446. *The H_0 Acidity Function in Aqueous Dioxan and in Methanol.*

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The degrees of protonation of three indicators, *o*-nitroaniline, *p*-nitroaniline, and 4-chloro-2-nitroaniline have been measured with various concentrations of perchloric acid in 60% water–40% dioxan and in 40% water–60% dioxan. Similar measurements have been made with methanesulphonic acid in methanol. The results indicate that for the two aqueous solvents the H_0 concept is applicable and values of H_0 for solutions containing up to about 4N-perchloric acid have been calculated. For methanesulphonic acid in methanol, however, the concept appears of doubtful value. The rates of hydrolyses of sucrose and of ethyl acetate in 40% water–60% dioxan containing perchloric acid have been shown to depend on the acidity function and stoichieometric acidity respectively. It is concluded that the Zucker–Hammett criterion of mechanism can be usefully applied to 40% and 60% aqueous dioxan solvents.

In 1939 Zucker and Hammett [1] suggested that for acid-catalysed reactions of initially uncharged substances in water, bimolecular and unimolecular mechanisms ($A2$ and $A1$, respectively, in Day and Ingold's terminology [2]) could be distinguished according to whether the logarithm of the first-order rate coefficient increases linearly with the logarithm of the stoicheiometric acidity or with Hammett's acidity function H_0. This criterion has now been widely used in the study of acid-catalysed reactions and mechanistic assignments based on its use have, in general, been in accord with expectations derived from other evidence.

Many reactions, for reasons of solubility, cannot be conveniently studied in water, and there is, therefore, a need for measurements establishing the H_0 scale for solvents other than water. However, for solvents of low dielectric constant it is probable that a H_0 scale constructed from indicator measurements in the normal way would have little generality or utility. It is necessary, therefore, to choose solvents, of high dielectric constant, in which organic substrates might be expected to be fairly soluble. Accordingly we have carried out measurements designed to test the validity of the H_0 concept and its kinetic utility in 40% and 60% aqueous dioxan and in methanol.

A number of previous studies of solvents other than water have been made and although in no case has the generality of the H_0 scale been firmly established, good correlations of reaction rates with indicator acidities have been reported. Gebhard and Adams,[3] for example, studied the rearrangement of benzopinacol to the corresponding pinacone in slightly aqueous acetic acid containing small concentrations of perchloric acid, and found that both the direct conversion and the conversion *via* an intermediate epoxide were dependent on H_0. The decomposition of trioxan has been studied [4] in both acetic acid and water, and the reported correlation of the rates through the H_0 values is good.

Eaborn [5] studied the acid-catalysed cleavage of a silane derivative in aqueous methanol and in aqueous dioxan and found good correlations between rates and H_0 values as measured by a single indicator (*p*-nitroaniline). More recently, however, he reported that in 27% aqueous methanol the plot of the logarithm of the indicator ratio for *p*-nitroaniline against that for *o*-nitroaniline does not give unit slope.[6]

An important contribution was made by Braude and Stern [7] who measured H_0 for two indicators, *p*- and *m*-nitroaniline, at two acid concentrations for a variety of solvents,

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[1] *J. Amer. Chem. Soc.*, 1939, **61**, 2791.
[2] Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686.
[3] Gebhard and Adams, *J. Amer. Chem. Soc.*, 1954, **76**, 3925.
[4] Walter and Chadwick, *Ind. Eng. Chem.*, 1947, **39**, 974.
[5] Eaborn, *J.*, 1953, 3148.
[6] *Idem, J.*, 1945, 1436.
[7] Braude, *J.*, 1948, 1971; Braude and Stern, *ibid.*, pp. 1976, 1982.

namely, ethanol, acetone, dioxan, and their aqueous mixtures. Although the results do not establish the validity of the H_0 concept in any of the solvents used, and have been criticised by Gutbezahl and Grumwald[8] on the grounds that for aqueous ethanol their criterion, based on the use of their activity postulate, shows the non-existence of an acidity function, significant correlations between reaction rates and indicator measurements were nevertheless obtained.

Recently Kreevoy[9] examined the H_0 scale in 50% aqueous dioxan containing perchloric acid, essentially by comparing the behaviour of an indicator, 4-chloro-2-nitroaniline, with the kinetic behaviour of four acetals and ketals. These results will be discussed later.

