Strongly Basic Systems. VII. The H_{2-} Acidity Scale

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Abstract: An H_{2-} scale has been established for four systems containing quaternary ammonium hydroxide–water, pyridine–water, sulfolane–water, and dimethyl sulfoxide–water. $H_{2-} = -\log a_{H^+}f_{A^{2-}}/f_{HA^-}$ and is a measure of the ability of a solvent to ionize an anionic acid. The 19 acids used to establish the scale were diphenylaminecarboxylic or -sulfonic acids or aminobenzoic acids containing nitro and other substituents. The acids varied in strength from 2,4,6-trinitrodiphenylamine-4′-sulfonate (pK = 9.73) to 2-nitrodiphenylamine-2′-carboxylate (pK = 20.64). The most basic system studied was 96.9 mole % dimethyl sulfoxide containing 0.011 M $(CH_3)_4N^+OH^-$; it has an H_{2-} value of 21.9. The H_{2-} scale appears to rise slightly less rapidly than the previously evaluated H_- scale and this may be caused by the different solvation requirements of mono- and dianions. The carboxylate group, CO_2^-, is found to be acid strengthening when *meta* or *para* but strongly acid weakening when *ortho*.

Previous papers in this series[1] have described the establishment of a self-consistent H_- scale for a number of solvent systems, based on the ionization of substituted anilines and diphenylamines. The acidity function, H_-, describes the ability of a system to remove a proton from a neutral acid and is defined as follows.[2]

$$HA \rightleftharpoons H^+ + A^-$$

$$H_- = -\log \frac{a_{H^+}f_{A^-}}{f_{HA}} = pK_{HA} + \log \frac{[A^-]}{[HA]} \qquad (1)$$

In a similar way the function H_{2-} describes the proton-removing properties of the system for anionic acids.

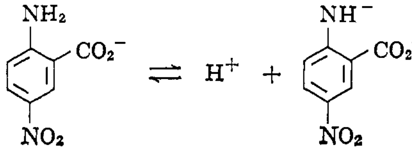
$$HA^- \rightleftharpoons H^+ + A^{2-}$$

$$H_{2-} = -\log \frac{a_{H^+}f_{A^{2-}}}{f_{HA^-}} = pK_{HA^-} + \log \frac{[A^{2-}]}{[HA^-]} \qquad (2)$$

Both H_- and H_{2-} become identical with pH in the aqueous region.

In strongly acid solution the functions H_0 (for cationic acids) and H_- (for neutral acids) are known to diverge,[3,4] but the kinds of molecules used to establish the two scales are quite different and it is difficult to determine the extent to which the difference in charge type of the acids is responsible.[5]

We have examined the effect of indicator charge type by constructing an H_{2-} scale using the systems aqueous pyridine, aqueous sulfolane, and aqueous dimethyl sulfoxide (DMSO), all containing 0.011 M $(CH_3)_4N^+OH^-$, and the system water containing varying amounts of benzyltrimethylammonium hydroxide, using the simple Hammett stepwise technique. This was done by the simple expedient of adding carboxylate groups to the aniline and diphenylamine indicators thereby ensuring that in the strongly basic solutions used the ionizing acids are anionic (for example, see the following equation).



Results and Discussion

All the amines used to construct the scale appeared to ionize by simple proton loss. Preliminary studies with aminophenolates, on the other hand, showed complicated spectral changes in solutions of low basicity, possibly because of zwitterion formation.

The pK_a values of the six indicators of strongest acidity were found directly using glycine buffers. The key indicators used in anchoring the system in the aqueous region and in bridging the pH and the H_{2-} regions are 2,4,6-trinitro-4′-chlorodiphenylamine-2′-carboxylic acid, 2,4,6-trinitrodiphenylamine-2′-carboxylic acid, and 4-chloro-2′,6′-dinitrodiphenylamine-4′-carboxylic acid (indicators 4, 5, and 6; Table I). The remaining indicator pK_a values then are obtained by stepwise comparison. The mean pK_a values then were used to set up the H_{2-} acidity scale for the four systems studied.

