[Contribution from the Department of Chemistry of the University of Canterbury]

Hammett Substituent Constants for Electron-withdrawing Substituents: Dissociation of Phenols, Anilinium Ions and Dimethylanilinium Ions

By M. M. Fickling, A. Fischer, B. R. Mann, J. Packer and J. Vaughan

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In order to gain more information concerning the σ-constant, the thermodynamic pK values, in water at 25°, of a number of substituted phenols, dimethylanilines and anilines have been measured. Discussion of substituent constants is concerned primarily with the p-NO_2, p-CN, 3,4-C_4H_4 and p-NO groups. The reaction constant for dimethylanilinium ion dissociation has been obtained and an explanation has been offered for differences noted between this series and the anilinium ion series.

In the correlation of rate and equilibrium data by means of the Hammett equation, three different types of substituent constant are now recognized. In illustration, a σ^+-value is required for an electron-donating (+M) substituent conjugated with an electron-withdrawing (−M) sidechain; the original Hammett σ-value applies to a substituent when there is little conjugation between substituent and side-chain; the σ^--value is applicable to an electron-withdrawing (−M) substituent conjugated with an electron-donating (+M) side-chain. The three types of substituent constant cover a large body of data with impressive accuracy; in particular, Brown and his associates[1] have demonstrated the consistency with which σ^+-values fit a variety of reactions in which conjugation between substituent and electron-deficient reaction center must vary in extent. The information on reactions to which σ^- is applicable is somewhat more limited and there is evidence that "intermediate" σ^--values may be needed, for some reactions, with particular substituents. For example, Bordwell and co-workers[2] have shown that σ^--values for the p-NO_2 and p-CH_3SO_2 groups, obtained from the dissociation constants of substituted thiophenols, are considerably smaller than the corresponding σ^--values derived from the dissociation constants of phenols, and these, in turn, are smaller than the values obtained from the dissociation constants of anilinium ions. Bordwell explained these results in terms of an increasing difference, between dissociated and undissociated forms, in resonance interaction of substituent with side-chain, on passing from thiophenols to phenols to anilinium ions. It also has been shown recently[3] that for the 3,4-benzo and p-NO_2 substituents in certain reactions of phenols and amines, a better Hammett fit is obtained with σ^--values which are lower than those normally used. No explanation was offered for these results.

Further information on the constancy of σ^--values is desirable and, clearly, the more accurate the data the more theoretical significance is likely to be attached to deviations from the Hammett plots. We now report the pK values, in water at 25°, of p-cyano-, p-nitro- and p-nitroso-phenol, p-cyanoaniline, p-cyano-, p-nitro- and p-nitroso-N,N-dimethylaniline and N,N-dimethyl-2-naphthylamine. Similar values of some other substituted phenols, anilines and N,N-dimethylanilines were also measured so that, with the aid of pK values already published, it was possible to determine with satisfactory accuracy the reaction constant ρ for each series and hence σ^- for the p-CN, p-NO_2, p-NO and 3,4-benzo substituents.

Experimental and Results

Physical constants, etc., of compounds examined were: **Phenols**: phenol, b.p. 184°; p-nitrophenol, m.p. 114°; m-cyanophenol,[4] m.p. 113.5°; p-cyanophenol (*cf.* ref. 4), m.p. 112.5°; p-nitrosophenol.[5] *Anal.* Calcd. for $C_6H_5O_2N$: C, 58.5; H, 4.1; N, 11.4. Found: C, 58.5; H, 4.1; N, 10.9.

Anilines and Dimethylanilines: aniline, b.p. 184°; m-nitroaniline, m.p. 113.5°; m-cyanoaniline (from m-amino-benzaldehyde, *cf.* ref. 4), m.p. 52°; p-cyanoaniline (from p-aminobenzaldehyde, *cf.* ref. 4), m.p. 86°; dimethylaniline, b.p. 194°, n^{18}_D 1.5600; p-methyl-N,N-dimethylaniline[6], b.p. 208°, n^{20}_D 1.5469; m-methyl-N,N-dimethylaniline (*cf.* ref. 6), b.p. 209°, n^{19}_D 1.5500; p-methoxy-N,N-dimethylaniline (*cf.* ref. 6), m.p. 47.5°; p-nitro-N,N-dimethylaniline,[7] m.p. 165.5°; m-nitro-N,N-dimethylaniline,[8] m.p. 60°; p-cyano-N,N-dimethylaniline (from p-dimethyl-aminobenzaldehyde, *cf.* ref. 4), m.p. 75°; p-bromo-N,N-dimethylaniline,[9] m.p. 54.5°; N,N-dimethyl-2-naphthylamine,[10] m.p. 46.5°; p-nitroso-N,N-dimethylaniline,[11] m.p. 85.5°. m-Cyano-N,N-dimethylaniline was prepared from m-dimethylaminobenzaldoxime. The oxime (10 g.) was refluxed with acetic anhydride (20 ml.) for 30 minutes. Distillation of the resulting solution in vacuum gave m-cyano-N,N-dimethylaniline (6.7 g., 75%), b.p. 118–122° (3 mm.) as a yellow oil. Three further distillations gave b.p. 98° (1 mm.), m.p. 19.5°, n^{21}_D 1.5800.

