562. *The Use of the Acidity Function H_0 as a Tool for the Study of Reaction Mechanism in Mixed Solvents.*
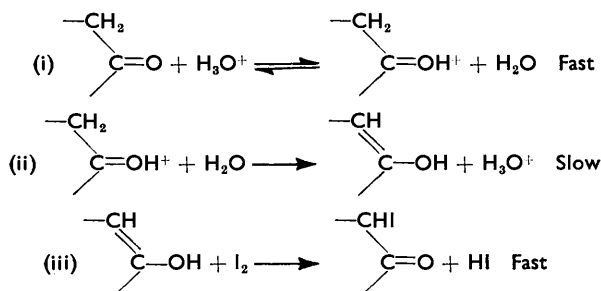
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Measurements of the rate of acid-catalysed iodination of acetone in water and in various ethanol–water mixtures are reported. The results indicate that the usefulness of the acidity function H_0 as a means of distinguishing between different acid-catalysed reaction mechanisms in mixed aqueous solvents is limited by a phenomenon which may prove even more restrictive than the lack of generality of H_0 scales in solvents of low dielectric constant.

The use of the acidity function H_0 for diagnosing reaction mechanism in aqueous solution is well known.[1] Certain acid-catalysed mechanisms lead to rates which correlate with the hydrogen-ion concentration $[H_3O^+]$, while others lead to correlations with h_0 ($=$ antilog $-H_0$). Zucker and Hammett's scheme has also often been invoked in connection with studies in mixed aqueous solvents, such as dioxan– and alcohol–water mixtures, but with little reason. The ultimate justification of the method is empirical and, so far, in no mixed solvent has the H_0 scale been shown to be reproducible, nor, which is perhaps more important, have detectably different correlations with acidity been demonstated for reactions known from independent evidence to proceed by different mechanisms. Particularly significant in the latter connection is Waters's study [2] of the solvolysis of phenyl acetate in ethanol–water mixtures. The mechanism of simple ester hydrolysis is of the type which, in water,[3] leads to correlation with $[H_3O^+]$ rather than with h_0. Waters's data refer to rather limited acidity ranges, but, so far as they go, suggest that in ethanolic solvents the rate of solvolysis tends to increase with acidity somewhat faster than strict proportionality to $[H_3O^+]$ demands, and that this tendency is greater the more ethanolic the medium. It seems unlikely that the mechanism of ester hydrolysis undergoes a gradual change in these media, and therefore the question obviously arises as to how ethanolic the solvent can become before the rate increases linearly with h_0 with a slope close to unity, and so makes impossible any distinction between such a mechanism and the type involving a unimolecular step, which should always correlate with h_0 if the scale is reproducible.[1]

Since much further work is clearly needed before mixed solvents can be used in diagnostic investigations along the Zucker–Hammett lines, a study of the iodination of acetone in ethanol–water mixtures has been made with hydrochloric and perchloric acids as catalysts.

The acid-catalysed halogenation of ketones in aqueous solution is one of the most fully studied of all reactions. The rate is general acid-catalysed, of the first order in ketone, and of zero order in halogen.[4] The generally accepted mechanism is : [5]

(i) $\begin{array}{c}-CH_2\\\diagdown\\C=O\\\diagup\end{array}$ $+\ H_3O^+ \rightleftharpoons$ $\begin{array}{c}-CH_2\\\diagdown\\C=OH^+\\\diagup\end{array}$ $+\ H_2O$ Fast

(ii) $\begin{array}{c}-CH_2\\\diagdown\\C=OH^+\\\diagup\end{array}$ $+\ H_2O \longrightarrow$ $\begin{array}{c}-CH\\\diagdown\\C-OH\\\diagup\end{array}$ $+\ H_3O^+$ Slow

(iii) $\begin{array}{c}-CH\\\diagdown\\C-OH\\\diagup\end{array}$ $+\ I_2 \longrightarrow$ $\begin{array}{c}-CHI\\\diagdown\\C=O\\\diagup\end{array}$ $+\ HI$ Fast

[1] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.
[2] Waters, *J.*, 1936, 1014.
[3] Bell, Dowding, and Noble, *J.*, 1955, 3106; Chmiel and Long, *J. Amer. Chem. Soc.*, 1956, **78**, 3326.
[4] Bell, " Acid–Base Catalysis," Oxford Univ. Press, 1941.
[5] Bell and Jones, *J.*, 1953, 88.

From the viewpoint of dependence on acidity, Zucker and Hammett[1] have observed the expected proportionality to $[H_3O^+]$ (and lack of it to h_0) for the iodination of acetophenone in aqueous perchloric acid.

