solvolysis of cyclic carbonate 8-monoacetate **22** deviated from pseudo-first-order kinetics after 1–2 hr.

pK_a' Determinations. The pK_a' values were determined by potentiometric titration in 80% Methyl Cellosolve–water (4:1) using a Radiometer pH meter with potassium chloride and glass electrodes or a Beckman expanded-scale pH meter with Beckman glass and potassium chloride electrodes. Approximately 3–6 mg was dissolved in 5–6 ml of 80% Methyl Cellosolve–water, and titrated with 0.01 *N* hydrochloric acid in 80% Methyl Cellosolve–water using an Ultra Buret whose tip was immersed in the solution. The solution was stirred with a magnetic stirring bar and pH′ readings were taken after each addition of acid. Determinations were done in duplicate with the reproducibility checked each day using the tetrol **1** as the standard.

Periodic Acid Titrations. The procedure followed was essentially that of Jackson.[46] Approximately 0.020 g of the substrate was dissolved in 0.54 *M* periodic acid (0.5–1.0 ml) and 2.0 ml of water. The reaction was allowed to proceed for approximately 20 hr. The sample was diluted with water to about 10 ml, and 1.5 g of sodium bicarbonate, 50 ml of 0.1 *N* sodium arsenite solution, and 1.0 ml of 20% potassium iodide solution was added. The solution was kept at room temperature for 10–15 min and then titrated with 0.1067 *N* iodine solution (Table III).

Table III. Periodic Acid Titrations

Compound	Consumption of periodic acid, molar equiv
6a,10a-Diol **13**	0.37
6a,8,9,10a-Tetrol **1**	1.15
6a,8,10a-Triol **36**	0.25

Acknowledgments. We take pleasure in thanking Professors K. A. Connors and J. J. Windheuser for stimulating discussions.

---

(46) E. L. Jackson, *Org. Reactions*, **2**, 341 (1944).

General Acid Cleavage of Allylmercuric Iodide[1a]

Maurice M. Kreevoy, Thomas S. Straub,
William V. Kayser,[1b] and John L. Melquist[1c]

Contribution from the School of Chemistry, University of Minnesota,
Minneapolis, Minnesota 55455. *Received October 12, 1966*

Abstract: Allylmercuric iodide is cleaved by a wide variety of acids. The Brønsted catalysis law is obeyed by carboxylic acids with high precision, but structurally dissimilar acids show substantial deviations. Bisulfate ion has a catalytic coefficient very similar to that of hydronium ion, explaining the anomalous effectiveness of H_2SO_4 in A-SE2 reactions. The Brønsted α, obtained from carboxylic acids, is 0.67, in excellent agreement with one of the possible α_i's obtained from isotope effects. The thermodynamic acid dissociation constants of chloroacetic, fluoroacetic, and difluoroacetic acids were redetermined to remove uncertainties in the latter two, and values of 1.33×10^{-3}, 1.75×10^{-3}, and 3.5×10^{-2} *M*, respectively, obtained.

A good deal of progress has recently been made in analyzing the relations that may exist among variously defined isotope effects and the Brønsted α for A-SE2 reactions,[2–5] that is, reactions in which proton transfer constitutes an important part of the reaction coordinate. In particular it has been possible to obtain a quantity, α_i, analogous to the Brønsted α, from a consideration of primary and secondary solvent isotope effects attending proton transfer from the aquated proton.[2,4] It is of considerable interest to know how closely α_i approximates α, obtained by a conventional study of molecular acids.[6] In addition it is of interest to know how widely the Brønsted catalysis law[6] is obeyed by reactions of this type, and what sorts of series of acids should be used to evaluate α. On this latter point some disagreement is evident.[7,8]

The present paper reports a study of the cleavage of allylmercuric iodide by acids other than the aquated proton. (Cleavage by the aquated proton has already been described.[2]) As before,[2] the reactions were carried out in the presence of a trace (4×10^{-5} *M*) of I^- to inhibit secondary reactions and small percentages of methanol (1–4%) to facilitate the assembly of reacting solutions. All of the rate constants given in this paper pertain to 25°, and except where otherwise noted, to an ionic strength of 0.2 *M* (maintained by suitable additions of $NaClO_4$). The course of the reactions was monitored by following, spectrophotometrically, the disappearance of the intense 248-mμ peak of allylmercuric iodide.[2]

