Acid strengths of some substituted picric acids

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The aqueous dissociation constants for a number of substituted picric acids and related compounds have been determined spectrophotometrically, and the values obtained correlated with the mid-equivalence potentials obtained by half-neutralization in acetone solution. Analysis of these results together with those obtained similarly for substituted benzoic acids shows that while the mid-equivalence potential method affords a rapid and convenient means of making a good estimate of the acid strength of a compound, it has its limitations and is only strictly applicable within the confines of a series of closely similar compounds. The observed pK_a values of a large series of polysubstituted phenols were correlated with the predicted values obtained from the Hammett relation, and good agreement obtained, even with substituted picric acids; styphnic acids appear to behave anomalously.

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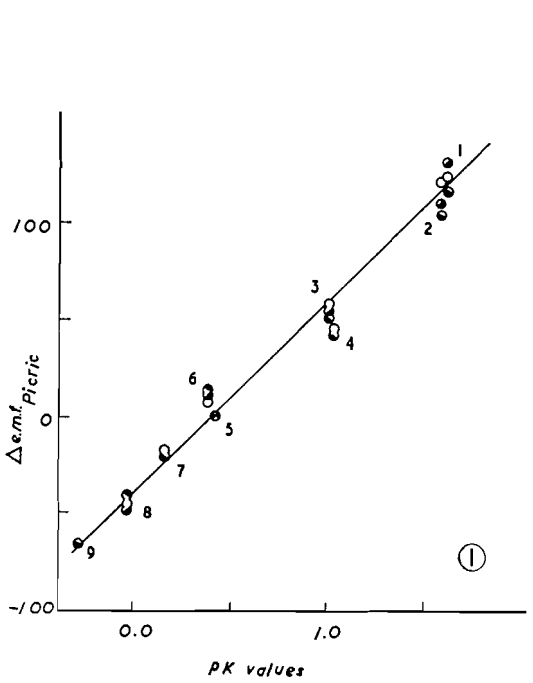
It has recently been suggested (1) that the aqueous dissociation constant of an acid may be rapidly estimated by measuring the glass electrode potential of a half-neutralized solution of the acid in acetone solution. The discrepancy between the dissociation constant of styphnic acid (2,4,6-trinitroresorcinol) inferred from such a mid-equivalence potential and the value we had obtained by spectrophotometric measurement led us to investigate the method in more detail. Experimental work consisted of (*a*) the determination of the dissociation constant in water of a large number of picric acids and related compounds and (*b*) the parallel measurement of the mid-equivalence potentials of the picric acids, and also of a large number of benzoic acids, the aqueous dissociation constants of which were known. An analysis was then made of the relationship between the mid-equivalence potential, the solvent in which it was determined, and the aqueous dissociation constant of the acid involved.

Discussion

Although it has long been recognized that picric acid is a very strong acid, there has been no common agreement as to what its exact dissociation constant is; the following values for the pK_a have been recorded: 0.29 (2), 0.33 (3), and 0.96 (4). For the related acids methylpicric and dimethylpicric pK_a values of 0.81 and 1.38 respectively have been found (5, 6). It has been accepted that the picric acids are too strong for the usual electrolyte methods to give good results, and the best values are based on spectrophotometric measurements. These are rather tedious and suffer from a lack of precision in the values assigned for the extinction coefficient of the undissociated acid.

Elder and Mariella (1) found that the mid-equivalence potential (the electromotive force (e.m.f.) as measured with a glass electrode/modified calomel electrode pair in a standard acetone solution of acid half-neutralized with tetrabutylammonium hydroxide) gave a measure of the relative acidity of a wide series of acids. These authors pointed out that there was a linear relationship between the relative acidities so determined and such aqueous dissociation constants (expressed as pK) as had been determined. This rapid and convenient method is in effect a simplified version of the potentiometric microtitration technique developed by Simon *et al.* (7–9). Simon has used this method extensively, working on the premise that the apparent pH of a solution at half-neutralization of the functional group to be determined is equivalent to pK'_{Solvent}, where K'_{Solvent} is the apparent dissociation constant for a given solvent system. Such apparent dissociation constants are functions of the nature of the solvent, the structure of the acid involved, concentration, and determination procedure. However, rigid standardization of the technique employed can give pK'_{Solvent} values dependent only on the structure of the acid being investigated and the solvent system used. It has been shown (10, 11) that such pK'_{Solvent} values may justifiably be interpreted in analogous fashion to thermodynamic pK values; however, it must be borne in mind that



