759. *The Hammett Acidity Function in Aqueous Iodic Acid and Aqueous Periodic Acid*

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The H_0 scale for iodic acid and that for periodic acid have been measured up to 6M and 2·5M, respectively. The H_0 results for iodic acid are in agreement with those calculated from an equation involving the water activity and the degree of dissociation, provided that the latter values are those derived from conductivity measurements. Poorer agreement was obtained by using degrees of dissociation obtained from proton magnetic resonance and Raman spectroscopy, and the implications of this are discussed.

FROM many experimental approaches, it is generally accepted that iodic acid and periodic acid are both weak acids.[1-5] The weakness of the individual acids, however, does not appear to have been measured quantitatively from the point of view of proton-donating power. The Hammett acidity function,[6] H_0, is a measure of this property, and the acidity scales of a number of acids have been established over wide ranges of concentration.[7-9] In a number of cases, the acidity function is known over the whole range from dilute aqueous solution up to the anhydrous acid. It is of interest, therefore, to compare the strengths of concentrated solutions of weak acids with those of strong acids. The H_0 values for iodic acid have been measured in this work up to 6M (57%) and those for periodic acid up to 2·5M (33%). The indicators used were *o*- and *p*-nitroaniline, which are known to behave simply as bases.[7] The absorption spectra of the protonated bases are quite well separated from those of the free bases, and the extent of protonation is conveniently measured spectrophotometrically.

EXPERIMENTAL

Solutions were made up by weight in graduated flasks, so that compositions by weight and molarity could be readily calculated. Indicator solutions were added to the acid solutions by pipette. The optical densities of the solutions were measured with a Hilger Uvispek against reference solutions of the same composition but without indicator. The ratios of protonated base to unprotonated base (indicator ratio), $[BH^+]/[B]$, were calculated in the normal way from the optical densities at maximum absorption.[7] The wavelengths of maximum absorption of the indicators were almost unaffected by concentration of acid.

Materials.—Concentrated solutions of iodic acid were made up from the AnalaR grade solid. Occasionally, a small quantity of undissolved solid remained, and this was removed by filtration through a sintered-glass crucible of porosity 4. The strengths of the solutions were obtained by normal acidimetry, and the solutions were diluted with weighed quantities of water for the H_0 measurements.

The periodic acid was of B.D.H. laboratory-reagent quality, 50% as H_5IO_6 (orthoperiodic acid, $HIO_4 \cdot 2H_2O$). In its analysis, an indicator that changed colour at the point corresponding to the first stage of neutralisation of orthoperiodic acid [10] [*i.e.*, $(pK_1 + pK_2)/2 = pH\ 5{\cdot}0$] was chosen; this was Methyl Red. Solutions for measurement were made from the concentrated acid by dilution with weighed quantities of water.

The indicator bases were of B.D.H. laboratory-reagent quality and were purified by recrystallisation twice from water; *p*-nitroaniline, m. p. 148°, and *o*-nitroaniline, m. p. 71°.

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[7] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.

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[9] K. N. Bascombe and R. P. Bell, *J.*, 1959, 1096.

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RESULTS AND DISCUSSION

The values of the indicator ratios, $[BH^+]/[B]$, for iodic acid and periodic acid are recorded in Tables 1 and 2, respectively. The usual procedure[7] of evaluating the pK of *p*-nitroaniline from the intercept of a plot of log $[BH^+]/[B]$ − log$[H^+]$ against molarity of acid could not be employed. The assumption implicit in this method is that $[H^+]$ can be put equal to the molarity of acid; with weak acids this is not possible, since the acid may be partly undissociated even in dilute solution. The pK values used here are the "best" values of Paul and Long,[7] and it was found that the H_0 results from the two indicators overlapped quite well in solutions of approximately the same concentrations. The H_0 values in Tables 1 and 2 were calculated from $H_0 = \mathrm{p}K - \log[BH^+]/[B]$.