Results

In all cases the change in optical density with time was accurately given by eq 1.[9] The symbols have their

$$k_1 = [2.303/(t - t_0)] \log [(D_0 - D_\infty)/(D_t - D_\infty)] \qquad (1)$$

usual significance.[2] Pseudo-first-order rate constants, k_1, were evaluated graphically. As in previous work, the typical deviations in k_1 values measured repetitively were 3–5%.

---

(1) (a) Supported, in part, by the National Science Foundation through GP-5088. (b) National Science Foundation Undergraduate Research Participant, Summer, 1965. (c) National Science Foundation Undergraduate Research Participant, Summer, 1966.

(2) M. M. Kreevoy, P. J. Steinwand, and W. V. Kayser, *J. Am. Chem. Soc.*, **88**, 124 (1966).

(3) A. J. Kresge and D. P. Onwood, *ibid.*, **86**, 5014 (1964).

(4) V. Gold and M. A. Kessick, *J. Chem. Soc.*, 6718 (1965).

(5) Earlier references are cited in ref 2–4.

(6) R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, England, 1949, Chapter V.

(7) A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **83**, 2877 (1961).

(8) R. J. Thomas and F. A. Long, *ibid.*, **86**, 4770 (1964).

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 29.

Table I. Dissociation Constants and Catalytic Coefficients

Acid	K_{HA},[a] M	K'_{HA}, M	k_{HA},[b] M^{-1} sec^{-1}	$10^6 I$,[b] sec^{-1}
CH_3COOH	1.75×10^{-5}	2.75×10^{-5}	2.1×10^{-5}[c]	*c*
$HCOOH$	1.77×10^{-4}	2.84×10^{-4}	$1.11 \pm 0.04 \times 10^{-4}$	2.7 ± 1.4
FCH_2COOH	1.91×10^{-3}[d]	3.00×10^{-3}	$5.4 \pm 0.1 \times 10^{-4}$	1.2 ± 1.8
$NCCH_2COOH$	3.40×10^{-3}	5.35×10^{-3}	$7.0 \pm 0.4 \times 10^{-4}$	0 ± 4
$H_3{}^+NCH_2COOH$	4.47×10^{-3}[e]	4.47×10^{-3}	$5.3 \pm 0.4 \times 10^{-4}$	2 ± 6
$F_2CHCOOH$	3.5×10^{-2}[f]	5.50×10^{-2}	$3.8 \pm 0.1 \times 10^{-3}$	-2 ± 13
$(COOH)_2$	5.36×10^{-2}	10.0×10^{-2}	$5.4 \pm 1.5 \times 10^{-3}$	50 ± 60
$CH_3NH(CH_2CH_2CN)_2{}^+$	4.6×10^{-5}[g]	4.6×10^{-5}	4.5×10^{-5}[g]	*g*
H_3PO_4	7.16×10^{-3}[h]	1.22×10^{-2}	$3.2 \pm 0.2 \times 10^{-3}$	0 ± 20
$HSO_4{}^-$	1.02×10^{-2}[i]	*j*	$1.34 \pm 0.06 \times 10^{-2}$	34 ± 16
H^+	55.5	55.5[k]	1.41×10^{-2}[l]	

[a] Taken from ref 24, except where otherwise indicated. [b] The uncertainties listed are 50% confidence limits. [c] Only two values of k_1 were obtained for CH_3COOH, both at high buffer concentration; CH_3COOH is so weak that even these reactions were very slow. Equation 2 was assumed to hold. No intercept or confidence limits are available. [d] This is the value of Bell and Kuhn,[25] which is confirmed by the present redetermination. [e] Value of E. J. King, *J. Am. Chem. Soc.*, **67**, 2178 (1945). [f] Determined in the present work. [g] Taken from ref 2; eq 2 was assumed to hold in evaluating K_{HA} and k_{HA}. [h] Value of P. Salomaa, L. L. Schaleger, and F. A. Long, *J. Am. Chem. Soc.*, **86**, 1 (1964). [i] Value of Young, Maranville, and Smith.[13] [j] Variable; described in the text. [k] Value of Bell.[25] [l] Infinite dilution value.