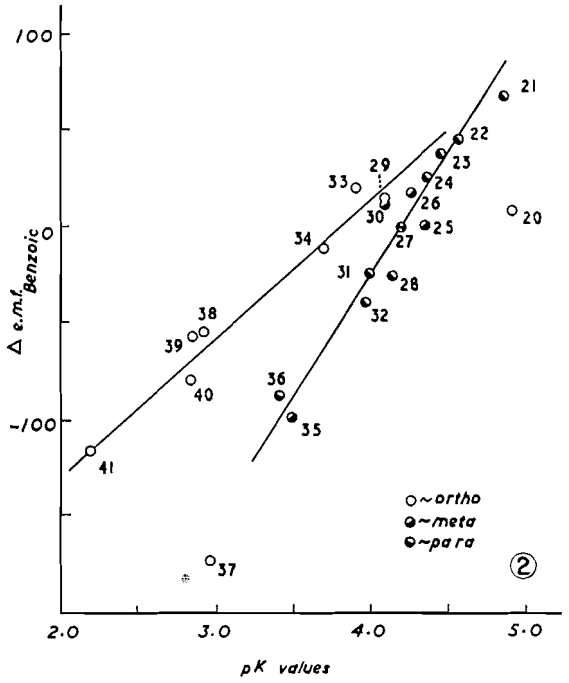


FIG. 1. Plot of mid-equivalence potential versus pK for substituted picric acids (in acetone solution).
FIG. 2. Plot of mid-equivalence potential versus pK for substituted benzoic acids (in acetone solution).

such values are specific to a given system, and that extensive extrapolation may not be warranted.

It is possible to derive an expression

$$pK'_{\text{Solvent}} = Q pK_a + \text{constant},$$

where Q is a term covering the various factors such as solvation energy inherent in the determination of pK'_{Solvent}. Since the mid-equivalence potential, $(\text{e.m.f.})_{1/2}$, and the apparent dissociation constant are merely different scale readings of the same galvanometer deflection, one may write $(\text{e.m.f.})_{1/2} = Q pK_a + C$ as the expression for the linear relationship that Elder and Mariella found. This relationship will only be general providing that the term Q remains constant; our results indicate that this is not so, and that while one given class of compounds (e.g. picric acids) have a certain linear relationship, this is not directly extensible to another class of acids (e.g. benzoic acids). Thus we conclude that while the mid-equivalence potential method affords a rapid means of making a good approximation of the pK_a value of an acid, it is really only valid within the confines of a series of closely related compounds, and that casual interpolation may give misleading results.

The relationship between mid-equivalence potential and dissociation constant for 8 picric acids is plotted in Fig. 1; a good straight line can be drawn through the plot. The results are also given in Table I, and from this it can be seen that the actual mid-equivalence potential recorded varied with the electrode system used. If, however, one takes the differences, Δ(e.m.f.), between the mid-equivalence potential of the test acid and that of a standard acid, in this case picric acid, both measured with the same electrode system, then consistent results are obtained.

The relationship between mid-equivalence potential and dissociation constant for 22 benzoic acids in two different solvent systems is plotted in Figs. 2 and 3 (cf. Table II). These plots show that, for a given solvent, one straight line cannot be drawn, but that two are necessary, one for the ortho-substituted benzoic acids and the other for the meta/para-substituted. As might be expected the slope of the plots is different in the

TABLE I

Mid-equivalence potentials of picric acids in acetone solution*

No.	Acid	pK_a	$(e.m.f.)_{1/2}$ observed			$\Delta(e.m.f.)_{Picric}$		
			A	B	C	A	B	C
1	*t*-Butylpicric	1.593	152	111	215	125	133	119
2	Dimethylpicric	1.215	150	90	202	123	112	106
3	Methylpicric	1.000	85	39	142	58	51	46
4	Ethylpicric	1.002	74	—	138	47	—	42
5	Picric	0.402	27	−12	96	0	0	0
6	Methoxypicric	0.367	35	2	107	8	10	11
7	Iodopicric	0.152	8	—	79	−19	—	−17
8	Bromopicric	−0.050	−18	−53	48	−45	−41	−48
9	Chloropicric	—	—	−58	37	—	−46	−59
10	Dichloropicric	—	—	—	30 to −9†	—	—	−66 to −105

*Electrode system: A = glass electrode/acetone solution/agar bridge/aqueous KCl/calomel electrode; B = glass electrode/acetone solution/methanolic KCl/calomel electrode; C = as B, but with different glass electrode.
†The initial reading was 30 mV, but this decreased slowly to −9.