TABLE 1

Results for iodic acid

Molarity	Wt. (%)	$[BH^+]/[B]$	H_0	Molarity	Wt. (%)	$[BH^+]/[B]$	H_0
p-*Nitroaniline*, pK = 0·99 (ref. 7)							
0·013	0·15	0·140	1·87	0·335	5·62	2·00	0·69
0·033	0·58	0·316	1·49	0·345	5·75	2·34	0·62
0·056	0·98	0·501	1·29	0·390	6·48	2·48	0·59
0·089	1·55	0·731	1·13	0·510	8·30	3·21	0·48
0·124	2·14	0·966	1·01	0·527	8·64	3·54	0·44
0·169	2·90	1·02	0·89	0·697	11·2	4·56	0·33
0·224	3·83	1·45	0·83	1·23	18·3	8·02	0·09
0·279	4·71	1·95	0·70	1·43	20·9	9·33	0·02
o-*Nitroaniline*, pK = −0·29 (ref. 7)							
0·331	5·55	0·123	0·62	2·11	28·3	0·700	−0·13
0·387	6·46	0·114	0·66	2·38	33·0	0·851	−0·22
1·052	16·1	0·387	0·13	2·69	34·1	0·968	−0·28
1·22	18·2	0·432	0·09	3·24	38·8	1·32	−0·41
1·41	20·6	0·490	0·03	4·03	44·9	1·80	−0·54
1·54	22·2	0·504	−0·01	4·67	49·2	2·09	−0·61
1·56	22·5	0·545	−0·02	5·71	55·4	2·85	−0·75

TABLE 2

Results for periodic acid

Molarity	Wt. (%)	$[BH^+]/[B]$	H_0	Molarity	Wt. (%)	$[BH^+]/[B]$	H_0
p-*Nitroaniline*, pK = 0·99 (ref. 7)							
0·021	0·41	0·0125	2·89	0·444	8·0	1·10	0·95
0·043	0·83	0·0957	2·01	0·533	9·4	1·28	0·88
0·064	1·22	0·130	1·88	0·573	10·0	1·47	0·84
0·082	1·58	0·203	1·68	0·594	10·4	1·33	0·86
0·147	2·80	0·448	1·34	0·641	11·1	1·65	0·77
0·163	3·03	0·533	1·26	0·741	12·7	1·77	0·74
0·214	4·00	0·693	1·19	0·889	14·9	2·12	0·66
0·278	5·1	0·782	1·10	1·04	17·0	2·69	0·56
0·296	5·4	0·750	1·12	1·06	17·2	2·96	0·52
0·342	6·2	0·912	1·03	1·09	17·6	2·94	0·52
0·399	7·2	1·03	0·98	1·28	20·1	3·48	0·45
0·428	7·8	1·11	0·94				
o-*Nitroaniline*, pK = −0·29 (ref. 7)							
1·07	17·3	0·148	0·54	1·87	26·5	0·440	0·07
1·27	20·0	0·251	0·39	1·96	28·1	0·520	−0·01
1·50	22·8	0·285	0·26	2·26	31·1	0·631	−0·09
1·72	25·3	0·337	0·18	2·51	33·4	0·759	−0·17

The acidity scales for the two acids are summarised in Table 3, where the figures for sulphuric acid[7] are given for comparison. The results for both acids are typical for weak acids, in that there is only a relatively small dependence of H_0 on molarity of acid when compared with a strong acid.

