

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

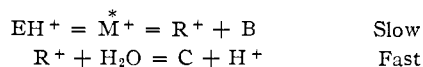
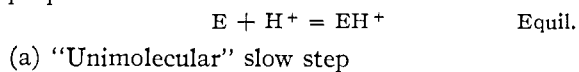
Acid-catalyzed Hydrolysis of Methylal. I. Influence of Strong Acids and Correlation with Hammett Acidity Function

BY DONALD MCINTYRE AND F. A. LONG

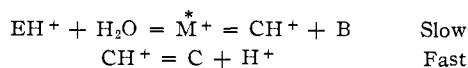
RECEIVED FEBRUARY 8, 1954

The acid-catalyzed hydrolysis of methylal has been studied at 25° in solutions of hydrochloric, sulfuric and perchloric acids at concentrations ranging from 0.4 to 4 *M* and also in mixed solutions of perchloric acid and sodium perchlorate having a total electrolyte concentration of 6 *M*. The first-order rate constants k_h increase very rapidly with increasing acid concentration and a plot of $\log k_h$ vs. the Hammett acidity function, H_0 , gives a straight line with a slope of -1.15 . This correlation is evidence that the activated complex for the reaction behaves like the conjugate acid of methylal and this in turn is added evidence for the "unimolecular" reaction mechanism already postulated by Ingold and by O'Gorman and Lucas for the acid-catalyzed hydrolysis of acetals.

Several recent investigations have involved the use of the Hammett acidity function H_0 to aid in the determination of the mechanisms of acid-catalyzed hydrolysis reactions.¹⁻⁴ The basic idea stems from a suggestion by Zucker and Hammett⁵ that for hydrolysis by concentrated solutions of strong acids the rate will correlate with H_0 if the activated complex does not contain a water molecule and will more closely correlate with concentration of hydrogen ion if water is involved in the activated complex. Consider, for example, the following schematic hydrolysis where two alternate slow steps are proposed



(b) "Bimolecular" slow step



For the "unimolecular" slow step it is reasonable to assume that the activated complex, M^* , will still structurally be the conjugate acid of E. With this slow step the Brönsted equation for medium effects on the first-order hydrolysis constant is

$$\log k_h = \log k_0 + \log C_{\text{H}^+} (f_{\text{H}^+} f_{\text{E}} / f_{\text{M}^*})$$

where the f 's are activity coefficients and C_{H^+} is concentration of hydrogen ion.

The Hammett acidity function is defined as

$$-H_0 = \log C_{\text{H}^+} (f_{\text{H}^+} f_{\text{B}} / f_{\text{BH}^+})$$

where f_{B} and f_{BH^+} are activity coefficients of a neutral base indicator and its conjugate acid, respectively. Since both of the ratios $f_{\text{B}}/f_{\text{BH}^+}$ and $f_{\text{E}}/f_{\text{M}^*}$ refer to a base and its conjugate acid, it is reasonable to suppose that they vary in the same way with medium changes and this will lead to a parallel behavior of $\log k_h$ and $-H_0$. For a mechanism which involves the "bimolecular" slow step (b) a parallelism between rate and H_0 would not be expected since one would no longer expect M^* to behave as the conjugate acid of E. A final point is

(1) F. A. Long and M. Purchase, *THIS JOURNAL*, **72**, 3267 (1950).
 (2) F. A. Long, W. F. McDevitt and P. Dunkle, *J. Phys. Chem.*, **55**, 813, 829 (1951).

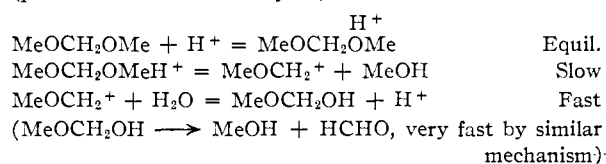
(3) M. Paul, *THIS JOURNAL*, **74**, 141 (1952).

(4) R. W. Taft, *ibid.*, **74**, 5372 (1952).

(5) L. Zucker and L. P. Hammett, *ibid.*, **61**, 2791 (1939)

that this diagnostic use of H_0 necessarily involves studies of the hydrolysis rates with strong acids at concentrations above roughly two molar since only above this concentration does $-H_0$ depart significantly from $\log C_{\text{H}^+}$.

In this paper we wish to report on the application of H_0 to the acid-catalyzed hydrolysis of methylal in aqueous solutions of strong acids. Ingold gives as the most likely mechanism for acetal hydrolysis (particularized to methylal)⁶



As evidence he adduces the stereochemical studies of O'Gorman and Lucas⁷ and the known large increase in rate with increase in number of alkyl substituents on the methylene group.⁸ This mechanism falls in the "unimolecular" category mentioned earlier and a parallelism of rate and H_0 should thus be added evidence for its correctness or, more specifically, for the fact that the activated complex is the conjugate acid of the reacting acetal.