TABLE II

Mid-equivalence potentials of benzoic acids

No.	Acid	pK_a*	Acetone solution		Ethanol solution	
			$(e.m.f.)_{1/2}$	$\Delta(e.m.f.)_{Benzoic}$ (mV)	$(e.m.f.)_{1/2}$	$\Delta(e.m.f.)_{Benzoic}$ (mV)
20	2-Aminobenzoic	4.91	581	9	470	22
21	4-Aminobenzoic	4.86	640	68	488	40
22	4-Hydroxybenzoic	4.57	617	45	471	23
23	4-Methoxybenzoic	4.47	610	38	458	10
24	4-Methylbenzoic	4.37	598	26	452	4
25	3-Aminobenzoic	4.36	572	0		
26	3-Methylbenzoic	4.27	590	18	445	−3
27	Benzoic	4.20	572	0	448	0
28	4-Fluorobenzoic	4.14	546	−26		
29	2-Methoxybenzoic	4.09	586	14		
30	3-Hydroxybenzoic	4.08	585	13	451	3
31	4-Chlorobenzoic	3.98	547	−25	423	−25
32	4-Bromobenzoic	3.97	532	−40		
33	2-Methylbenzoic	3.91	592	20	438	−10
34	1-Naphthoic	3.70	567	−5	421	−27
35	3-Nitrobenzoic	3.49	472	−100	392	−56
36	4-Nitrobenzoic	3.42	485	−87	377	−71
37	2-Hydroxybenzoic	2.97	399	−173	351	−97
38	2-Chlorobenzoic	2.92	518	−54	385	−63
39	2-Iodobenzoic	2.86	516	−56		
40	2-Bromobenzoic	2.85	494	−78		
41	2-Nitrobenzoic	2.17	457	−115	353	−95

*pK_a values taken from McDaniell and Brown (27).

two solvents. These results indicate how the Q term may not only vary from solvent to solvent, but also how it may vary between different types of acid. It should be noted that in both solvents the 2-hydroxybenzoic acid and to a lesser extent the 2-aminobenzoic acid do not fit the ortho relationship. This deviation, which is probably the result of powerful intermolecular hydrogen bonding, illustrates the dangers of casual interpolation.

A check on the objectivity of the results is given by Fig. 4, where our mid-equivalence potentials determined in acetone solution are plotted against the apparent dissociation constants determined by Simon in a methylcellosolve/water system (9). The data for both ortho and meta/para acids group onto the same line, suggesting that the variation of the Q term as a function of the structure of the acid involved is similar in both solvent systems.