An interesting finding is the acid-strengthening effect of the *meta* and *para* carboxylate substituents. Data on the ionization of di- and tricarboxylic acids suggest, after the appropriate statistical corrections are applied, that the carboxylate substituent has very little effect on the strength of a *meta* or *para* carboxyl group. Thus terephthalic acid has a pK_2 of 4.34 at 20° with μ = 0.1, whereas the pK of benzoic acid is 3.99 under the same conditions.[4] The true pK_2 of terephthalic acid is 0.3 unit (log 2) lower, however, because of the two sites for protonation of the dianion and the one site of proton loss in the monoanion. There is good evidence, however, for the carboxylate substituent exerting a definite acid-strengthening effect on the ionization of phenols. Thus the pK values of phenol, *m*-hydroxybenzoate ion, and *p*-hydroxybenzoate ion, are reported as 9.80, 9.61, and 8.99, respectively.[6] Other determinations give similar results.[7,8]

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(1) R. Stewart and J. P. O'Donnell, *J. Am. Chem. Soc.*, **84**, 493 (1962); *Can. J. Chem.*, **42**, 1681 (1964).

(2) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 269; M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(3) R. H. Boyd, *J. Am. Chem. Soc.*, **83**, 4288 (1961); *J. Phys. Chem.*, **67**, 737 (1963).

(4) J. N. Phillips, *Australian J. Chem.*, **14**, 183 (1961).

(5) H_0 and H_+ seem to be very close: see M. Isaks and H. H. Jaffé, *J. Am. Chem. Soc.*, **86**, 2209 (1964); M. W. Fuller and W. M. Schubert, *ibid.*, **85**, 108 (1963); J. C. D. Brand, W. C. Horning, and M. B. Thornley, *J. Chem. Soc.*, 1374 (1952).

(6) A. V. Willi and J. F. Stocker, *Helv. Chim. Acta*, **38**, 1279 (1955); see also ref 7, p 364.

(7) G. Kortum, M. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworth and Co. (Publishers) Ltd., London, 1961, pp 373–375.

(8) J. Hermans, S. J. Leach, and H. A. Scheraga, *J. Am. Chem. Soc.*, **85**, 1390 (1963).

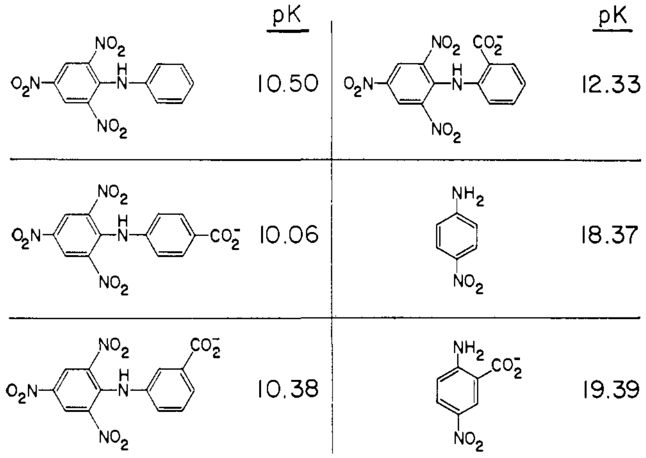

Figure 1. Acidities of some aromatic amines.

The discrepancy between the effect of the carboxylate ion on carboxyl and phenolic hydroxyl acidities seems much too great to be accounted for by the higher ρ for phenol ionization. Some degree of conjugation such as the following may be involved for *p*-hydroxybenzoate ion. It is difficult to interpret unequivocally the small acid-strengthening effect of the *m*-carboxylate ion.

The present results on aniline and diphenylamine acidities show generally similar substituent effects to phenols. However, Stewart and O'Donnell,[9] and Buckley, Dolman, and Stewart,[10] have shown that substituent effects on the ionization of diphenylamines and nitro-substituted diphenylamines are best correlated by σ_0;[11] in the case of both 2,4,6-trinitro-, and 2,4-dinitrodiphenylamines, ρ is found to be 1.9. This value is close to that obtained for the ionization of phenols (2.11).[12] The acid-strengthening effect of $m\text{-}CO_2^-$ is about the same (*ca.* 0.2 p*K* unit) for both phenols and the nitrodiphenylamines. However, both $p\text{-}CO_2^-$ and $p\text{-}SO_3^-$ (both of which are capable of direct interaction with the negative site of the dianion) have a smaller acid-strengthening effect on the diphenylamines than on the phenols (*ca.* 0.55 compared to 0.88, and 0.77 compared to 1.29,[7] respectively). This is in agreement with the need to use σ_0 rather than σ_- to correlate substituent effects in this system.