Studies of the acid-catalyzed hydrolysis of methylal have been reported previously by Skrabal,⁹ Palomaa and Salonen¹⁰ and Lobering and Fleischmann,¹¹ but in all cases data are available for only fairly low concentrations of catalyst acid. The reaction goes to completion, and, as expected, the rate is first order in both methylal and hydrogen ion concentrations and hence pseudo-unimolecular for a given concentration of acid. The best value of the bimolecular rate constant at 25° appears to be that of Palomaa and Salonen who obtained by dilatometry a value of 1.87×10^{-3} l./mole min. in a solution of 0.333 *M* hydrochloric acid.

Experimental

For the majority of the kinetic studies the reaction was followed by dilatometry. The dilatometers had volumes of about 50 ml. and were of two types, one type with only one capillary tube for volume measurement and with a stopcock to close off the other side^{1,2} and the open, double capillary,

(6) C. K. Ingold, "Structure and Mechanisms in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 334.

(7) J. M. O'Gorman and H. J. Lucas, *THIS JOURNAL*, **72**, 5489 (1950).

(8) A. Skrabal and M. Zlatewa, *Z. physik. Chem.*, **122**, 349 (1926).

(9) A. Skrabal, *ibid.*, **99**, 290 (1921).

(10) M. H. Palomaa and A. Salonen, *Ber.*, **67**, 424 (1934).

(11) I. Lobering and A. Fleischmann, *ibid.*, **70**, 1713 (1937)

type used by Benford and Ingold.¹² Both gave highly reproducible results particularly at the lower acidities. The least accurate runs (errors up to $\pm 10\%$) are those at the highest acidities where it is difficult to fill the dilatometer before a sizable fraction of the methylal has reacted and where there is the most trouble from heat of reaction errors of the type discussed by Tong and Olson.¹³ In all of the dilatometric studies the methylal concentration was in the range 0.17 to 0.23 mole per liter. First-order rate constants, k_h , were calculated from the dilatometric data using the method of Guggenheim.¹⁴

For a few kinetic experiments the rate was followed by removing aliquots, neutralizing the acid to stop the reaction and titrating the formaldehyde present by the sodium sulfite method.¹⁵ The titration procedure is less reproducible than the dilatometric, but within the limits of the titration errors the two methods agreed well.

All experiments were made in a 25° water-bath whose temperature was controlled to $\pm 0.002^\circ$.

The solutions of acids were made up from reagent grade materials and redistilled water. The methylal used was a reagent grade product which was freed from methanol by reaction with sodium and subsequent distillation over sodium. The refractive index of the purified methylal was n_D^{20} 1.3554 and the corrected boiling point was 42.3°.

Results and Discussion

Table I gives the hydrolysis data for varying concentrations of three strong acids, hydrochloric, sulfuric and perchloric and also for mixtures of perchloric acid and sodium perchlorate at a total perchlorate concentration of six molar. The first two columns give acid and its concentration; column three gives the calculated bimolecular rate con-

TABLE I
METHYLAL HYDROLYSIS AT 25°

Acid	Acid concn., mole/l.	$k_h' \times 10^3$, l./mole min.	$k_h \times 10^3$, min. ⁻¹	$-H_0$
HCl	0.371	2.02	0.752	-0.43
HCl	.371	2.06	.766	-.43
HCl	.371	1.95 ^a	.726 ^a	-.43
HCl	.495	2.05 ^a	1.02 ^a	-.31
HCl	.495	2.17	1.08	-.31
HCl	.507	2.17	1.10	-.31
HCl	1.303	3.81	4.96	.24
HCl	2.606	7.74	20.2	.74
HCl	3.909	35.9	140	1.30
HClO ₄	0.453	1.98	0.90	-0.29
HClO ₄	0.906	2.32	2.10	-.04
HClO ₄	1.460	2.96	4.33	.41
HClO ₄	1.813	4.46	8.08	.60
HClO ₄	2.719	8.69	23.7	.97
HClO ₄	3.395	16.0	54.2	1.25
HClO ₄	4.30	49.2	211	1.74
H ₂ SO ₄	1.226	3.65	4.48	0.26
H ₂ SO ₄	1.718	5.03	8.63	.53
H ₂ SO ₄	1.963	5.94	11.68	.64
{ 0.5 M HClO ₄ , 5.5 M NaClO ₄ }		71.6	35.8	1.00
{ 1 M HClO ₄ , 5 M NaClO ₄ }		99.8	99.8	1.31
{ 2 M HClO ₄ , 4 M NaClO ₄ }		119	238	1.73

^a Rate by titration instead of dilatometry.

(12) G. A. Benford and C. K. Ingold, *J. Chem. Soc.*, 929 (1938).