The rate of iodination of acetone in aqueous hydrochloric acid for acid concentrations up to 1M was measured by Dawson and Powis.[6] The present results, shown in Table 1, extend their measurements into the region where h_0 and $[H_3O^+]$ are significantly different. Dawson and Powis used an acetone concentration of 0·273M and all the rate constants

FIG. 1. *Correlation of iodination rates with acid concentration.*

For all Figures :

a, ● H_2O; b, △ 7·2; c, ■ 16·9; d, ◑ 24·4; e, ◇, 44·4; f, ◐ 63·8 moles % of EtOH in H_2O.
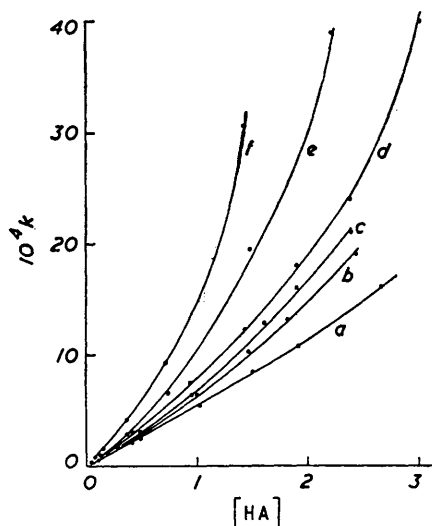

FIG. 2. *Logarithmic correlation of iodin- ation rates with acid concentration.*
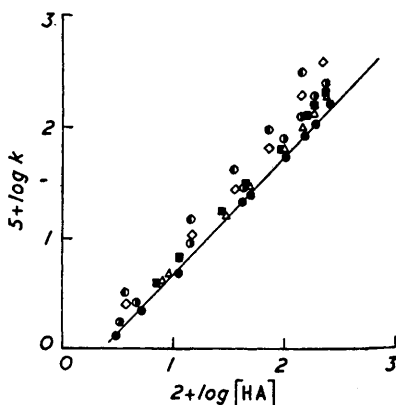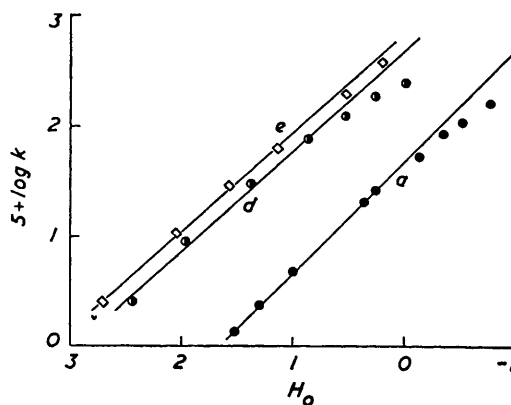

FIG. 3. *Correlation of iodination rates with acidity function.*

given in the present paper are calculated on the basis of that concentration so that a comparison with their data can easily be made. The agreement is, in fact, quite good. Figs. 1, 2, and 3 show that the proportionality between $[H_3O^+]$ and k found by Dawson and Powis is reasonably maintained at higher acidities and that there is a definite lack of parallelism with h_0. Thus the iodination of acetone, as expected, shows in water the same type of acidity dependence as the iodination of acetophenone.

In alcohol–water mixtures the acid-catalysed reaction rate remains of zero order in halogen. The results obtained in five different ethanol–water media are given in Tables 2—7. In Fig. 1, k is plotted against [HA], and in Fig. 2, log k against log [HA], where

* Dawson and Powis, *J.*, 1913, 2135.

[HA] represents the stoicheiometric acid concentration.   In the alcohol–water mixtures used both hydrochloric acid and perchloric acid will be essentially completely dissociated at all the concentrations employed, the highest being only 3·0M.   Further it is probable that, at any rate above 45 mole % of water, effectively all the ionisation will be to give hydroxonium rather than ethoxonium ions.[7]   In any case, for the comparatively low acid concentrations used, there will exist for any given alcohol–water mixture some particular value of the ratio $[H_3O^+]/[EtOH_2^+]$ which will stay practically constant with changing acid concentration.   In other words the rate of a general acid-catalysed reaction would be expected to be reasonably proportional to [HA] in the solvents used, as in water, always provided the activity coefficient ratios involved in the rate equation remain approximately constant.[1]

TABLE 1.   *Iodination of* 0·273M-*acetone in water at* 25°.

[HCl] *	0·030	0·051	0·112	0·420	0·487	1·03	1·50	1·91	2·66
10^4k	0·132	0·230	0·490	2·12	2·52	5·40	8·40	10·75	16·0
H_0	1·52	1·30	1·00	0·34	0·26	−0·13	−0·35	−0·52	−0·79

   * In all Tables, k is the rate of disappearance of iodine (moles l.⁻¹ min.⁻¹) and brackets [ ] denote stoicheiometric molarity.