An *ortho* carboxylate group sharply reduces the acidity of the amino group (Figure 1) and this is undoubtedly caused by hydrogen bonding between the amino hydrogens and the adjacent carboxylate anion. Again this is similar to the situation with phenols.[7,8]

Figure 2 shows the difference between H_- and H_{2-} for aqueous DMSO solutions. (Similar effects exist for the other mixed solvent systems studied (Table II) but not for the purely aqueous solutions (Table III)). The rise in H_{2-} as the DMSO content of the solution is increased is less than the rise of the H_- function although the difference is not great.[13] From eq 1 and 2 it follows that

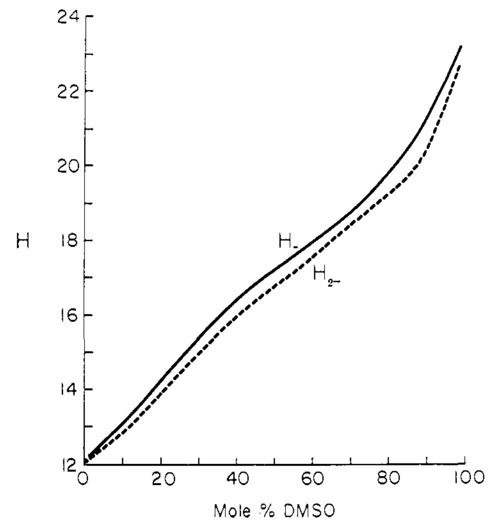

Figure 2. H_- and H_{2-} functions for aqueous dimethyl sulfoxide systems,[19] containing 0.011 *M* $(CH_3)_4N^+OH^-$.

$$H_- - H_{2-} = -\log\frac{f_{A^-}f_{HA^-}}{f_{HA}f_{A^{2-}}} \qquad (3)$$

As the water content of the system decreases the activity coefficient of the anions will increase. The positive value of $H_- - H_{2-}$ means that the activity coefficient quotient in eq 3 is less than 1, and this, presumably, reflects a very large increase in the activity coefficient of the dianion as a result of its high solvation requirements. The difference in the two functions might, indeed be greater if the indicators used had the doubly negative charge concentrated on the same or adjacent atoms.

Experimental Section

Preparation of Indicators. The indicators were synthesised according to standard procedures. The trinitrodiphenylamine acids (indicators 1, 2, 3, 4, and 5) were prepared by the reaction of picryl chloride with the appropriate amino acid.[14] The dinitrodiphenylaminecarboxylic acids were synthesised either by the reaction of 1-bromo-2,4-dinitrobenzene and an aminobenzoic acid[15] (indicators 7, 9, and 13) or the reaction of a chlorodinitrobenzoic acid with an aniline[16] (indicators 6, 8, 10, and 11). The reaction of a bromonitrobenzene with an aminobenzoic acid was used to prepare the nitrodiphenylaminecarboxylic acids[17] (indicators 14, 17, and 19). The dinitroaminobenzoic acids were prepared by the reaction of alcoholic ammonia solution and the appropriate chlorodinitrobenzoic acid[16] (indicators 12 and 15). The nitration of an acetylated aminobenzoic acid, followed by deacetylation, was used to prepare the nitroaminobenzoic acids[18] (indicators 16 and 18).

The indicators then were recrystallised several times from ethanol, aqueous acetic acid, or acetic acid to constant melting point. The

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[9] R. Stewart and J. P. O'Donnell, *Can. J. Chem.*, **42**, 1694 (1964).

[10] A. Buckley, D. Dolman, and R. Stewart, unpublished results.

[11] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

[12] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963.

[13] As the DMSO concentration approaches 0 the H_- and H_{2-} scales must converge at $H_- = H_{2-} = 12$ since the hydroxyl ion concentration is 10^{-2} *M* and water is the standard state. On the other hand in DMSO–methanol–sodium methoxide systems the H_- and H_{2-} scales differ considerably and do not converge as the DMSO concentration approaches 0: A. Buckley and R. Stewart, unpublished results.

[14] E. Wedekind, *Ber.*, **33**, 426 (1900).