Evaluation of Catalytic Coefficients. In most studies of general acid catalysis, the catalytic coefficients, k_{HA}, are evaluated from the increase in k_1 attending an increase in the general acid concentration, while the (H^+) is held constant by holding the buffer ratio and ionic strength constant. That procedure had to be modified for some of the present acids because they were so strong that their degree of dissociation changed with concentration, even at constant buffer ratio and ionic strength. Accordingly, eq 2, which implicitly takes

$$k = k_H(H^+) + k_{HA}(HA) \tag{2}$$

account of any change in degree of dissociation, was used. With all the acids except $HSO_4{}^-$, (H^+) was evaluated from eq 3 which follows directly from the mass action expression in cases where (H^+) is an appreciable fraction of the stoichiometric acid concentration, $(HA)_0$. The apparent dissociation constants

$$(H^+)^2 + (H^+)[K'_{HA} + (A^-)_0] - K'_{HA}(HA)_0 = 0 \tag{3}$$

used in eq 3, K'_{HA}, were the thermodynamic dissociation constants, K_{HA}, corrected to the appropriate ionic strength by means of the Debye–Hückel first approximation,[10] and corrected for the methanol content of the solutions by analogy.[11] Values of K'_{HA}, as well as K_{HA}, are given in Table I.

Degree of Dissociation of $HSO_4{}^-$. This method of evaluating (H^+) and (HA) did not seem reliable for $HSO_4{}^-$ because of the very marked susceptibility of $K'_{HSO_4{}^-}$ to medium effects. Two separate, empirical methods were used instead, on three kinds of solutions. With unbuffered $NaHSO_4$ and with $NaHSO_4$–Na_2SO_4 buffers in the ratio of unity the degree of dissociation of the $HSO_4{}^-$ ion was taken from Baes,[12] or interpolated from his values. These values are based on reasonable assumptions about activity coefficients and also fitted to the results of quantitative Raman spectroscopy.[13] Measurement of pH with a meter was also used to determine (H^+) in both these solutions, and in a third set, in which the ratio, $NaHSO_4$:Na_2SO_4, was 2. In these last solutions, as the concentration of buffer was reduced, the $NaHSO_4$ was replaced with $NaClO_4$, and the Na_2SO_4 was replaced with $CH_2(SO_3)_2Na_2$, so that the charge type of the electrolytes as well as the total ionic strength was held constant. The latter was 0.2. The Debye–Hückel first approximation[10] was again used to provide the activity coefficients required to convert pH to (H^+). In the two sets of solutions where (H^+) was evaluated by the two methods, the average discrepancies were 12 and 9%, respectively, with the values based on pH measurement generally tending to be higher.

Electrolyte Effects on k_H. In previous work it was shown that k_H increased with $(NaClO_4)$ and, for all the acids except $HSO_4{}^-$, a value appropriate to $(NaClO_4)$, 0.2 M, was used: 1.83×10^{-2} M^{-1} sec^{-1}. To get a better approximation for the variation of k_H with the concentration of the ions in the $NaHSO_4$–Na_2SO_4 systems k_H was obtained as a function of $CH_2(SO_3)_2Na_2$ concentration, between zero and 0.15 M, using 3.6×10^{-2} M $HClO_4$ as the acid. At all four salt concentrations k_H was indistinguishable from its dilute solution value, 1.41×10^{-2} M^{-1} sec^{-1}. In a solution containing 3.6×10^{-2} M CH_3SO_3H and 0.141 M CH_3SO_3Na k_H was 1.25×10^{-2} M^{-1} sec^{-1}, which may or may not be significantly different from the dilute solution value, but, in any event, does not differ by very much. Accordingly, 1.41×10^{-2} M^{-1} sec^{-1} was used for k_H throughout the $HSO_4{}^-$ work. These approximations of k_H are accurate in the limit of zero buffer concentration. Their appropriateness at the higher buffer concentrations can only be surmized.