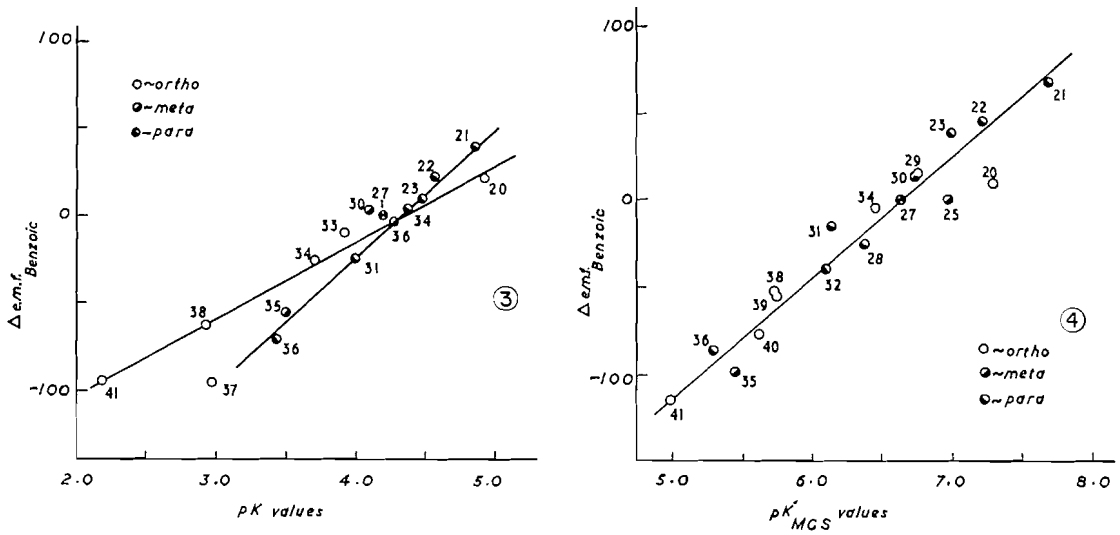


FIG. 3. Plot of mid-equivalence potential versus pK for substituted benzoic acids (in ethanol solution).
FIG. 4. Plot of mid-equivalence potential (in acetone) versus pK'_{MCS} (in 80% methylcellosolve/20% water) for substituted benzoic acids.

When the results for the picric acids and for the benzoic acids are combined into a single plot (cf. Fig. 5), it can clearly be seen that there is no unique relationship between the mid-equivalence potential and aqueous dissociation constant for all acids, but rather a family of lines, one for each class of acids. It is possible that this concept of a strictly limited relationship explains why a simple interpolation of the observed mid-equivalence potentials of styphnic acid and of trinitrophloroglucinol suggests dissociation constants markedly different from those we determined spectrophotometrically. The mid-equivalence potentials of 4 styphnic acids, 5 dinitrophenols, and 8 picric acids are plotted against pK_a values in Fig. 6 (cf. Table III). Examination prompts the following suggestions. (1) Our determination of the primary dissociation constants of styphnic acid and trinitrophloroglucinol would have to be reduced by two orders of magnitude for them to fall on the picric acid line. (2) It seems probable that with the removal of one ortho-nitro group the dinitrophenols no longer fall on the picric acid line, but form another family with a lower Q value. As with the benzoic acids the ortho-amino compound does not conform. (3) It is possible that the styphnic acids constitute another family, with a line of steeper slope.

Some calculations were made to see whether the experimentally determined acid strengths checked with those predicted by the Hammett relation $\log K = \rho\sigma \log K_0$ (12). Barlin and Perrin (13) have shown that pK values may be predicted for polysubstituted phenols provided that appropriate σ constants are used. The values suggested by these authors are satisfactory except for ortho-methoxy (where 0.04 gives better results than the suggested 0.00) and ortho-nitro. The results from polynitrophenols indicate that a value of 1.40 is the correct one for ortho-nitro substitution, even though for 2-nitrophenol itself this predicts a lower pK than is actually observed. Using a least mean square analysis for a series of 86 phenols it was found that the pK could be predicted by the relation: $pK = 9.94 - 2.26\ \Sigma\sigma$, with a relative deviation of 0.18. The observed and calculated results and σ constants used are given in Tables IV and V. Examination of the predicted values shows that serious deviation from the observed values normally only occurs when there are substituents on both sides of a nitro group. The effect of such grouping would be to hinder the coplanarity of the nitro group with the benzene ring, and by thus reducing the resonance effect give an observed pK value higher than that predicted. A single very bulky substituent between two nitro groups will produce the same effect. Such deviation can be noticed for 3,5-dimethyl-4-