[15] G. Schraeter and O. Eisleb, *Ann.*, **367**, 101 (1909).

[16] F. Ullmann, *ibid.*, **366**, 82 (1909).

[17] I. Goldberg, *Ber.*, **39**, 1691 (1906).

[18] E. Borel and H. Deuel, *Helv. Chim. Acta*, **36**, 801 (1953).

[19] H_- values for low dimethyl sulfoxide concentrations (0–10%) have been redetermined by A. Albagli, A. Buckley, and R. Stewart (unpublished results). H_- values for high dimethyl sulfoxide concentrations (70–95%) are those of D. Dolman and R. Stewart (unpublished results).

Table I. Acidities and Physical Data[a] for H_{2-} Indicators

No.	Substituted acids	pK_a	λ_{max} Carboxylate anion[b] mμ	ϵ	Dianion mμ	ϵ
1	2,4,6-Trinitrodiphenylamine-4′-sulfonic acid	9.73	377	14,600	438	21,500[c]
2	2,4,6-Trinitrodiphenylamine-4′-carboxylic acid	10.06	382	15,500	442	23,000[c]
3	2,4,6-Trinitrodiphenylamine-3′-carboxylic acid	10.38	393	15,600	438	21,800[c]
4	2,4,6-Trinitro-4′-chlorodiphenylamine-2′-carboxylic acid	11.78	400	17,100	441	21,700[d]
5	2,4,6-Trinitrodiphenylamine-2′-carboxylic acid	12.33	395	15,900	436	23,600[d]
6	4-Chloro-2′,6′-dinitrodiphenylamine-4′-carboxylic acid	12.73	415	5,740	570	6,710[d]
7	2,4-Dinitrodiphenylamine-4′-carboxylic acid	13.14	373	18,400	435	20,000[d]
8	2,6-Dinitrodiphenylamine-4-carboxylic acid	13.19	425	8,140	578	7,040[d]
9	2,4-Dinitrodiphenylamine-3′-carboxylic acid	13.48	368	18,600	430	19,400[d]
10	4-Chloro-2′,4′-dinitrodiphenylamine-6′-carboxylic acid	14.58	383	16,900	460	19,000[d]
11	2,4-Dinitrodiphenylamine-6-carboxylic acid	15.34	383	16,800	458	19,000[d]
12	3,5-Dinitro-4-aminobenzoic acid	15.34	436	9,100	554	8,730[d]
13	2,4-Dinitrodiphenylamine-2′-carboxylic acid	15.45	383	20,800	425	20,800[d]
14	2-Nitrodiphenylamine-4′-carboxylic acid	17.04	483	7,010	550	9,800[d]
15	3,5-Dinitro-2-aminobenzoic acid	17.10	353	14,500	421	14,900[d]
16	3-Nitro-4-aminobenzoic acid	17.39	419	5,750	520	8,360[d]
17	4-Nitrodiphenylamine-2′-carboxylic acid	18.04	440	20,000	493	27,600[d]
18	5-Nitro-2-aminobenzoic acid	19.39	395	17,700	476	28,300[d]
19	2-Nitrodiphenylamine-2′-carboxylic acid	20.64	455	7,450	546	9,980[d]