Values of k_{HA}. Plots of $k_1 - k_H(H^+)$ against (HA), constructed with the values of (H^+), (HA), and k_H obtained as described, were linear, with zero intercept, within the precision of the points, as required by eq 2. This lends some additional support to the approximations used. A typical example of such a plot for a carboxylic acid is shown in Figure 1. Figure 2 shows all the results for $HSO_4{}^-$. For each plot the slope, k_{HA}, the intercept, and the 50% confidence limits for both were obtained by the method of least squares.[14] They are all shown in Table I. It can be seen that the inter-

---

(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, pp 64–66, 508–512.

(11) J. Julliard, *Bull. Soc. Chim. France*, 3069 (1964).

(12) C. F. Baes, Jr., *J. Am. Chem. Soc.*, **79**, 5611 (1957).

(13) T. F. Young, L. F. Maranville, and H. M. Smith, "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p 35.

(14) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1954, pp 36–40, 231.

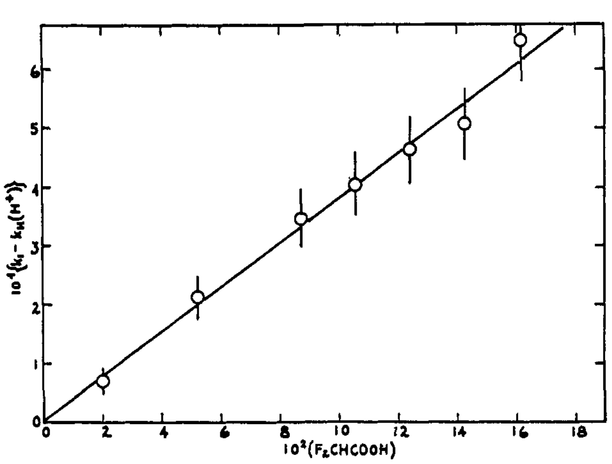

Figure 1. A plot of $k_1 - k_H(HA)$ for the acid. $F_2CHCOOH$, at 25°, in water containing 4% methanol. The solid line is the least-squares line through the points. The vertical bars represent the error that would have to be introduced by a 5% error in k_1.

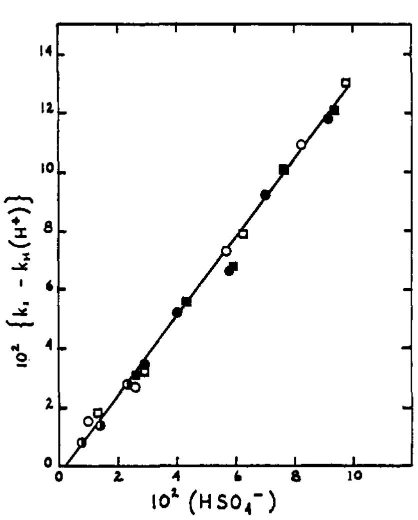

Figure 2. The plot of $k_1 - k_H(H^+)$ for HSO_4^-, at 25°, in water containing 1% methanol. Open points refer to unbuffered $NaHSO_4$, half-open points to 2:1 mixtures of $NaHSO_4$ and Na_2SO_4, closed points to 1:1 mixtures of $NaHSO_4$ and Na_2SO_4. The squares are points for which (H^+) and (HA) were evaluated from the dissociation quotients of Baes.[12] The circles are points for which (H^+) and HA were evaluated from pH measurement. For the 2:1 mixtures the ionic strength and charge type were held constant by additions of $NaClO_4$ and $CH_2(SO_3)_2Na_2$ as needed.

cepts are never much larger, and generally smaller, than their 50% confidence limits (probable error).