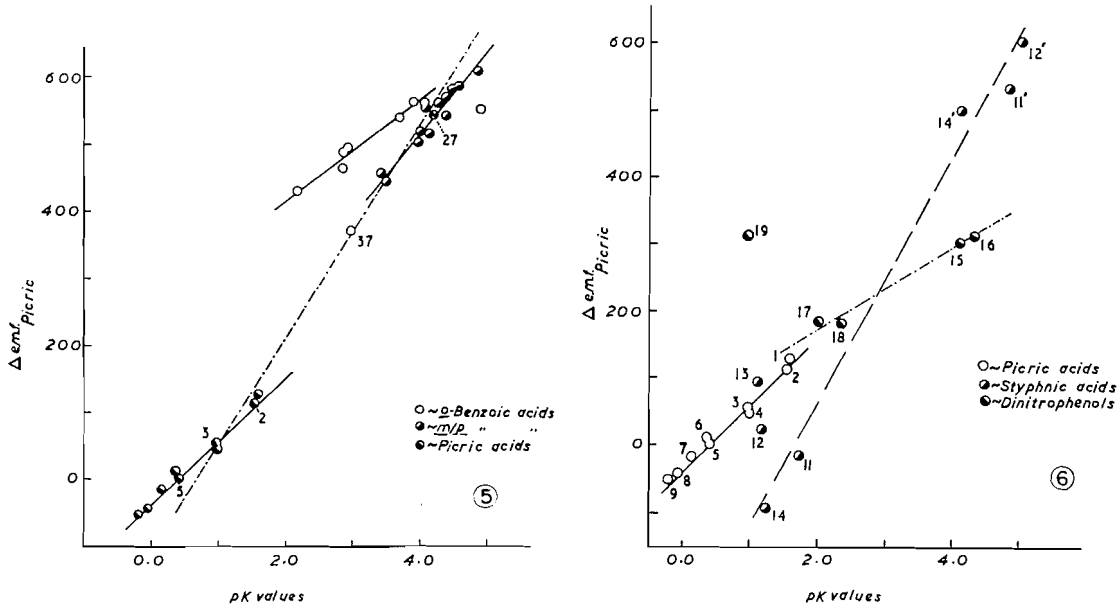


FIG. 5. Plot of mid-equivalence potential versus pK for three series of acids. (The numbered acids and pecke line indicate the relationship originally described.)
FIG. 6. Plot of mid-equivalence potential versus pK for various di- and tri-nitrophenols.

TABLE III

Mid-equivalence potentials of styphnic acids and dinitrophenols in acetone solution

No.	Compound	pK_a	$(e.m.f.)_{1/2}$	$\Delta(e.m.f.)_{Picric}$ (mV)
11	Styphnic acid	1.74	10	−17
		4.86	561	534
12	Methylstyphnic acid (Trinitroorcinol)	1.17	48	21
		5.04	632	605
13	Chlorostyphnic acid	1.13	122	95
		—	640	613
14	Hydroxystyphnic acid (Trinitrophloroglucinol)	1.26	−71	−98
		4.16	528	501
		7.66	791	764
15	2,4-Dinitrophenol*	4.13	329	302
16	6-Methyl-2,4-dinitrophenol*	4.35	339	312
17	6-Chloro-2,4-dinitrophenol	2.01	210	183
18	6-Bromo-2,4-dinitrophenol	2.35	209	182
19	6-Amino-2,4-dinitrophenol	1.00	343	316

*pK value taken from literature (28, 29), the others were determined in this laboratory.

nitro-, 3,5-dimethyl-2,4,6-trinitro-, and 3-*t*-butyl-2,4,6-trinitro-phenol. Allowing for this effect the predicted strength of the picric acids agrees well with the experimentally determined values. The Hammett relationship can be extended to the di- and tri-hydroxyphenols, with a good measure of agreement for simple substitution (the discrepancy for 2-methyl-*p*-hydroquinone is quite exceptional), but it breaks down with the introduction of a third nitro group.

One might expect a correlation between the pK_a value and the OH stretching frequency for the picric acids, and indeed Fig. 7 (cf. Table VI) shows the normal type of plot. It should be noted that the styphnic acid values do not fall on this plot. A similar form of correlation, though over