RESULTS

(a) *Indicator Measurements.*—The ratios of unprotonated to protonated base ($[B]/[BH^+]$) $= I$ for three indicators were determined by spectrophotometric means at various acid strengths in 60% (v/v) and 40% aqueous dioxan and in methanol. Perchloric acid was used in the two aqueous solvents, and the solutions were made up so that the ratio of water to dioxan, in terms of volumes added together, was constant for each solvent irrespective of acidity. The choice of acid for methanol presented some difficulty. Hydrochloric, nitric, and sulphuric acids were found to react too fast with the solvent; the use of perchloric acid required the inconvenient preparation and use of the anhydrous acid. Methanesulphonic acid, which would be expected to be a reasonably strong acid in methanol and to produce only a slow esterification, was found to be suitable.

Values of H_0 were calculated from the equation:

$$H_0 = \log I + \mathrm{p}K_{\mathrm{B}} \qquad (1)$$

where

$$\mathrm{p}K_{\mathrm{B}} = -\log \frac{a_{\mathrm{H^+}}a_{\mathrm{B}}}{a_{\mathrm{BH^+}}} \qquad (2)$$

The values of $\mathrm{p}K_{\mathrm{B}}$ used in the calculation were referred to water as solvent and were those recently reported by Paul and Long;[10] they are a little different from the values originally used by Hammett and Deyrup[11] and amended by Hammett and Paul.[12] Table 1 gives the collected values

For each of the two aqueous solvents the H_0 values for the three indicators form a continuous curve of H_0 against stoicheiometric acidity, *i.e.*, the separate curves for the three indicators overlap without discontinuity. Figs. 1 and 2 show the curves, judged visually as representing the best fit, for the two aqueous solvents. It will be seen that some of the points obtained by using *o*-nitroaniline at low acidities are significantly displaced from the curves. These points, however, are subject to relatively large experimental errors since they represent measurements of small degrees of protonation. Within the limits of accuracy of the experimental procedure, therefore, the values of H_0 may be taken as independent of the nature of the indicator used.

In methanol solvent, however, the situation is different. A continuous curve can be drawn, as in Fig. 3, only if the $\mathrm{p}K_{\mathrm{B}}$ value for 4-chloro-2-nitroaniline is taken as $-1{\cdot}23$ instead of $-1{\cdot}03$, the true value. The values of H_0 so obtained are shown in Table 1 in parentheses and have been used in constructing Fig. 3.

By extrapolating the plots of $-\log c_{\mathrm{H^+}}I$ against $c_{\mathrm{H^+}}$ to infinite dilution, the data can be used to find approximate values of the ionisation constants ($\mathrm{p}K_{\mathrm{B}}$) of the conjugate acids of the three indicators in the various solvents. The values so obtained are listed in Table 2 and can be used, if desired, to find H_0 values referred to infinite dilution in the particular solvent as standard state.

(b) *Kinetic Measurements.*—The rates of hydrolysis of sucrose and of ethyl acetate in 40% water–60% dioxan at various concentrations of perchloric acid were measured, by polarimetric

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[8] Gutbezahl and Grunwald, *J. Amer. Chem. Soc.*, 1953, **75**, 559, 565.

[9] Kreevoy, *J. Amer. Chem. Soc.*, 1956, **78**, 4237.

[10] Paul and Long, *Chem. Rev.*, in the press.

[11] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

[12] Hammett and Paul, *ibid.*, 1934, **56**, 827.

and dilatometric methods respectively, at 25°. The results are given in Table 3. It will be seen that the acid concentrations used were in the range where the H_0 values change much more rapidly than the corresponding values of $-\log c_{H^+}$.