Anal. Calcd. for $C_9H_{10}N_2$: C, 73.9; H, 6.9; N, 19.2. Found: C, 74.0; H, 6.5; N, 19.1.

Acid dissociation constants were measured by a spectrophotometric method as described by Robinson and Biggs.[12] Optical densities (range 0.2 to 1.0) were determined using a Hilger Uvispek instrument. The jacketed 1- or 2-cm. quartz cells were kept at 25.0 ± 0.2°. Beer's law was obeyed by the absorbing species over the required concentration range. Buffers used were: (A) borax, accurate pwH ($= -\log a_H f_{Cl}$) values for these buffers are available from results reported by workers at the National Bureau of Standards[13]; (B) sodium dihydrogen phosphate–disodium hydrogen phosphate, $pK_{HX} = 7.198$[14]; (C) acetic acid–sodium acetate (fractionally crystallized, "Analar" grade, acetic acid added to standard CO_2-free, sodium hydroxide solution), $pK_{HX} = 4.756$.[15]

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(1) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(2) F. G. Bordwell and H. M. Andersen, This Journal, **75**, 6019 (1953).

(3) A. Fischer, J. Packer, J. Vaughan, A. F. Wilson and E. Wong, *J. Org. Chem.*, **24**, 155 (1959).

(4) J. B. Culbertson, E. L. Carpenter and E. K. Nielsen, *Proc. Iowa Acad. Sci.*, **37**, 248 (1930).

(5) H. H. Hodgson and F. H. Moore, *J. Chem. Soc.*, **127**, 2260 (1925).

(6) H. H. Hodgson, *ibid.*, **133**, 77 (1928).

(7) J. B. Tingle and F. C. Blanck, This Journal, **30**, 1405 (1908).

(8) H. M. Fitch, *Org. Syntheses*, **27**, 62 (1947).

(9) K. Fries, *Ann.*, **346**, 187 (1906).

(10) G. T. Morgan, *J. Chem. Soc.*, **77**, 814 (1900).

(11) G. M. Bennett and E. V. Bell, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p. 223.

(12) R. A. Robinson and A. I. Biggs, *Trans. Faraday Soc.*, **51**, 901 (1955).

(13) G. G. Manov, N. J. De Lollis, P. W. Lindvall and S. F. Acree, *J. Research Natl. Bur. Standards*, **36**, 543 (1946).

(14) R. G. Bates and S. F. Acree, *ibid.*, **30**, 129 (1943).

(15) H. S. Harned and R. W. Ehlers, This Journal, **54**, 1350 (1932).

pK_{HB} for an acid HB in a buffer mixture of HX and X was obtained using one of the equations

$$pK_{HB} = pwH - \log m_B/m_{HB} - \log f_B/f_{Cl}f_{HB} \quad (1)$$

$$pK_{HB} = pK_{HX} + \log m_X/m_{HX} - \log m_B/m_{HB} - \log f_B f_{HX}/f_{HB} f_X \quad (2)$$

where m_B is the molality of B, the conjugate base of HB, and f_B is the activity coefficient of B, etc. From the electroneutrality condition and the conditions that $m_B + m_{HB} = m_B^* + m_{HB}^*$ and $m_X + m_{HX} = m_X^* + m_{HX}^*$ (where asterisks denote stoichiometric values) it may be shown that

$$m_X/m_{HX} = (m_X^* + \{m_B^* - m_B + m_H - m_{OH}\})/(m_X^* - \{m_B^* - m_B + m_H - m_{OH}\}) \quad (3)$$

The term in braces is usually small by comparison with the quantities m_X^* and m_{HX}^*, and hence

$$\log m_X/m_{HX} = \log m_X^*/m_{HX}^* + \{(m_B^* - m_B + m_H - m_{OH})/2.3\}(1/m_X^* + 1/m_{HX}^*) \quad (4)$$