[a] Melting points (literature melting points) and references for compounds **1–19** are as follows: **1**, >300° (see footnote *e*); **2**, 304–305° (292–293°: see ref 14); **3**, 241–243° (233–234°: see ref 14); **4**, >300° (see footnote *f*); **5**, 286–287° (271–272°: see ref 14); **6**, 285–286° (see footnote *g*); **7**, 308–310° (>225°: B. Linke, *J. Prakt. Chem.*, **91**, 202 (1915)); **8**, 249–250° (245°: H. Lindemann and W. Wessel, *Ber.*, **58**, 1221 (1925)); **9**, 267–269° (>225°: B. Linke, J. *Prakt. Chem.*, **91**, 202 (1915)); **10**, 194–195° (see footnote *h*); **11**, 216–217° (214°: T. Zincke, *J. Prakt. Chem.*, **82**, 17 (1910)); **12**, 272–273° (259–271°: J. C. Clayton, G. F. Green, and B. A. Hems, *J. Chem. Soc.*, 2467 (1951)); **13**, 268–269° (264°: see ref 15); **14**, 282–283° (272–274°: V. C. Barry, M. L. Conalty, and D. Twomey, *Proc. Roy. Irish Acad.*, **55B** 157 (1953); see *Chem. Abstr.*, **48**, 1378 (1954)); **15**, 271–272° (268°: M. G. C. Van Dorp, *Rec. Trav. Chim.* **23**, 301 (1904)); **16**, 285–286° (285°: see ref 18); **17**, 214–215° (211°: see ref 17); **18**, 277–278° (278°: M. T. Bogert and G. Scatchard, *J. Am. Chem. Soc.*, **41**, 2502 (1919)); **19**, 218–219° (219°: F. Ullmann and W. Bader, *Ann.*, **355**, 323 (1907)). [b] Solvent is aqueous buffer of sufficient basicity to ionize the carboxyl group completely. [c] Solvent is 0.1 *M* sodium hydroxide solution. [d] Solvent is 0.011 *M* tetramethylammonium hydroxide in dimethyl sulfoxide–water of just sufficient basicity to ionize the dianion completely. [e] Compound previously reported[14] but no physical constants given. *Anal.* Calcd for $C_{12}H_8N_4O_9S$: C, 37.51; H, 2.10. Found: C, 36.98; H, 2.22. [f] Compound not previously reported. *Anal.* Calcd for $C_{13}H_7ClN_4O_8$: C, 40.80; H, 1.84; Cl, 9.27; N, 14.64. Found: C, 41.00; H, 1.96; Cl, 9.20; N, 14.54. [g] Compound not previously reported. *Anal.* Calcd for $C_{13}H_8ClN_3O_6$: C, 46.24; H, 2.39; N, 12.44. Found: C, 46.22; H, 2.44; N, 12.18. [h] Compound not previously reported. *Anal.* Calcd for $C_{13}H_8ClN_3O_6$: C, 46.24; H, 2.39; N, 12.44. Found: C, 46.53; H, 2.57; N, 12.32.

Table II. H_{2-} Values for Aqueous Solutions of Dimethyl Sulfoxide (DMSO), Pyridine, and Sulfolane, all 0.011 *M* in Tetramethylammonium Hydroxide

Mole % nonaq component	H_{2-} DMSO	Pyridine	Mole % sulfolane	H_{2-}
1.0	12.04	12.03	1.0	11.95
5.0	12.32	12.29	9.9	12.25
9.9	12.70	12.47	14.8	12.42
14.9	13.24	12.77	19.7	12.63
19.8	13.85	13.15	29.4	13.05
24.7	14.34		39.0	13.55
29.6	14.84	13.76	48.3	14.06
34.5	15.39		57.8	14.66
39.3	15.77	14.04	62.6	14.99
44.1	16.18		67.2	15.48
48.8	16.59	14.34	71.9	15.77
53.7	16.96		76.5	16.12
58.6	17.32	14.65	81.3	16.56
63.5	17.70	15.69	85.9	17.12
68.3	18.18	*a*	90.6	17.74
73.2	18.48		95.1	18.56
78.0	18.88			
82.8	19.30			
87.5	19.84			
90.9	20.27			
92.3	20.71			
94.6	21.31			
96.9	21.92			

[a] Further measurements in this system could not be made because of immiscibility of the base solution.

Table III. H_{2-} Values for Aqueous Benzyltrimethylammonium Hydroxide

Hydroxyl ion, *M*	H_{2-}
0.0114	12.00
0.0536	12.35
0.111	12.74
0.196	13.22
0.402	13.79
0.770	14.21
1.065	14.77
1.45	15.09
2.18	15.48
2.48	16.30

relevant details of the indicators are given in Table **I**, together with the analytical results for the previously unreported compounds.

Acidity Measurements. The pK and H_{2-} values were measured as has been previously reported.[1] A Bausch and Lomb Spectronic 502 spectrophotometer was used. The solvent dependence of the spectra over the ionization range was small and often the measurements could be made at a wavelength where the monoanion did not absorb.

The ionizations of the indicators were all completely and instantaneously reversible. Only 3,5-dinitro-2-aminobenzoic acid slowly formed a new, nonreversible species (λ_{max} at 450 mμ) in sulfolane–water–base and no measurements were made with this indicator in that solvent system.

Overlap between each pair of adjacent indicators used to construct the scale was checked as previously described[1] and was found to be very satisfactory.

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