FIG. 1. *H_0 for perchloric acid in 60% water–40% dioxan.*

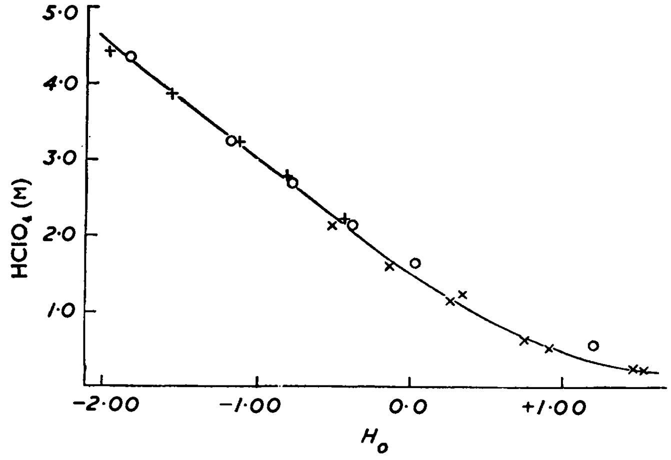
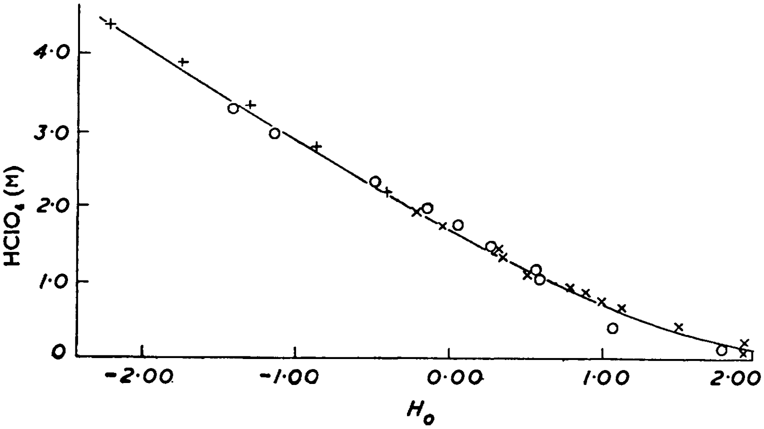


FIG. 2. *H_0 for perchloric acid in 40% water–60% dioxan.*



FIGS. 1 *and* 2. ×, p-*Nitroaniline*; ○, o-*nitroaniline*; +, 4-*chloro*-2-*nitroaniline*.

The rate of hydrolysis of ethyl acetate is clearly proportional to the stoicheiometric acidity, *i.e.*, k_2 is sensibly constant and log k_1 plotted against $-\log c_{H^+}$ gives a straight line of unit slope. The rate of hydrolysis of sucrose, however, increases very much more rapidly, by a factor of 6·6 over the range of acidities studied, than does the stoicheiometric acid concentration and is clearly dependent on H_0. A plot of log k_1 against H_0 for the sucrose reaction gives a straight line of nearly unit slope (1·02). This line (○), together with a plot (×) of the values obtained by Leininger and Kilpatrick [13] with hydrochloric acid in water as solvent, is shown in Fig. 4. The broken line indicates the expected curve if the rate in 40% aqueous dioxan were linearly dependent on stoicheiometric acidity.

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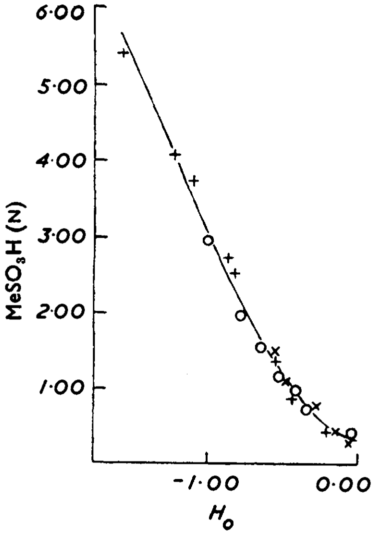
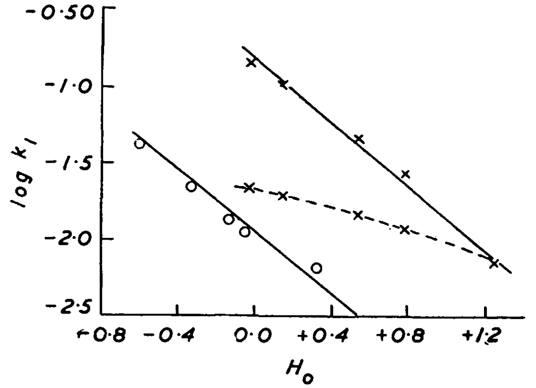
[13] Leininger and Kilpatrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2891.