Of the terms m_H and m_{OH}, usually one and often both are negligible.

pwH values, for solutions containing only buffer, require correction when either B or HB is introduced. A formula for this correction, rather more simple than that of Robinson and Kiang,[16] may be obtained as

$$pwH = pK_{HX} + \log m_X/m_{HX} + \log f_X/f_{HX}f_{Cl} \quad (5)$$

When B and HB are present, let pwH become pwH' etc.; then pK_{HX} may be eliminated from equations 5 and 5′. If the ionic strength, and hence the activity coefficient term, may be regarded as constant, then

$$pwH' - pwH = \log m'_X/m'_{HX} - \log m_X/m_{HX} \quad (6)$$

From (3) $pwH' - pwH =$

$$\log \frac{m_X^* + m_B^* - m_B + m'_H - m'_{OH}}{m_{HX}^* - m_B^* + m_B - m'_H + m'_{OH}} - \log \frac{m_X^* + m_H - m_{OH}}{m_{HX}^* - m_H + m_{OH}} \quad (7)$$

Usually it is sufficiently accurate to write $m'_H = m_H$ and $m'_{OH} = m_{OH}$; in addition if, as is usual, $(m_B^* - m_B)$ is small compared with both the terms $(m_X^* + m_H - m_{OH})$ and $(m_{HX}^* - m_H + m_{OH})$, then

$$pwH' - pwH = (m_B^* - m_B)\{1/(m_X^* + m_H - m_{OH}) + 1/(m_{HX}^* - m_H + m_{OH})\}/2.3 \quad (8)$$

If, as is also usual, $(m_H - m_{OH})$ is small compared with both m_X^* and m_{HX}^*, then

$$pwH' - pwH = (m_B^* - m_B)(1/m_X^* + 1/m_{HX}^*)/2.3 \quad (9)$$

The pwH corrections in Table I were made using this equation.

Spectrophotometric measurements gave $(\epsilon - \epsilon_{HB})/(\epsilon_B - \epsilon)$, $= m_B/m_{HB}$, where ϵ is the extinction coefficient of the mixture of HB and B measured in the buffer, ϵ_{HB} was measured in 0.1 N hydrochloric acid for phenols and for amines of $pK > 4$, and in 6 N acid for amines of $pK < 4$, and ϵ_B was measured in 0.1 N sodium hydroxide. The activity coefficient term (equations 1 and 2) was obtained using Guggenheim's extension[17] of the Debye–Hückel equation

$$-\log \pi(f_i) = (\Sigma z_i^2)\, 0.5085 I^{1/2}/(1 + I^{1/2}) + \beta I \quad (10)$$

where β is an adjustable parameter. Values of pK' ($= pK - \beta I$) were obtained over a range of ionic strengths up to $I = 0.1$. From these, thermodynamic pK figures were obtained by adjusting β until the resultant pK values showed no systematic variation with ionic strength.

For some of the amines pH_{HB} values were derived from measurement in dilute hydrochloric acid–potassium chloride solutions ("buffer" D). In this case

$$pK_{HB} = pcH - \log m_B/m_{HB} - \log f_H f_B/f_{HB} \quad (11)$$

where $pcH = -\log m_H = -\log(m_H^* - m_B^* + m_B)$. The other terms were obtained as described above.

Results for substituted phenols, anilines and dimethylanilines are given in Tables I, II and III, respectively. For each buffer one result is given in detail.

TABLE I

pK VALUES OF SUBSTITUTED PHENOLS

Phenol, at $\lambda = 290$ mμ, $\epsilon_{HB} = 5$, $\epsilon_B = 2445$

Borax[a] molality (= 0.5 I)	Phenol molality × 10^4	pwH	ϵ	$-\log m_B/m_{HB}$	pwH correction	pK'	pK^b
0.01	4.17	9.240	367	0.759	0.003	9.996	9.994
.025	4.17	9.258	379	.742	.001	9.999	9.994
.025	8.35	9.258	378	.743	.002	9.999	9.994
.05	8.35	9.307	413	.697	.001	10.003	9.993

p-Cyanophenol,[c] at $\lambda = 275$ mμ, $\epsilon_{HB} = 1388$, $\epsilon_B = 21700$