TABLE 2.   *Iodination of* 0·273M-*acetone in* 7·2 *moles* % *of ethanol in water at* 25°.

[HCl]	0·077	0·094	0·292	0·490	0·980	1·47	1·82	2·43
10^4k	0·417	0·464	1·58	2·90	6·28	10·2	13·1	19·1

TABLE 3.   *Iodination of* 0·273M-*acetone in* 16·9 *moles* % *of ethanol in water at* 25°.

[HCl]	0·071	0·118	0·290	0·460	0·960	1·60	1·89	2·40
10^4k	0·402	0·680	1·74	2·93	6·30	12·9	16·0	21·1

TABLE 4.   *Iodination of* 0·273M-*acetone in* 24·4 *moles* % *of ethanol in water at* 25°.

[HCl]	0·032	0·047	0·141	0·430	0·950	1·44	1·90	2·37
10^4k	0·174	0·258	0·88	2·89	7·60	12·3	18·0	24·1
H_0	—	2·45	1·95	1·36	0·85	0·51	0·25	−0·02

TABLE 5.   *Iodination of* 0·273M-*acetone in* 24·4 *moles* % *of ethanol in water at* 25°.

[HClO₄]	0·048	0·144	0·430	1·05	1·42	1·73	2·42	3·00
10^4k	0·263	0·860	2·77	8·18	12·0	16·3	25·6	40·0

TABLE 6.   *Iodination of* 0·273M-*acetone in* 44·4 *moles* % *of ethanol in water at* 25°.

[HClO₄]	0·038	0·148	0·369	0·740	1·48	2·22	2·96
10^4k	0·261	1·07	2·80	6·51	19·4	39·0	62·0
H_0	2·69	2·03	1·56	1·14	0·54	0·19	—

TABLE 7.   *Iodination of* 0·273M-*acetone in* 63·8 *moles* % *of ethanol in water at* 25°.

[HClO₄]	0·036	0·144	0·362	0·720	1·44
10^4k	0·320	1·49	4·07	9·33	30·5

   Examination of Figs. 1 and 2 shows that, as the ethanol content of the medium rises, (*a*) the amount of deviation from essentially exact dependence on concentration shown in water increases, and (*b*) the rate of iodination increases somewhat at constant acid concentration.

   (*a*) This result is analogous to that of Waters.   In Fig. 3 the logarithms of the rate constants obtained in water and in mixtures containing 24·4 and 44·4 moles % of ethanol are plotted against the H_0 values for these media (H_0 values for water are taken from refs. 3 and 8 and those for the ethanolic media are as measured by use of the base *p*-nitro-aniline).   As previously mentioned the correlation in water is poor, and in 24·4 moles % ethanol it is, if anything, somewhat worse, but by the time 44·4 moles % ethanol is reached it is quite good.   For this medium the correlation between log k and H_0 is, in fact, rather better than that between log k and log [HA] (Fig. 2).   As the ethanol content rises the

   [7] Braude and Stern, *J.*, 1948, 1976.
   [8] Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 827.

change in H_0 for a given change in acid concentration increases, but so also does the change in reaction velocity. In the present case the latter effect begins to overhaul the former after about 25 moles % of ethanol. It is clear that at a composition somewhat below 44 moles % of ethanol it has become impossible to say whether correlation with log [HA] or with H_0 is the better, and that from this composition onwards this difficulty will always be present, any decision being in favour of a correlation with H_0.

It seems rather unlikely that the mechanism of acid-catalysed halogenation of ketones will change as the medium becomes more ethanolic. In particular it is difficult to visualise a change to a mechanism involving a rate-determining, unimolecular reaction of the conjugate acid of the keto-form—the only mechanism which should show a correlation with H_0 on the Zucker–Hammett basis. An important reason for the increasing departure from simple concentration dependence is probably that the sort of ratio of activity co-efficients, which must be assumed to remain constant if mechanisms of the ketone halogenation type are to give correlations with [HA], becomes, in fact, less and less constant with increasing acid concentration as the ethanol content of the medium is raised. Whether or not this is the only reason, it must be concluded that even if a reproducible H_0 scale is eventually established in any ethanol–water mixture containing more than about 40 moles % of ethanol, as seems quite possible, studies of the variation of reaction rate with acidity in such a solvent will nevertheless be inadequate for diagnostic purposes : one anomaly of the present kind makes all other correlations equivocal. Since different reactions possessing a mechanism of type (b) will show different degrees of departure from simple concentration dependence, it will not be possible to give a definite safety limit beyond which results will become ambiguous. However, it is probably safe to use the ethanol–water media containing more than 70 moles % of water, though for mixed media whose organic components have dielectric constants lower than that of ethanol, more water may be necessary. The use of higher acid concentrations than was possible in the present work may improve the situation, though consideration of the curvature exhibited in Fig. 1 is discouraging to hopes of any great improvement.