FIG. 3. *H_0 for methanesulphonic acid in methanol.*



×, p-*Nitroaniline*; ○, o-*nitroaniline*; + 4-*chloro-2-nitroaniline* (*adjusted to fit the curve*).

FIG. 4. *Hydrolysis of sucrose at 25°.*



×, *in 40% water–60% dioxan with* $HClO_4$.
○, *in water with* HCl.[13]
Broken curve is that expected if reaction followed molar acidity.

TABLE 1.

(a) 60% *Water–40% dioxan.*

$HClO_4$ (M)	log I	H_0	$HClO_4$ (M)	log I	H_0
p-Nitroaniline, pK_B = 0·99					
0·217	0·53	1·52	1·086	−0·70	0·29
0·222	0·51	1·50	1·108	−0·66	0·33
0·543	−0·07	0·92	1·63	−1·11	−0·12
0·653	−0·23	0·76	2·172	−1·48	−0·49
o-Nitroaniline, pK_B = − 0·29					
0·543	1·51	1·22	2·715	−0·48	−0·77
1·629	0·32	0·03	3·25	−0·86	−1·15
2·172	−0·10	−0·39	4·344	−1·55	−1·84
4-Chloro-2-nitroaniline, pK_B = − 1·03					
2·22	0·61	−0·42	3·878	−0·53	−1·56
2·77	0·25	−0·78	4·423	−0·92	−1·95
3·324	−0·11	−1·14			

(b) 40% *Water–60% dioxan.*

$HClO_4$ (M)	log I	H_0	$HClO_4$ (M)	log I	H_0
p-Nitroaniline					
0·195	0·95	1·94	0·976	−0·21	0·78
0·230	0·96	1·95	1·15	−0·45	0·54
0·460	0·50	1·49	1·313	−0·61	0·38
0·586	0·25	1·24	1·464	−0·67	0·32
0·689	0·14	1·13	1·75	−1·03	−0·04
0·781	0·01	1·00	1·95	−1·21	−0·22
0·875	−0·11	0·88			
o-Nitroaniline					
0·195	2·09	1·80	1·72	0·34	0·05
0·587	1·37	1·08	1·95	0·08	−0·21
1·09	0·88	0·59	2·30	−0·21	−0·50
1·15	0·85	0·56	2·93	−0·85	−1·14
1·464	0·56	0·27	3·28	−1·13	−1·42
4-Chloro-2-nitroaniline					
1·641	1·03	0·00	3·28	−0·28	−1·31
2·188	0·61	−0·42	3·849	−0·72	−1·75
2·735	0·16	−0·87	4·376	−1·20	−2·23

(c) *Methanol*

Me·SO_3H (M)	log I	H_0	Me·SO_3H (M)	log I	H_0
p-Nitroaniline					
0·367	−1·05	−0·06	1·101	−1·47	−0·48
0·441	−1·15	−0·16	1·468	−1·54	−0·55
0·734	−1·28	−0·29			
o-Nitroaniline					
0·380	0·24	−0·05	1·52	−0·34	−0·63
0·76	−0·05	−0·34	1·94	−0·48	−0·77
0·97	−0·14	−0·43	2·91	−0·68	−0·97
1·14	−0·22	−0·51			
4-Chloro-2-nitroaniline					
0·441	1·05	0·02 (−0·18)	2·50	0·42	−0·61 (−0·81)
0·882	0·80	−0·23 (−0·43)	2·70	0·38	−0·65 (−0·85)
1·35	0·69	−0·34 (−0·54)	3·69	0·15	−0·88 (−1·08)
1·373	0·68	−0·35 (−0·55)	4·05	0·03	−1·00 (−1·20)
			5·40	−0·30	−1·33 (−1·53)

TABLE 2.

	60% Aqueous dioxan	40% Aqueous dioxan	Methanol
p-Nitroaniline	0·00	−0·34	1·55
o-Nitroaniline	−1·40	−1·58	0·20
4-Chloro-2-nitroaniline	−2·08	−2·35	−0·67

TABLE 3.*

$HClO_4$ (M)	10^2k_1	10^2k_2	H_0	$HClO_4$ (M)	10^2k_1	10^2k_2	H_0
(1) Sucrose hydrolysis				(2) Ethyl acetate hydrolysis			
0·591	0·743	1·26	1·25	0·470	0·246	0·523	1·43
0·948	2·8	2·95	0·77	0·948	0·54	0·570	0·77
1·171	4·64	3·96	0·53	1·860	1·17	0·630	−0·15
1·578	10·4	6·60	0·13	2·230	1·31	0·588	−0·49
1·740	14·5	8·33	−0·03				

* k_1 is the first-order rate coefficient in min.$^{-1}$. k_2 is k_1/c_{H^+} in min.$^{-1}$ mole^{-1} l.