NaH_2PO_4[d,e] molality × 10^3	I × 10^2	ϵ	$-\log m_B/m_{HB}$	$\log m_X/m_{HX}$	$\Phi(I^{1/2})$	pK'	pK^f
2.5	1.75	5522	0.593	0.293	0.119	7.965	7.969
5.0	3.5	5316	.620	.297	.160	7.955	7.962
7.5	5.25	5109	.649	.299	.189	7.957	7.968
10.0	7.0	4960	.671	.299	.213	7.955	7.969

m-Cyanophenol, at $\lambda = 318.5$ mμ, $\epsilon_{HB} = 38$, $\epsilon_B = 3693$

I^a	0.02	0.05	0.075	0.1
pK'	8.612	8.619	8.622	8.629
pK^g	8.608	8.609	8.607	8.609

p-Nitrophenol, at $\lambda = 401$ mμ, $\epsilon_{HB} = 28$, $\epsilon_B = 17480$

$I^{d,h}$	0.01	0.015	0.02	0.03	0.04
pK'	7.152	7.148	7.140	7.144	7.138
pK^i	7.155	7.153	7.146	7.153	7.150

At $\lambda = 317$ mμ, $\epsilon_{HB} = 9480$, $\epsilon_B = 1472$

$I^{d,h}$	0.01	0.015	0.02	0.03	0.04
pK'	7.141	7.145	7.138	7.139	7.132
pK^i	7.144	7.150	7.144	7.148	7.144

p-Nitrosophenol, at $\lambda = 395.5$ mμ, $\epsilon_{HB} = 205$, $\epsilon_B = 27390$

$I^{d,h}$	0.01	0.02	0.03	0.04
pK'	6.353	6.367	6.359	6.366
pK^j	6.353	6.367	6.359	6.366

[a] Buffer A, equation 1. [b] $\beta = -0.1$. [c] Concentration = 7.03×10^{-5} molal. [d] Buffer B, equation 2. [e] $m_X^*/m_{HX}^* = 2$. [f] $\beta = 0.2$. [g] $\beta = -0.2$. [h] $m_X^*/m_{HX}^* = 1$. [i] $\beta = 0.3$. [j] $\beta = 0$.

TABLE II

pK VALUES OF SUBSTITUTED ANILINES

Aniline,[a] at $\lambda = 280$ mμ, $\epsilon_{HB} = 1$, $\epsilon_B = 1379$

NaOAc[b] molality × 10^2 (= I)	HOAc molality × 10^2	ϵ	$-\log m_B/m_{HB}$	$-\log m_X/m_{HX}$	$\Phi(I^{1/2})$	pK'	pK^c
5.28	5.32	665	0.031	0.000	0.190	4.597	4.634
5.28	10.04	462	.299	.275	.190	4.590	4.627
5.28	16.65	318	.525	.495	.190	4.596	4.633

m-Nitroaniline,[d] at $\lambda = 359$ mμ, $\epsilon_{HB} = 92$, $\epsilon_B = 1402$

HCl[e] molality × 10^3	KCl molality × 10^2	I × 10^2	ϵ	$\log m_B/m_{HB}$	pcH	pK'	pK^f
2.374	0.00	0.2	874	0.171	2.637	2.466	2.465
1.187	5.06	5.2	1065	.461	2.941	2.480	2.464
2.374	5.39	5.6	862	.154	2.637	2.483	2.466
4.749	5.24	5.7	631	− .155	2.332	2.487	2.470

m-Cyanoaniline, at $\lambda = 307$ mμ, $\epsilon_{HB} = 4$, $\epsilon_B = 2392$

I^e	0.052	0.056	0.057
pK'	2.758	2.764	2.773
pK^f	2.742	2.747	2.756

p-Cyanoaniline, at $\lambda = 285$ mμ, $\epsilon_{HB} = 28$, $\epsilon_B = 12725$

I^e	0.01	0.01	0.019
pK'	1.742	1.739	1.747
pK^f	1.739	1.736	1.741

[a] Concentration = 3.24×10^{-4} molal. [b] Buffer C, equation 2. [c] $\beta = 0.7$. [d] Concentration = 1.648×10^{-4} molal. [e] Buffer D, equation 11. [f] $\beta = -0.3$; *cf.* ref. 18.

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(16) R. A. Robinson and A. K. Kiang, *Trans. Faraday Soc.*, **51**, 1398 (1955).

(17) E. A. Guggenheim, "Thermodynamics," 3rd ed., North-Holland Publishing Co., Amsterdam, 1957, p. 356.