TABLE IV

Experimental and predicted pK values for phenols*

Substituent	pK Found	pK Calcd.	Substituent	pK Found	pK Calcd.
2-Me	10.28	10.23	2-Br	8.39	8.36
3-Me	10.09	10.10	3-Br	9.03	9.06
4-Me	10.26	10.32	4-Br	9.34	9.33
2,3-Me_2	10.42	10.39	2-I	8.46	8.52
2,4-Me_2	10.61	10.62	3-I	9.06	9.15
2,5-Me_2	10.22	10.39	4-I	9.31	9.26
2,6-Me_2	10.59	10.53	2-NO_2	7.21	6.78
3,4-Me_2	10.42	10.48	3-NO_2	8.35	8.34
3,5-Me_2	10.15	10.25	4-NO_2	7.15	7.14
2,4,5-Me_3	10.57	10.78	2,6-Me_2-4-NO_2	7.22	7.73
2,4,6-Me_3	10.88	10.91	3,5-Me_2-4-NO_2	8.24	7.45
2-Et	10.2	10.23	2,4,6-Me_3-3-NO_2	8.98	9.31
3-Et	9.9	10.10	2,4-$(NO_2)_2$	4.09	3.97
4-Et	10.0	10.28	2,5-$(NO_2)_2$	5.22	5.17
3-Et-5-Me	10.1	10.25	2,6-$(NO_2)_2$	3.71	3.61
2-Ph	9.97	9.94	3,4-$(NO_2)_2$	5.42	5.53
3-Ph	9.64	9.80	2,4-$(NO_2)_2$-6-Me	4.35	4.27
4-Ph	9.55	9.60	2,4-$(NO_2)_2$-6-Cl	2.01	2.44
2-CH_2OH	9.92	9.85	2,4-$(NO_2)_2$-6-Br	2.35	2.39
3-CH_2OH	9.83	9.76	2,6-$(NO_2)_2$-4-Cl	2.97	3.09
4-CH_2OH	9.82	9.76	2,4,6-$(NO_2)_3$	0.40	0.81
2-CH_2OH-4-Me	10.15	10.23	2,4,6-$(NO_2)_3$-3-Me	1.00	0.97
2,4-$(CH_2OH)_2$	9.77	9.67	2,4,6-$(NO_2)_3$-3-Et	1.00	0.97
2,6-$(CH_2OH)_2$	9.66	9.76	2,4,6-$(NO_2)_3$-3,5-Me_2	1.57	1.13
2,6-$(CH_2OH)_2$-4-Me	9.92	10.14	2,4,6-$(NO_2)_3$-3-tBu	1.59	1.04
2,4,6-$(CH_2OH)_3$	9.66	9.58	2,4,6-$(NO_2)_3$-3-MeO	0.37	0.63
2-MeO	9.98	9.85	2,4,6-$(NO_2)_3$-3-Cl	−0.20	−0.03
3-MeO	9.65	9.76	2,4,6-$(NO_2)_3$-3-Br	−0.05	−0.07
4-MeO	10.21	10.19	2,4,6-$(NO_2)_3$-3-I	0.15	0.02
2-MeO-4-CHO	7.40	7.52	2,4,6-$(NO_2)_3$-3,5-Cl_2	−0.7	−0.86
2-MeO-5-CHO	8.89	9.04			
2-MeO-6-CHO	7.91	8.15			
3-Ac	9.19	9.08			
4-Ac	8.05	8.04	2-OH	9.85	9.85
3-MeS	9.53	9.60	3-OH	9.15	9.17
4-MeS	9.53	9.47	4-OH	10.85	10.78
3-$MeSO_2$	8.40	8.40	2-Me-4-OH	10.20	11.07
4-$MeSO_2$	7.83	7.86	2,3,5,6-Me_4-4-OH	11.51	11.68
3,5-Me_2-4-$MeSO_2$	8.13	8.18	2,6-Cl_2-4-OH	7.33	7.70
3-CN	8.57	8.56	2-NO_2-4-OH	7.63	7.61
4-CN	7.95	7.95	2,6-$(NO_2)_2$-4-OH	4.42	4.45
2,6-Me_2-4-CN	8.27	8.54	2-NO_2-6-OH	6.70	6.69
3,5-Me_2-4-CN	8.21	8.27	2,3-$(OH)_2$	9.01	9.08
2-F	8.81	8.72	3,5-$(OH)_2$	8.45	8.40
3-F	9.28	9.17	2,4,6-$(NO_2)_3$-3-OH	1.74	0.04
4-F	9.81	9.80	2,4,6-$(NO_2)_3$-3-OH-5-Me	1.17	0.20
2-Cl	8.48	8.40	2,4,6-$(NO_2)_3$-3-OH-5-Cl	1.13	−0.79
3-Cl	9.08	9.10	2,4,6-$(NO_2)_3$-3,5-$(OH)_2$	1.26	−0.73
4-Cl	9.42	9.42			
2,3-Cl_2	7.70	7.57			
2,4-Cl_2	7.85	7.88			
2,5-Cl_2	7.51	7.57			
2,6-Cl_2	6.79	6.87			
3,4-Cl_2	8.59	8.58			
3,5-Cl_2	8.19	8.27			

*Experimental pK values taken from literature (29) unless determined in this laboratory.