(13) L. K. J. Tong and A. R. Olson, *THIS JOURNAL*, **65**, 1704 (1943).

(14) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 428 (1926).

(15) J. F. Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1944, p. 255.

stant, $k_h' = k_h/C_{H^+}$, and column four the observed first-order rate constant, k_h . The last column gives $-H_0$ values from the data of Hammett and Deyrup,¹⁶ Hammett and Paul¹⁷ and Harbottle.¹⁸ The bimolecular rate constant for solutions of 0.37 M hydrochloric acid, $k_h' = 2.01 \times 10^{-3}$ l./mole min., is in reasonable agreement with the results of Palomaa and Salonen for 0.33 M acid.

The most obvious aspect of the data of Table I is the lack of parallelism between rate and concentration of acid at the higher acidities. Thus an increase in hydrochloric acid concentration of from 2.6 to 3.9 M causes the first order-rate constant to increase by 7-fold. Another point is the marked salt effect indicated by a comparison of the data for perchloric acid and for perchloric acid-sodium perchlorate mixtures.

Figure 1 is a plot of $\log k_h$ vs. $-H_0$ and, although there is some scatter in the points, it is evident that the rate parallels the acidity as measured by the Hammett acidity function and does not parallel the acidity as measured by concentration of hydrogen ion. In terms of the earlier discussion this result indicates that the activated complex for the hydrolysis behaves like the conjugate acid of the methylal. This in turn is strong support for the "unimolecular" mechanism proposed by Ingold and by O'Gorman and Lucas.

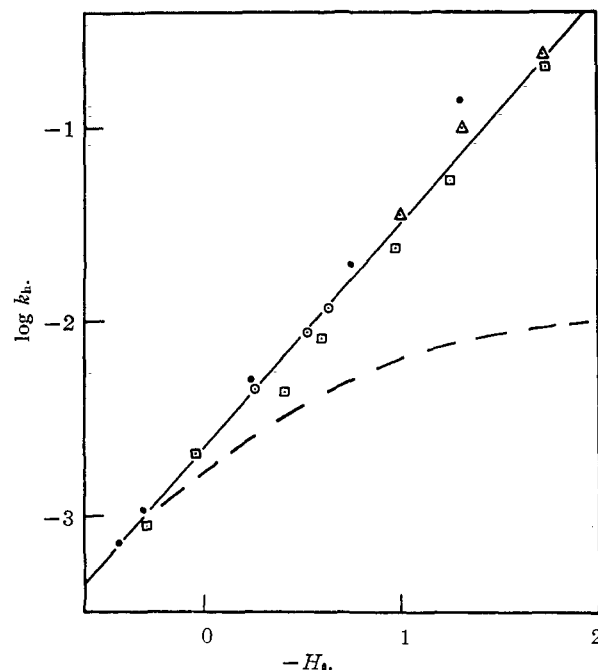


Fig. 1.— $\log k_h$ vs. $-H_0$ for hydrolysis of methylal at 25°: dashed line is predicted curve for $\log k_h$ linear with $\log CH^+$: ●, HCl; ○, H₂SO₄; □, HClO₄; △, HClO₄-NaClO₄.

Although the agreement of the rate data with H_0 is good, certainly far better than with concentration of hydrogen ion, it is not exact. Complete parallelism of rate and H_0 implies a slope of unity for a plot of $\log k_h$ vs. $-H_0$. The slope of the straight line of

(16) L. P. Hammett and A. J. Deyrup, *THIS JOURNAL*, **54**, 2721 (1932).

(17) L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

(18) G. Harbottle, *ibid.*, **73**, 4024 (1950).

Fig. 1 is actually 1.15, indicating that the rate of the reaction increases somewhat *faster* than does $-H_0$. A more detailed analysis of the requirements for parallelism between rate and H_0 suggests an explanation for this small discrepancy. Assuming the "unimolecular" mechanism for the hydrolysis of methylal, the Brönsted equation for the dependence of the first-order rate constant on medium changes is

$$k_h = k'_{h0} C_{H^+} (f_H + f_M / f_M^*) \quad (1)$$

where f_M and f_M^* are activity coefficients of methylal and the activated complex, respectively. Taking logarithms and adding and subtracting H_0 gives the equation

$$\log k_h = -H_0 + \log \frac{f_M f_{BH^+}}{f_M^* f_B} + \text{const.} \quad (2)$$

where f_B is the activity coefficient of the neutral indicator base used in the experimental determination of H_0 and f_{BH^+} is the activity coefficient of its conjugate acid. It follows from this equation that a precise parallelism between $\log k_h$ and $-H_0$ will occur only if the activity coefficient ratios f_M/f_M^* and f_B/f_{BH^+} change in exactly the same way with changing medium. However, many studies are available on the influence of electrolytes (including strong acids) on the activity coefficients of neutral molecules¹⁹ and these show that the magnitudes of the "salt effects" vary considerably with size and