Limits of Reliability. The 50% confidence limits on the k_{HA} values are generally consistent with the reproducibility of the k_1 values. Their accuracy is probably not this high, however, because of uncertainty about the behavior of k_H under changes in electrolyte type. In any event, it is unlikely that the value of k_H used could have been in error by as much as 25%, as this is the magnitude of the total electrolyte effect at 0.2 *M* electrolyte. An error of this magnitude in k_H would introduce no more than a similar error in k_{HA}, so this is an upper limit on the uncertainty in the latter. The relative values of k_{HA} are much more reliable than this, because the errors introduced by a poor value of k_H would be about the same in each case. This is, undoubtedly, the reason that the Brønsted correlation, described below, can be so good. Electrolyte effects involved in the determination of k_{HSO_4} were specifically estimated by analogy, so its uncertainty, if anything, is a little less than that of the others.

Dissociation Constants. The thermodynamic dissociation constants, K_{HA}, for several of the acids were determined by the spectrophotometric indicator method of Klotz[15] which leads to eq 4. In that equation,

$$\frac{S[(NaA) - (H^+)_0(1 - S)]}{1 - S} = \frac{\gamma_{HA}K_{HA}}{\gamma_H\gamma_A} \tag{4}$$

(NaA) is the stoichiometric concentration of the salt of the "weak" acid added to a solution of perchloric acid, of concentration $(H^+)_0$. Equation 5 defines *S*.

$$S \equiv \left(\frac{A_N - A_a}{A_N - A_b}\right)\left(\frac{A_{NaA} - A_b}{A_{NaA} - A_a}\right) \tag{5}$$

All the *A*'s are optical densities due to the indicator, methyl orange. The subscripts indicate the solutions in which they were measured: *a* refers to a perchloric acid solution sufficiently acidic to protonate the methyl orange completely; *b* refers to a slightly basic solution in which the indicator is completely unprotonated; NaA refers to the solution in which the salt of the "weak" acid has been added to a known concentration of perchloric acid; and N refers to a solution in which sodium perchlorate has been added to the same standard perchloric acid, so as to make its ionic strength identical with that of the NaA solution. Thus, although an indicator is used, its dissociation constant does not influence the measured value of K_{HA}. The only requirement on the indicator is that it show measurable spectroscopic changes in the region of pH being studied.

Three acids were studied in this way, chloroacetic, fluoroacetic, and difluoroacetic. In each case, 8–10 determinations of the apparent dissociation constant, $K_{HA}\gamma_{HA}/\gamma_H\gamma_A$, were made on 4–5 separate NaA solutions, in the concentration range 0.02–0.003 *M*. Two sets of measurements were made for each solution, one at the wavelength of maximum absorption of the protonated form of the indicator and one at the wavelength of maximum absorption of the unprotonated form. In calculating K_{HA}, the activity coefficients of the neutral acids, γ_{HA}, were assumed to be unity, and $\gamma_H\gamma_A$ was taken to be the square of the mean ion activity coefficient given by Debye-Hückel theory.[10] Interionic distances were assumed to be 6 A, but they do not have great influence on the derived constants, nor do they have much physical significance. The K_{HA} values obtained are 1.33×10^{-3}, 1.75×10^{-3}, and 3.5×10^{-2} *M* for chloroacetic, fluoroacetic, and difluoroacetic acids, respectively, with average deviations from the mean of 3–8%.

Discussion

The logarithmic form of the Brønsted relation is shown in eq 6.[6] The quantities, *p* and *q*, are statistical

$$\log(k_{HA}/p) = \alpha\log(K_{HA}q/p) + C \tag{6}$$

factors; *p* is the number of equivalent acidic protons in the acid, HA, and *q* is the number of equivalent basic sites in the conjugate base. These definitions

---

(15) I. M. Klotz, Doctoral Thesis, University of Chicago, 1940.