It will be interesting to see how the limits of validity of the H_0 scales in mixed media compare with the rather ill-defined boundaries set by the phenomenon now reported.

(b) The slight increase in rate at a fixed acid concentration as the alcohol content of the medium is raised might be expected for at least two reasons. First, any contribution to the total rate from ethoxonium ions will increase with alcohol content. Secondly, reactions which involve the dispersion of charge in the transition state are favoured by movement to media of lower dielectric constant.

The H_0 values for the mixed media used are considerably more positive than those for aqueous media of the same acid concentration and, therefore, from this point of view, the rates of iodination show no tendency to follow the acidity function. Waters's results also do not show quantitative dependence on H_0 in this respect. It seems likely that, since at low acid concentrations, the changes in H_0 with alcohol content are quite large,[7] variation of solvent composition at a fixed acid concentration will prove a more powerful method of establishing the presence or absence of correlations with H_0 in these media than the variation of the acid concentration.

EXPERIMENTAL

Materials.—" AnalaR " acetone, absolute alcohol (99·5 wt.%), and perchloric acid were used. Iodine was resublimed and *p*-nitroaniline was recrystallised, m. p. 148°.

Kinetic Experiments.—The disappearance of iodine was followed colorimetrically with a Beckman spectrophotometer. Iodine was shown to obey Beer's law in the various media used. The iodination is reversible,[1] the equilibrium lying closer to the free iodine side the higher the acid concentration and the more ethanolic the medium. This difficulty can be overcome by the addition of sufficient sodium nitrite to re-oxidise the iodide ions which are produced to iodine.[1] This method has the incidental advantage that all, instead of half, the

iodine is used, so that the reaction takes twice as long to complete and higher acid concentrations are thus made accessible.

The useful iodine concentrations for a 1 cm. path are in the range 10^{-3}—10^{-4}M. The acetone was always in at least a ten-fold excess. The sodium nitrite concentration used was 5×10^{-3}M. In making up the reaction mixtures, calculated volumes of water, ethanolic (or aqueous) iodine and concentrated aqueous hydrochloric (or perchloric) acid were mixed, together with the sodium nitrite when necessary, in a stoppered flask. The flask and contents were brought to $25°$ in a thermostat bath and the reaction started by the addition of a small quantity of aqueous acetone. Samples of reaction mixture were withdrawn at suitable intervals, and their light absorption measured. It was shown that inappreciable cooling took place during the optical measurements. In calculating the concentrations of the reactants allowance was made for the small volume changes involved on mixing the various solutions.

Good zero-order plots were obtained for all the quoted rate constants. In water and the more aqueous mixed media at low acid concentrations, the reaction goes to completion even in the absence of nitrite, and it was verified that the observed specific rates in the presence and absence of nitrite were identical.[1] For the media containing 24·4 moles % of ethanol experiments were conducted with both hydrochloric acid and perchloric acid. The two sets of values agree closely, as it is to be expected if dissociation is complete. The reason for the change to perchloric acid at this point was that in the more ethanolic media good kinetic plots were not obtained with hydrochloric acid as the catalyst, while perchloric acid solutions behaved perfectly.

Measurements of Acidity Function.—The H_0 values for the media containing 24·4 moles % of ethanol and hydrochloric acid and for those containing 44·4 moles % of ethanol and perchloric acid, were measured by the usual methods [9] with a Beckman spectrophotometer. The temperature was $18° \pm 1°$ and the indicator p-nitroaniline. No sodium nitrite was added, the reasonable assumption [9] being made that a neutral-salt concentration of 5×10^{-3}M would have a negligible effect on H_0. The H_0 values were calculated on the basis of the pK_a value for p-nitroaniline recommended by Long and Paul,[9] *viz.*, 0·99.

H_0 values for 0·1- and 1·0-M-hydrochloric acid in a medium containing 24·4 moles % of ethanol can be interpolated from the work of Braude and Stern [7] who covered the whole composition range at these acidities. The corresponding values now obtained differ more in magnitude and are somewhat more positive than theirs. It is pointed out that the same is true of values recently obtained by Baines and Eaborn [10] for a more ethanolic medium.

[9] Long and Paul, *Chem. Rev.*, in the press.
[10] Baines and Eaborn, *J.*, 1956, 1436.