The Hammett acidity function is often used as a criterion of mechanism in the study of reactions which are catalysed by acid.[11] Some attention has been given, however, to the use of the Hammett function in the interpretation of the constitution of acid solutions.[12,13] The changes in H_0 values in concentrated solutions of strong acids can be correlated with the primary hydration of the proton to $H_9O_4^+$, and the large deviations from ideality of such solutions can be accounted for by a simple hydration treatment. Furthermore, it has been shown that H_0 is a common function of the water activity for completely dissociated acids.[13] The difference between H_0 for a strong acid and that for a weak acid, when compared *at the same water activity,* is related to the degree of dissociation, α of the weak acid.[13] If the weak acid is behaving in a simple manner, this is,

$$(H_0)_{\text{weak}} - (H_0)_{\text{strong}} = \log(1 + \alpha)/2\alpha \qquad (1)$$

Equation (1) has been tested and shown to be quite accurate for aqueous nitric acid solutions [8] up to 17M (75%). The values of H_0 for iodic acid and sulphuric acid [7] at the same water activities [2,14] are given in Table 4, along with the corresponding values of α calculated from equation (1). It is seen that the values of α are anomalous and increase with increasing concentration of acid. It has been suggested that iodic acid is polymerised in aqueous solution. Measurements [3] of pH and ultrasonic absorption [4] indicate polymerisation at concentrations as low as 0·1M, whereas proton magnetic resonance [5] suggest the onset of polymerisation at 1·85M. Other complications may be expected in view of the existence of salts of the type $KIO_3(HIO_3)_n$, and some evidence suggesting the formation of complex anions in solutions of the acid, has been obtained.[15]

TABLE 3

H_0 Scales for iodic acid, periodic acid, and sulphuric acid [7]

Molarity	H_0 iodic acid	H_0 periodic acid	H_0 sulphuric acid [7]	Molarity	H_0 iodic acid	H_0 periodic acid	H_0 sulphuric acid [7]
0·025	1·60	—	—	1·75	−0·06	0·14	−0·72
0·05	1·36	2·00	1·00	2·0	−0·13	0·01	−0·84
0·01	1·10	1·58	0·83	2·25	−0·19	−0·10	−0·99
0·20	0·86	1·22	0·57	2·5	−0·25	−0·18	−1·12
0·35	0·63	1·03	0·31	3·0	−0·36	—	−1·38
0·50	0·48	0·91	0·13	3·5	−0·46	—	−1·62
0·75	0·30	0·74	−0·07	4·0	−0·54	—	−1·85
1·00	0·18	0·58	−0·26	4·5	−0·60	—	−2·06
1·25	0·08	0·43	−0·42	5·0	−0·66	—	2·28
1·50	0·00	0·28	−0·56	5·5	−0·72	—	−2·51

TABLE 4

Calculation of α for iodic acid from equation (1)

Molarity of HIO_3	a_{H_2O} [2]	H_0 (HIO_3)	H_0 (H_2SO_4) [7,14]	α
0·10	0·997108	1·10	0·93	0·51
0·20	0·994775	0·86	0·71	0·55
0·30	0·992748	0·70	0·55	0·55
0·50	0·989368	0·48	0·39	0·69
0·69	0·986650	0·34	0·29	0·81
0·97	0·983556	0·19	0·20	1·04
1·43	0·980031	0·02	0·11	1·61
1·88	0·977800	−0·08	0·06	2·22

The values of α for iodic acid from Raman spectra,[5] proton magnetic resonance,[5] and conductance [2] are not compatible. Hood, Jones, and Reilly [5] claim satisfactory agreement

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[11] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 935.

[12] K. N. Bascombe and R. P. Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158.

[13] P. A. H. Wyatt, *Discuss. Faraday Soc.*, 1957, **24**, 162.

[14] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955, Appendix 8.4, p. 462.

[15] N. Rajeswara Rao, *Discuss. Faraday Soc.*, 1957, **24**, 130.

for the Raman and proton magnetic resonance (p.m.r.) values, but at one point they vary by 50%. Furthermore, the calculations of α from the experimental results are based on a simple dissociation scheme. The reason for the widely differing values of α in the more concentrated solutions may be due to the chemical complexity of iodic acid in solution.