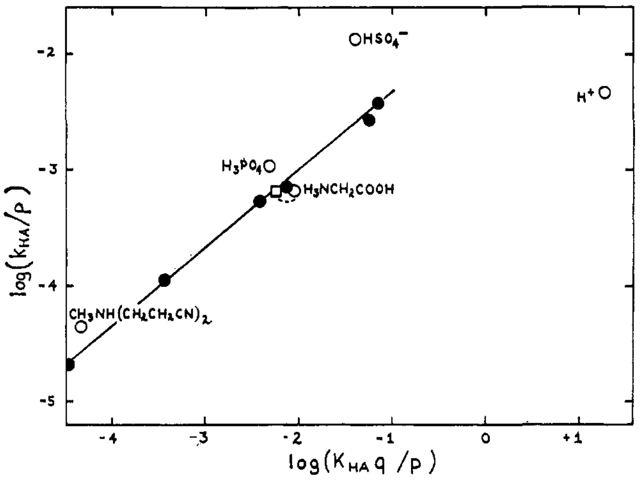

Figure 3. The Brønsted plot for cleavage of allylmercuric iodide, made up from data in Table I. Closed circles are neutral carboxylic acid points. Other acids are open circles, and are identified. The square for the glycine point represents its position relative to the other carboxylic acids if K'_{HA} were used instead of K_{HA}. The line is that obtained by the method of least squares, applied to the neutral carboxylic acids, and has a slope of 0.67.

of p and q are those of Brønsted[16] and equivalent to those of Bishop and Laidler[17] (and also to those of Gold[18] in all the present cases) but somewhat different from those of Bell.[6] Fortunately, as it will develop, few of the qualitative conclusions depend on the definitions of p and q. The parameter, C, is arbitrarily chosen to fit the data. The parameter, α, also obtained by fitting, is a measure of the degree to which the group A, in the transition state, has progressed from its structure in HA toward its structure in the aquated conjugate base, A^-. The application of the Brønsted relation to the present data is shown in Figure 3.

The data for neutral carboxylic acids are correlated by the Brønsted relation with excellent precision. There are six of them, spanning over three powers of ten in acidity, and over two powers of ten in rate. They define a line with slope, α, of 0.67 ± 0.02. The slope and its 50% confidence limits were determined by the method of least squares.[14] The average vertical deviation of a point from the line is 0.02 logarithmic unit—equivalent to a 5% error in k_{HA}. This is comparable to the precision with which the k_{HA}'s were measured, and considerably better than their estimated reliability. As pointed out above, there is, undoubtedly, considerable cancellation of systematic errors.

The Brønsted α, defined by these carboxylic acids, is indistinguishable from one of the possible values of α_i obtained from the secondary solvent isotope effect (0.65) and qualitatively similar to another (0.79).[2] This agreement lends considerable confidence in the physical significance of α. The electronic restructuring of the A fragment has proceeded *ca.* two-thirds of the way from HA to A^- in the transition state, as measured by two different techniques. The practical identity of the Brønsted α and α_i, as derived from the model with $n = 0$,[2] lends some support to that model, although the large deviation of H^+ from the Brønsted correlation for carboxylic acids signals caution.

Acids that deviate in structural type or in charge from neutral carboxylic acids generally give rise to significant deviations from the Brønsted correlation. The glycine cation can be brought onto the line if K'_{HA} values were used instead of K_{HA} values. (In Figure 3 this is shown by an equivalent displacement of the glycine cation point, to avoid cluttering the figure by showing an alternative for each neutral carboxylic acid.) However, a similar correction applied to the $CH_3NH(CH_2CH_2CN)_2^+$ point would displace it still further from the line. In the case of bisulfate, the range of ionic strengths studied corresponds to a change of a factor of ten in K'_{HA}, and the data is extensive enough to show a change in K_{HA} if a marked change occurred, but no such change is obvious. Phosphoric acid is too effective by comparison with the neutral carboxylic acids, and H^+ fails so widely that no reasonable correction for its charge type could bring it into agreement. These observations, together with those of Thomas and Long,[8] suggest that A-SE2 reactions generally do not show accurate Brønsted correlations for divergent acid types. The success of Kresge and Chiang[7,19] in such a correlation may have been partly fortuitous, partly due to the very large range of K_{HA} values included, so that smaller structural specificities were obscured.