DISCUSSION

For the acidity function concept to be applicable to a given solvent the activity coefficient ratio, f_B/f_{BH^+}, for a neutral base and its conjugate acid, must be essentially independent of the nature of the base. When this is true, values of H_0, calculated by equation 1 (and using pK_B values referring to water as solvent) from data obtained with different indicators, should depend only on acid concentration. If, as is usually the case, the indicators cover different ranges of acidities, the corresponding curves of H_0 against acid concentration should overlap without discontinuity. This is essentially the criterion originally used by Hammett and Deyrup.[11] In the present case the results for the two aqueous solvents satisfy this criterion and, within the limits imposed by the nature of the three amine indicators chosen, it may be concluded that the H_0 concept is applicable to both solvents.

On the other hand, the values of H_0 for methanesulphonic acid in methanol are not independent of the indicator used, and a continuous curve of H_0 against acidity cannot be drawn. However, if the pK_B value of one of the indicators (4-chloro-2-nitroaniline) is arbitrarily decreased by 0·2 unit, the major discontinuity in the curve is removed (Fig. 3), but this procedure has no theoretical significance and it must be concluded that in this system the H_0 concept has little generality.

The same conclusions emerge by plotting the logarithms of the indicator ratios (log *I*) for pairs of indicators at a series of acidity values. This procedure essentially determines whether, in the overlap region, the curves of log *I* against acidity for two indicators are parallel. If they are not, clearly no continuous curve for H_0 can be drawn. The test is rather a severe one for the present results since the overlap region for any two indicators necessarily includes the least accurate values of the indicator ratios. The slopes of the plots are given in Table 4, which also includes values obtained from Hammett and Deyrup's original data [11] for perchloric acid in water.

TABLE 4.

	Water	60% Aqueous dioxan	40% Aqueous dioxan	Methanol
Log I_A/log I_B	0·99	0·98	1·08	1·12
Log I_C/log I_B	1·03	1·06	0·97	0·84

A = *p*-nitroaniline; B = *o*-nitroaniline; C = 4-chloro-2-nitroaniline.

The results for perchloric acid in the two aqueous dioxan solvents are not much worse, on this test, than those for water. For methanesulphonic acid in methanol, however, the plots are not quite linear and the average slopes are significantly different from unity; this system clearly does not satisfy the test.

It must be pointed out that, although the results show that for the three indicators used an acidity function exists in aqueous dioxan, it is not our view that the same result would necessarily be obtained whatever indicators were used. In other words, the use of three indicators with similar structures is not sufficient to satisfy the very stringent criterion for the existence of an acidity function given by Gutbezahl and Grunwald.[8] It seems to us that the H_0 concept does not have complete generality in any solvent, and we regard the present results primarily as indicating the probable usefulness of the concept as a diagnostic tool for reactions occurring in aqueous dioxan.

The results for methanol, on the other hand, do not support the view that there is an acidity function in this solvent, but this may be partly due to the choice of acid, since large anions are known to produce abnormally large activity effects under certain conditions.[14] However, even if the H_0 values for methanol in Table 1 were true acidity-function values they would be of little interest to the kineticist, since the rate of change of H_0 is not very different from the rate of change of $-\log c_{H^+}$. For example, in the range 1—4M methanesulphonic acid, where $-\log c_{H^+}$ changes by 0·60, the change in H_0 is 0·77, whereas in 40% aqueous dioxan the corresponding change for perchloric acid is 2·66. Although the reasons for this behaviour are not known it illustrates the limitations of a comparison of the acidities of different solvents at fixed acid concentrations.