For a simple weak acid the values of H_0 should always be higher (more positive) than those for a strong acid *at the same water activity*.[13] Table 4 shows, however, that, at water activities of $<0{\cdot}984$, the H_0 values for iodic acid are lower than those for sulphuric acid. In other words, at a given value of H_0, *i.e.*, at a given acidity, the water activities of the solutions are higher than one would expect for concentrated solutions of a weak acid. This could be explained if $[IO_3(HIO_3)_n]^-$ is formed in preference to $[IO_3(H_2O)_m]^-$ in the more concentrated solutions.

An alternative procedure has been suggested by Bascombe and Bell,[12] to correlate H_0 results with constitution of acid solutions. In its simplest form, and by assuming that the water activities are equal to the mole fractions of free water, it was shown that the large changes in H_0 for the strong acids with increasing concentration could be accounted for. The method was also successful when applied to weak acids, including nitric acid.[9] However, the simple method of calculating H_0 values based on equation (5) of reference 12, *i.e.*,

$$-H_0 = \log c - h \log[(c/m)(1 - 0{\cdot}018hm)]$$

when modified for weak acids, gave poor agreement with the observed H_0 values when degrees of dissociation, α, from p.m.r.,[5] Raman spectroscopy,[5] and conductivity [2] were used in the calculation. The terms c and m represent molarity and molality of acid, respectively, and h is the number of water molecules in the primary hydration shell of the proton, which is taken to be 4. This poor agreement might be expected if the constitution of the anion is not simple.

TABLE 5

Use of equation (2) for iodic acid

Molarity of HIO_3	H_0 (p.m.r.)	H_0 (Raman)	H_0 (Conductance)	H_0 (Observed)
0·025	1·64	1·63	1·64	1·60
0·05	1·40	1·35	1·37	1·36
0·10	1·13	1·08	1·10	1·10
0·20	0·93	0·84	0·85	0·85
0·35	0·84	0·69	0·65	0·63
0·50	0·81	0·63	0·52	0·48
0·75	0·83	0·72	0·39 *	0·30
1·00	0·89	0·73	—	0·18
1·25	0·92	0·83	—	0·08
1·50	1·01	0·96	—	0·00

* Calculated by using extrapolated α value.

TABLE 6

Comparison of α values for iodic acid

Molarity of HIO_3	α (p.m.r.) [5]	α (Raman) [5]	α (Conductance) [2]	α (Eqn. (2))
0·025	0·91	0·94	0·92	1·00
0·05	0·84	0·89	0·86	0·90
0·10	0·74	0·83	0·79	0·80
0·20	0·58	0·71	0·70	0·72
0·35	0·40	0·57	0·63	0·69
0·50	0·30	0·45	0·58	0·69
0·75	0·19	0·24	0·53 *	0·71(?)
1·00	0·12	0·17	—	—
1·25	0·09	0·11	—	—
1·50	0·06	0·08	—	—

* Extrapolated value.

It is possible, however, to calculate H_0 values from the degrees of dissociation, without speculating as to the exact nature of the anion, provided that the water activities are known. This involves the use of a modification of equation (3) of reference 12, and is,

$$-H_0 = \log \alpha c + 4\log a_{H_2O}, \qquad (2)$$

where c represents molarity of acid, and a_{H_2O} is activity of water. By using the water activities [2] and the three sets [2,5] of values of α, the values of H_0 for iodic acid have been calculated from equation (2), and they are compared with the measured values in Table 5. The observed values agree most closely with those calculated from the results obtained from conductance measurements.

From the measured values of H_0 and equation (2), values of α have been calculated and are compared with those from other methods in Table 6. As is to be expected, the best agreement is with the conductance values. Although simplifying assumptions are made in the derivation [12] of equation (2), and certain assumptions are made to calculate α values from conductance data, both these methods of obtaining degrees of dissociation are less sensitive to complications (such as polymerisation and formation of complex ions) than are the spectroscopic methods which depend on the adoption of a particular dissociation scheme.

It is probable that the apparent weakness of both iodic acid and periodic acid is due to polymerisation and formation of complex anions.

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