TABLE V

Apparent σ constants for substituents in phenols* ($pK = 9.94 - 2.26\,\Sigma\sigma$)

Substituent	σ_{ortho}	σ_{meta}	σ_{para}
Methyl	−0.13	−0.07	−0.17
Ethyl	−0.13	−0.07	−0.15
t-Butyl		−0.10	
Phenyl	0.00	0.06	0.15
Methylol	0.04	0.08	0.08
Methoxy	0.04′	0.08	−0.11
Methylthio		0.15	0.21
Methylsulfonyl		0.68	0.92
Formyl	0.75	0.36	1.03
Acetyl		0.38	0.84
Fluoro	0.54	0.34	0.06
Chloro	0.68	0.37	0.23
Bromo	0.70	0.39	0.27
Iodo	0.63	0.35	0.30
Cyano		0.61	0.88
Nitro	1.40′	0.71	1.24
Hydroxy	0.04′	0.34′	−0.37

*Constants marked ′ differ from those previously proposed (13).

a much smaller range of wavenumbers, is found for the OH bending frequency. An interesting observation is that aminostyphnic acid has no peak in the 3100–3200 cm^{-1} range; the peak at 3410 cm^{-1} is undoubtedly NH stretching, and so probably is the less intense peak at 3290 cm^{-1}.

Experimental

All but one (no. 10) of the picric acids were prepared by mixed acid nitration of the corresponding phenol; they were purified by recrystallization from ethanol or acetone to constant melting point, and the purity then checked by thin layer chromatography on silica gel using a variety of solvent mixtures, of which methylene chloride/acetic acid 20/1 was typical. Trinitroorcinol was prepared by mixed acid nitration of orcinol, trinitrophloroglucinol by treatment of triacetoxybenzene with cold 98% nitric acid. The monopyridinium salt of trinitrophloroglucinol was treated with phosphorus oxychloride to give chlorostyphnic acid, m.p. 117 °C (Found: C, 24.5; H, 1.5; N, 14.0. $C_6H_2ClN_3O_8.H_2O$ requires C, 24.2; H, 1.3; N, 14.1), and this was converted via 5-ethoxytrinitroresorcinol to aminostyphnic acid, which was identical with that prepared by alkaline hydrolysis of pentanitroaniline. The pyridinium salt of chlorostyphnic acid was treated with phosphorus oxychloride to give dichloropicric acid. Melting points were determined on a Kofler hot-stage microscope; the melting points observed (and corresponding previous references) were: *t*-butylpicric acid 171° (14), dimethylpicric 108° (15), methylpicric 109° (16), ethylpicric 88° (4), picric 122° (17), methoxypicric 86° (18), iodopicric 196° (19), bromopicric 147° (20), chloropicric 114° (21), dichloropicric 138° (22), 2,4,6-trinitroresorcinol 174° (23), 5-methyltrinitroresorcinol 164° (23), 5-chlorotrinitroresorcinol 117°, 5-aminotrinitroresorcinol 240° (24), trinitrophloroglucinol 167° (25).

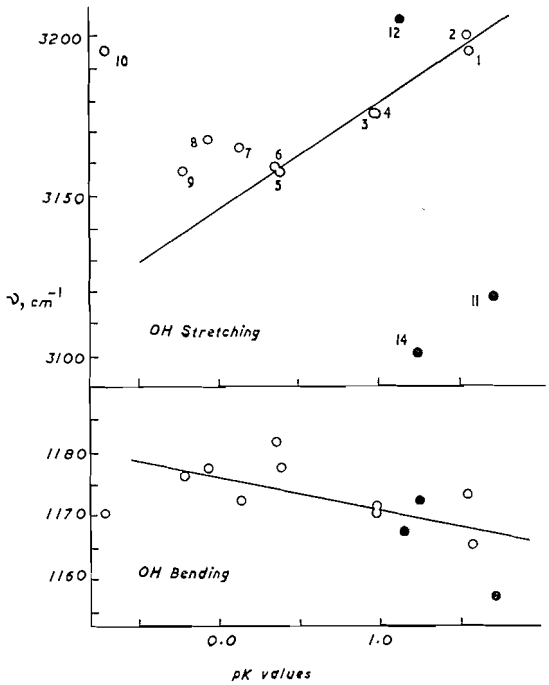


FIG. 7. Plot of infrared frequencies for (○) picric and (●) styphnic acid series.