Our results are compared with those of other workers in Table 5, which gives H_0 values at M-acid in aqueous dioxan. Kreevoy's data, which have been adjusted so as to refer to infinite dilution in water as standard state, are not wholly consistent with ours; this may be partly due to his method of making up solutions which is such that the dioxan–water ratio varies with the acidity. Braude and Stern's results show that aqueous dioxan solutions of M-hydrochloric acid are less acidic than those of M-perchloric acid. For both acids, at this concentration, 40% dioxan solutions are the more strongly acidic, although, as can be seen by reference to Table 1, this situation is reversed for perchloric acid solutions above 2·25M.

TABLE 5.

Authors	Acid	60% of water	50% of water	40% of water
Braude and Stern	HCl	0·89	—	1·24
Kreevoy	$HClO_4$	—	0·33	—
This work	$HClO_4$	0·48	—	0·72

The rate of hydrolysis of ethyl acetate in water has been shown by Bell, Dowding, and Noble [15] to follow stoicheiometric acidity. As can be seen from Table 3 the same result is obtained in 40% aqueous dioxan. The actual rates at corresponding acidities are not very different in the two solvents; 10^3k_2 is 7·8 and 5·6 min.$^{-1}$ mole^{-1} l., in water and 40% aqueous dioxan respectively. Application of the Brönsted equation to a mechanism involving attack by a water molecule on the conjugate acid of a substrate (S) in the rate-determining stage leads [16] to the equation:

$$k = k_2 k_e [OH_3^+] \frac{f_S f_{OH_3^+}}{f_T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where k is the experimental first-order rate coefficient, k_2 is the true rate coefficient for the rate-determining stage, *i.e.*, is the rate coefficient under the chosen standard-state conditions, all variation in the rate being taken up by the activity coefficients, k_e is the equilibrium constant for the protonation of the substrate (S), and T^+ refers to the transition state, which in this case contains a water molecule. The product k_2k_e should be independent of environment, and k will depend on $[OH_3^+]$ alone if the activity ratio term is constant. The results obtained indicate that for a change of solvent from water to 40% aqueous dioxan this condition is approximately fulfilled.

The rate of hydrolysis of sucrose in water is dependent on H_0.[17] In 40% aqueous dioxan the same dependence is observed, the slopes of the plots of log k_1 against H_0 being virtually the same in the two cases. Hence, the clear-cut distinction between the mechanisms of hydrolyses of sucrose and of ethyl acetate in water is equally well shown in

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[14] Long and McDevit, *Chem. Rev.*, 1952, **51**, 119.

[15] Bell, Dowding, and Noble, *J.*, 1955, 3106.

[16] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, p. 276.

[17] Ref. 16, p. 274.

aqueous dioxan, and this supports the view that the Zucker–Hammett criterion of mechanism may be usefully employed in aqueous dioxan solvents.

Kreevoy's results[9] on the hydrolysis of acetals and ketals indicate that these reactions in 50% aqueous dioxan also depend on the acidity function. However, his demonstration of the validity of the concept in this solvent involves the joint use of indicator and kinetic data. Our view is that the H_0 scale should be established by indicator measurements alone, as was done originally for water solution, and that the Zucker–Hammett hypothesis, since it involves additional assumptions, should be tested subsequently by kinetic methods.

The actual rates of hydrolysis of sucrose in 40% aqueous dioxan, at particular values of H_0, differ appreciably from those in water. The comparison is shown in Fig. 4,* from which it can be seen that the reaction in water is the slower by a factor of *ca.* 13·4. If a rate coefficient for the rate-determining step be defined in the usual way by

$$\text{Rate} = k'[\text{SH}^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

then combining it with equation (1) we have

$$\text{Rate} = k'[\text{S}]h_0k_\text{B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where H_0 is $-\log h_0$. Hence:

$$k_1 = k'h_0k_\text{B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where k_1 is the experimentally determined first-order rate coefficient for given acidity. For two different solvents with the same substrate and acidity-function value, the relative values of k' are given by the relative values of the experimental rate coefficients, k_1. This is independent of mechanism and of the assumptions involved in the Zucker–Hammett hypothesis and assumes only the validity of the H_0 concept in the solvents used. However, differentiation of mechanism requires the application of the Brönsted equation, and this leads for a unimolecular heterolysis of the conjugate acid of S to the equation:[18]