Brønsted correlations frequently fail for H^+, usually by predicting too high a value of k_H. In the present case this negative deviation of k_H is combined with a value of k_{HSO_4} larger than that predicted by the correlation, so that the two constants are practically indistinguishable. This is probably characteristic of reactions with A-SE2 mechanisms, as it has often been pointed out that H_2SO_4 is a better catalyst for such reactions than strong monobasic acids.[20,21] The present result makes it seem unlikely that the ionic strength effect on K_{HSO_4} in moderately concentrated acids is responsible for its anomalous effectiveness as a catalyst, which had been suggested.[20] As has been pointed out, Figure 2 shows no obvious sign of an electrolyte effect on k_{HSO_4}, although K'_{HSO_4} changes by a factor of more than ten over the range of conditions studied. A possible explanation of the catalytic effectiveness of HSO_4^- may lie in its preferred solvation, in which the solvent shell around the SO_4 fragment probably resembles that of the transition state and the ultimate product rather closely, so that not much solvent rearrangement has to take place to reach the transition state of lowest energy. Since the time required for the actual transfer of the proton may be only 10^{-12}–10^{-13} sec,[22,23] the transition-state solvation actually achievable may not be ideal. Such circumstances would favor a catalyst in which a minimal solvent rearrangement was required. They would also account for the lack of responsiveness of k_{HSO_4} to changes in ionic strength, in spite of the sensitivity of K_{HSO_4}. Further work to test this hypothesis is clearly necessary, and is being undertaken.

The K_{HA} for chloroacetic acid was redetermined to evaluate the method used, and the good agreement with

---

(16) J. N. Brønsted, *Chem. Rev.*, **5**, 322 (1928).

(17) D. M. Bishop and K. J. Laidler, *J. Chem. Phys.*, **42**, 1688 (1965).

(18) V. Gold, *Trans. Faraday Soc.*, **60**, 738 (1964).

(19) A. J. Kresge, *Discussions Faraday Soc.*, **39**, 46 (1965).

(20) A. J. Kresge, L. E. Hakka, S. Mylonakis, and Y. Sato, *ibid.*, **39**, 75 (1965).

(21) M. M. Kreevoy, *J. Am. Chem. Soc.*, **79**, 5927 (1957).

(22) T. Ackermann, *Z. Physik. Chem.*, **27**, 34 (1961).

(23) M. M. Kreevoy and C. A. Mead, *Discussion Faraday Soc.*, **39**, 166 (1966).

its well-established value, 1.36 × 10^{-3},[24] lends confidence in it. Two, quite different, values of K_{HA} for fluoroacetic acid have been previously reported, neither obviously flawed. The present redetermination is in good agreement with that of Bell and Kuhn,[25] shown in Table I. The Bell and Kuhn value would also improve the fit of fluoroacetic acid in the Kresge and Chiang correlation.[7] No precise value of K_{HA} could be found for difluoroacetic acid. Judging by success in the other two cases, the value presently reported should not be uncertain by more than its imprecision, ±8%.

Experimental Section

Allylmercuric iodide was prepared as previously.[2] All inorganic reagents were of analytical reagent quality and were used without further purification. Aqueous inorganic acids and bases were made up and standardized in the usual ways.[26] Acetic, formic, and oxalic acid were also of analytical reagent quality. The identity and purity of the latter was further verified by titration. The former two were used as supplied. Fluoroacetic and difluoroacetic acids were purchased from K and K Laboratories. They were distilled under vacuum and fractions of narrow boiling range were used. Their identity was verified by C and H analysis of their sodium salts. The same procedures were used for chloroacetic acid, which was purchased from Eastman Kodak Co. Cyanoacetic acid was purchased from Aldrich Chemical Co., and used as supplied. Its identity was verified by C and H analysis of its sodium salt. Glycine was purchased from Eastman Kodak Co. Its identity and purity were verified by titration with base in the presence of excess formaldehyde.