Spectrophotometric Determination of pK Values

The method used was that of Richard and Sykes (26), which does not require a knowledge of the extinction coefficients involved. If an acid dissociates according to the expression

$$HA \overset{K}{\rightleftharpoons} H^+ + A',$$

then assuming that both the undissociated acid and the anion absorb light in the wavelength range studied, one may write

$$d(K + c) = E_{HA}ca + E_{A'}Ka,$$

where d is the optical density per unit cell length, c is the hydrogen ion concentration, E is the appropriate extinction coefficient, and a is the initial concentration of acid. If at a standard acid concentration c_0 one obtains an optical density d_0 for any given wavelength, then one may write

$$\frac{c - c_0}{d - d_0} = \frac{(K + c_0)(K + c)}{a(E_{A'} - E_{HA})}.$$

It follows that a plot of $(c - c_0)/(d - d_0)$ versus c at constant wavelength should be linear, with slope $= (K + c_0)/a(E_{A'} - E_{HA})$ and intercept $= K(K + c_0)/a(E_{A'} - E_{HA})$, and that intercept/slope should equal K.

Mixtures of varying proportions of 5 *N* perchloric acid and 5 *N* sodium perchlorate (total volume 4.8 ml) were made up to 50 ml with 0.003 *M* solutions of the picric acids, the resultant ionic product being 0.5. The optical density was measured over the range 340–430 mμ, and then $(c - c_0)/(d - d_0)$ plotted against the hydrogen ion

TABLE VI

Correlation of pK_a with OH stretching and bending frequencies

No.	Acid	pK_a	OH stretching (cm^{-1})	OH bending (cm^{-1})
1	*tert*-Butylpicric	1.59	3195	1165
2	Dimethylpicric	1.57	3200	1173
3	Methylpicric	1.00	3175	1170
4	Ethylpicric	1.00	3175	1171
5	Picric	0.40	3157	1177
6	Methoxypicric	0.37	3158	1181
7	Iodopicric	0.15	3165	1172
8	Bromopicric	−0.05	3167	1177
9	Chloropicric	−0.20	3157	1176
10	Dichloropicric	−0.7	3195	1170
11	Styphnic	1.74	3118	1157
14	Hydroxystyphnic	1.26	3100	1172
12	Methylstyphnic	1.17	3205	1167

concentration for various wavelengths. Under the best conditions the intercept/slope ratio was the same for all wavelengths; with acids stronger than picric the plots tended to be curved, and thus the ratios were less precise. The mass dissociation constants obtained in this were transformed, approximately, into thermodynamic aqueous dissociation constants by applying the Debye–Huckel expression. For simplicity it was assumed that the second ionization of the styphnic acids did not start until the first was complete. The average difference of three units between pK_I and pK_{II} makes this a fair assumption, but our failure to get a satisfactory differential plot for pK_{II} of chlorostyphnic acid suggests that it is not an inviolate one.

Determination of Mid-Equivalence Potential

The preparation of tetrabutylammonium hydroxide solution and the general conditions for determining the mid-equivalence potential followed those of Elder and Mariella (1). An Electronic Instruments Ltd. (E.I.L.) Model 23 direct reading pH meter was used, with an E.I.L. or a Cambridge Instruments Ltd. wide-range glass electrode. It was found that the use of an agar bridge with a normal calomel electrode (electrode system A) gave quicker and more reproducible results than did a modified calomel electrode (electrode systems B and C). In the case of polybasic acids after the initial reading a further 1/3 mmole of alkali was added to determine the second mid-equivalence potential.

Infrared spectra were determined in carbon tetrachloride solution, using 4 cm Infrasil cells for the 4000–2500 cm^{-1} region, and as Nujol and Florube mulls, using a Perkin–Elmer 237 instrument.

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