$$k = k_2k_\text{e}a_{\text{H}^+}f_\text{S}/f_{\text{T}^+}$$

f_{T^+} referring to the transition state, which in this case, does not contain a water molecule, and the other symbols having the same significance as before. In so far as $f_\text{S}/f_{\text{T}^+}$ is equal to $f_\text{B}/f_{\text{BH}^+}$, the logarithm of the rate coefficient should depend only on H_0,† k_2k_e being independent of the environment.[19] The failure of the rates in water and in aqueous dioxan to correlate through the H_0 values is surprising, expecially since the slopes of the log k–H_0 plots are very close to unity in both cases. However, no formal incompatability arises here since the unit slopes in the log k–H_0 dependence require not that $f_\text{S}/f_{\text{T}^+}$ shall equal $f_\text{B}/f_{\text{BH}^+}$ where B represents an indicator, but that their first derivatives with respect to acid concentration shall be the same over the range of acidities studied. Whether this condition, which is sufficient for diagnosis, holds more generally than the more extreme requirement of equality of the two activity ratios, can only be established by more attempts to correlate rates in different solvents through H_0 values.

EXPERIMENTAL

(a) *Materials.*—Commercial *o*-nitroaniline, *p*-nitroaniline, and 4-chloro-2-nitroaniline were recrystallised from water three times. Dioxan was purified as described by Vogel.[20] Methanesulphonic acid was twice distilled in an all-glass apparatus. Anhydrous methanol was obtained by distillation from a suspension of magnesium methoxide in absolute methanol.

Solutions of methanesulphonic acid in methanol were found to give constant titres, against alkali, over the period of the experiments.

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* Leiniger and Kilpatrick's data refer to concentrations of sucrose similar to those used by us.

† For two different solvents this will be true providing, of course, that the H_0 values have been referred to the same standard state.

[18] Ref. 19, p. 275.

[19] Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, 1941, p. 404.

[20] Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 175.

(b) *Solutions.*—The 40% water–60% dioxan solutions were made up as follows : 40 volumes of water and 60 volumes of dioxan were mixed together. An appropriate amount of 72% " AnalaR " perchloric acid, previously standardised against borax, was added. The volume of water in this amount of acid was calculated, and an amount of dioxan, such that the ratio of its volume to the volume of water present in the perchloric acid was 60 : 40, was then also added. This procedure ensured that, whatever the acid concentration, the amounts of water and dioxan remained in constant ratio. A similar procedure was used for the other aqueous solvent.

(c) *Indicator Measurements.*—An appropriate amount of indicator, usually giving a solution *ca.* 10^{-3} times the concentration of acid, was dissolved in the appropriate solvent, and the optical densities at four wavelengths across the absorption peak were measured with a Unicam S.P. 500 Spectrophotometer. At the wavelengths chosen, Beer's law was obeyed for all three indicators, and the completely protonated forms gave negligibly small absorptions.

(d) *Kinetic Measurements.—Hydrolysis of sucrose.* Each solution was made by dissolving sucrose (*ca.* 0·1—0·2 g. in 10 c.c.) in 40% water–60% dioxan containing a known concentration of perchloric acid. The reaction was followed by placing the solution in a polarimeter tube, at 25° (thermostat), and reading the rotatory power at suitable times. The following results, which are typical, were obtained with a solution 1·578M in perchloric acid.

Time (min.)	0	0·75	1·83	2·83	3·55	4·33
Rotation	0·519°	0·460°	0·385°	0·332°	0·295°	0·264°
k_1 (min.$^{-1}$)	—	0·112	0·110	0·104	0·103	0·099
Time (min.)	5·66	7·00	11·00	15·10	18·30	∞
Rotation	0·194°	0·142°	0·018°	−0·058°	−0·090°	−0·214°
k_1 (min.$^{-1}$)	0·104	0·103	0·105	0·103	0·097	—

Hydrolysis of ethyl acetate. Solutions of 40% water–60% dioxan containing known concentrations of perchloric acid were degassed by quick pumping on a filter pump. Portions (25 c.c.) were kept at 25°; freshly distilled ethyl acetate (*ca.* 0·5 c.c.) was added, the whole was mixed, and a tap dilatometer (of *ca.* 20 c.c. volume and with a capillary of 0·4 mm. bore) was filled by suction. Readings were commenced 10 min. after filling. Good first-order rate coefficients, calculated by Guggenheim's method,[31] were obtained in all cases.

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[31] Guggenheim, *Phil. Mag.*, 1926, **7**, 538.