**, 3662^5 (1939).

(23) I. M. Kolthoff, *Rec. trav. chim.*, **39**, 674 (1920).

(24) J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.*, **49**, 1140 (1953).

(25) Kuhn and Zumstein determined the acidity of the mono- and di-hydrochlorides of *m*- and *p*-phenylenediamine,[26] but as Kuhn and Wassermann[19] point out their calculations of ionic strength effects were made incorrectly. We have therefore plotted their uncorrected data *versus* the square root of the ionic strength. In the two cases ($K_1{}^{\text{m}}$ and $K_2{}^{\text{p}}$) in which there was no clear trend, the data were averaged while in the other two cases a linear extrapolation to zero ionic strength was made. The resultant $pK_1{}^{\text{p}}$ and $pK_2{}^{\text{p}}$ values of 2.79 and 6.16 give a log (K_1/K_2) value of 3.37 in reasonable agreement with the value 3.50 that may be obtained from the data of Kolthoff and Bosch at 18°.[27] For the *meta* values of 2.26, 4.98 and 2.72, respectively, there appear to be no other reports completely suitable for comparison. The agreement with the data of Willi and Meier[28] determined at an ionic strength of 0.1 seems reasonable for both the *m*- and *p*- compounds, however.

(26) R. Kuhn and F. Zumstein, *Ber.*, **59B**, 488 (1926).

(27) I. M. Kolthoff and W. Bosch, *Rec. trav. chim.*, **48**, 37 (1929).

(28) A. V. Willi and W. Meier, *Helv. Chim. Acta*, **39**, 318 (1956).

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

RECEIVED SEPTEMBER 2, 1958

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).