Rate Measurements. Most of the rate measurements were made by the techniques previously described.[2] However, in the case of oxalic acid, the buffer solutions were too strongly absorbing to permit this, so aliquots were withdrawn periodically, the allylmercuric iodide was extracted from the buffer with isooctane, and its optical density determined. For a pseudo-first-order reaction, such as the present one, it is not necessary that the allylmercuric iodide be quantitatively extracted, nor that the mercuric iodide or buffer be quantitatively excluded. It is only necessary that the amounts of each substance extracted be proportional to its concentration in the reaction mixture, and that the changes in optical densities produced be reliably measurable.[9] These conditions are reasonably met in the present case. Although there is more scatter from eq 1 in these experiments than in those not involving the extraction, there is no discernible systematic deviation.

Spectra and Optical Densities. Continuous spectra were obtained as needed, with a Beckman DK-2 spectrophotometer. Most optical density measurements at a single wavelength were made on a Beckman DU spectrophotometer, but a few were made on the DK-2 spectrophotometer, set so as to record optical density as a function of time at a single wavelength. The temperature in the cell compartments of both instruments was controlled by pumping water of known temperature through their jackets. Direct measurements in the cells verified that these did not vary by more than 0.1° from the temperature of the water bath.

---

(24) G. Kortum, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworth and Co. Ltd., London, 1961, p 293.

(25) R. P. Bell and A. T. Kuhn, *Trans. Faraday Soc.*, 59, 1789 (1963).

(26) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The MacMillan Co., New York, N. Y., 1943.

Catalysis of α-Hydrogen Exchange. III. Exchange of Isobutyraldehyde-2-*d* in the Presence of Methylammonium Ions[1]

Jack Hine,[2a] Fritz C. Kokesh,[2b] K. Gerald Hampton,[2c] and Julien Mulders

Contribution from the Evans Laboratory of Chemistry,
The Ohio State University, Columbus, Ohio 43210, and the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia. *Received October 14, 1966*

Abstract: The kinetics of the dedeuteration of isobutyraldehyde-2-*d* in the presence of methylammonium chloride have been investigated using 2,6-lutidine–2,6-lutidinium chloride buffers and sodium acetate–acetic acid buffers. The results obtained are consistent with the view that much of the dedeuteration is due to the rate-controlling attack of the various bases present on the iminium ion, $Me_2CDCH{=}NHMe^+$. The acidity constant of the 2,6-lutidinium ion is found to be decreased to the same extent by added methylammonium chloride or sodium chloride but increased by added 2,6-lutidine or 2,6-lutidinium chloride. Specific medium effects of this type are blamed for differences between the values for certain kinetic constants determined in aqueous solutions with different buffers present.

In the presence of several tenths molar methylamine and methylammonium ions, conditions under which isobutyraldehyde exists largely in the form of its N-methylimine, the deuterium exchange of isobutyraldehyde-2-*d* is largely due to a term in the kinetic equation that may be written[1b]

$$k[Me_2CDCH{=}NMe][MeNH_3^+]$$

or alternatively

$$k'[Me_2CDCH{=}NHMe^+][MeNH_2]$$

Inasmuch as the exchange reaction is much too slow for a proton transfer from methylammonium ions to the imine to be the rate-controlling step, it seems highly probable that the rate-controlling step is the removal of deuterium from the iminium ion by the attack of methylamine.

In a number of reactions of aldehydes and ketones, the salts of primary and secondary amines have been found to be catalysts under conditions where not more than a very small fraction of the carbonyl compound is present as the imine or iminium ion. To learn more

(1) (a) This investigation was supported in part by Public Health Service Research Grant AM 06829 MCB from the National Institute of Arthritis and Metabolic Diseases. (b) For the preceding paper in this series see J. Hine, B. C. Menon, J. H. Jensen, and J. Mulders, *J. Am. Chem. Soc.*, 88, 3367 (1966).

(2) (a) The Ohio State University; (b) U. S. Public Health Service Predoctoral Fellow, 1965–1967; (c) U. S. Public Health Service Postdoctoral Fellow, 1965–1966.