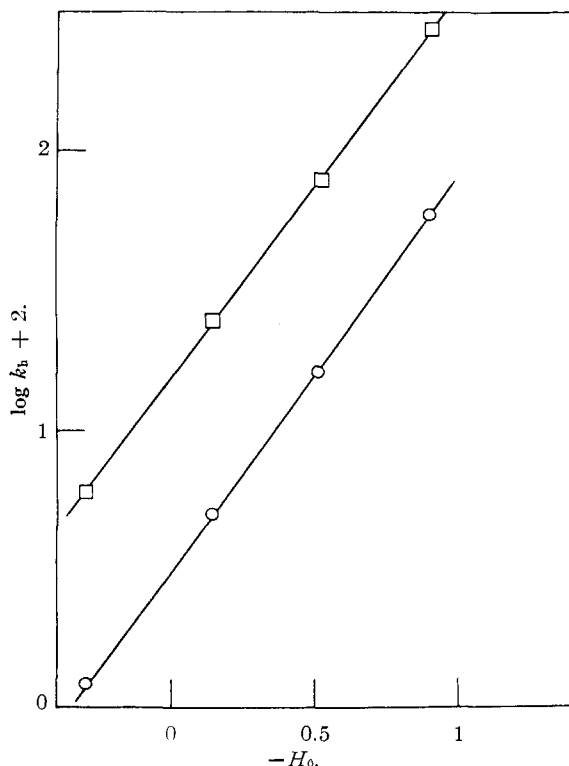


Fig. 2.—Leininger and Kilpatrick's data for hydrolysis of acetal in solutions of hydrochloric acid: upper curve is for 10°, slope is 1.38; lower curve is for 0°, slope is 1.41.

(19) F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

chemical nature of the neutral molecule. Hence one would normally expect the influence of increasing acid concentration to be different for f_M and f_B and only in the unlikely event of complete compensation by the changes in f_M^* and f_{BH^+} would one expect the ratio $f_M f_{BH^+} / f_M^* f_B$ to remain at precisely the value unity.

It is shown in the following paper²⁰ that for hydrochloric acid solutions f_M does not change with electrolyte concentration whereas f_B (for the case of a typical Hammett indicator, *p*-nitroaniline) probably decreases with increasing concentration of hydrochloric acid, *i.e.*, there is salting in. This means that the ratio f_M/f_B increases with increasing concentration of hydrochloric acid. If one can now assume that the ratio f_{BH^+}/f_M^* is relatively independent of electrolyte concentration it follows that the term $\log (f_M f_{BH^+} / f_M^* f_B)$, increases with acid concentration. This leads to a slope greater than unity for a plot of $\log k_h$ vs. $-H_0$, in agreement with the observed results.

A subsidiary point is to note in Fig. 1 that the slopes of $\log k_h$ vs. $-H_0$ are actually slightly different for the three strong acids, being about 1.25 for hydrochloric, 1.15 for sulfuric and 1.08 for perchloric acid. This slight variation is to be expected in terms of the previous discussion. Salt effects are generally somewhat specific and are known to vary somewhat for these three acids.¹⁹ One would thus expect the change in the ratio f_M/f_B with electrolyte concentration to depend on the particular strong acid employed as the catalyst.

This problem of the relation of salt effects to H_0 is considered more fully in the following paper which gives data on salt effects for a variety of electrolytes. However, the tentative conclusion from the present data is that complete parallelism between rate and H_0 is not generally to be expected even though the activated complex does in fact behave like the conjugate acid of the reacting neutral molecule.

Leininger and Kilpatrick²¹ have studied the hydrolysis of ethylal at 0 and 10° in concentrated solutions of hydrochloric acid and have found that, as with methylal, the rate increases very rapidly with increasing concentration of acid. Figure 2 is a plot of $\log k_h$ for these data against $-H_0$ (values for 25°). As may be seen, fairly good straight lines are obtained with, however, a slope of 1.4, *i.e.*, there is an even greater departure from slope unity than for methylal. In terms of the previous discussion this is quite understandable. Ethylal is a larger molecule and would be expected to be "salted out" more by electrolytes, and in particular by hydrochloric acid, than is methylal. This means a relatively greater increase of the ratio f_M/f_B with increasing hydrochloric acid concentration and hence from eq. 2 a still larger slope for a plot of $\log k_h$ vs. $-H_0$.

ITHACA, NEW YORK

(20) F. A. Long and D. McIntyre, *THIS JOURNAL*, **76**, 3243 (1954).

(21) P. Leininger and M. Kilpatrick, *THIS JOURNAL*, **61**, 2510 (1939).