Table III

Dimethylaniline, at λ = 243 mμ, ϵ_{HB} = 147, ϵ_B = 8000

I[a]	0.046	0.051	0.051
pK'	5.036	5.030	5.033
pK[b]	5.068	5.066	5.069

m-Methyldimethylaniline, at λ = 245 mμ, ϵ_{HB} = 141, ϵ_B = 8373

I[a]	0.046	0.049	0.051
pK'	5.318	5.302	5.309
pK[b]	5.350	5.336	5.345

p-Bromodimethylaniline, at λ = 254 mμ, ϵ_{HB} = 192, ϵ_B = 12310

I[a]	0.026	0.053	0.053	0.053	0.070	0.079	0.105
pK'	4.214	4.192	4.196	4.199	4.176	4.181	4.157
pK[b]	4.232	4.229	4.233	4.236	4.225	4.236	4.230

p-Methyldimethylaniline, at λ = 242 mμ, ϵ_{HB} = 99, ϵ_B = 9401

I[a]	0.049	0.051	0.060
pK'	5.585	5.595	5.590
pK[b]	5.619	5.631	5.632

p-Methoxydimethylaniline, at λ = 239 mμ, ϵ_{HB} = 202. ϵ_B = 10320

I[a]	0.051	0.060	0.10
pK'	5.816	5.813	5.786
pK[b]	5.852	5.855	5.856

p-Nitrosodimethylaniline, at λ = 258 mμ. ϵ_{HB} = 674, ϵ_B = 3781

I[a]	0.033	0.046	0.051
pK'	4.520	4.510	4.510
pK[b]	4.543	4.542	4.546

Dimethyl-β-naphthylamine, at λ = 245 mμ. ϵ_{HB} = 1601, ϵ_B = 29720

I[a]	0.026	0.026	0.053	0.053
pK'	4.538	4.547	4.537	4.530
pK[b]	4.556	4.565	4.574	4.567

m-Nitrodimethylaniline, at λ = 248 mμ, ϵ_{HB} = 6460, ϵ_B = 17460

I[c]	0.001	0.004	0.011	0.036	0.050	0.058	0.103
pK'	2.625	2.627	2.629	2.640	2.644	2.651	2.669
pK[d]	2.625	2.625	2.625	2.626	2.624	2.628	2.628

p-Nitrodimethylaniline, at λ = 420 mμ, ϵ_{HB} = 0, ϵ_B = 18970

I[c]	0.11	0.11	0.12
pK'	.659	.645	.654
pK[d]	.615	.601	.606

m-Cyanodimethylaniline, at λ = 260 mμ. ϵ_{HB} = 473, ϵ_B = 8435

I[a]	0.001	0.002	0.10	0.10
pK'	2.969	2.968	3.006	3.015
pK[d]	2.969	2.968	2.966	2.975

p-Cyanodimethylaniline, at λ = 297 mμ, ϵ_{HB} = 14, ϵ_B = 24400

I[c]	0.010	0.013	0.016	0.021
pK'	1.787	1.783	1.777	1.785
pK[d]	1.783	1.778	1.771	1.777

[a] Buffer C, equation 2. [b] For *p*-bromodimethylaniline β = 0.7 and this value was used for all amines in buffer C. [c] Buffer D, equation 11. [d] For *m*-nitrodimethylaniline β = −0.4 and this value was used for all dimethylanilines in buffer D.

Table IV

pK Values for Phenols and Amines

Substituent	H	*p*-NO_2	*m*-NO_2	*p*-CN	*m*-CN	*p*-NO
Phenols	9.99	7.15	..	7.97	8.61	6.36
Lit. values	10.00[19]	7.15[12]		7.95[20]	..	..
Anilines	4.63	..	2.47	1.74	2.75	..
Lit. values	4.58[21] 4.62[22]	..	2.43[23] 2.57[18]	..	..	..
Dimethylanilines	5.07	0.61	2.63	1.78	2.97	4.54
Lit. values	5.06[21]	0.92[24]	2.47[24]	..	..	..

Substituent	*p*-Me	*m*-Me	*p*-Br	*p*-OMe	3,4-C_4H_4
Dimethylanilines	5.63	5.34	4.23	5.85	4.57
Lit. values	5.50[21]	5.24[21]	..	..	..

Discussion of Results

***pK* Values and Hammett Plots.**—Mean *pK* values, together with available literature values, are given in Table IV. Estimated maximum errors in *pK* are ±0.01 unit for phenols and ±0.02 unit for amines.

The major discrepancy in Table IV is that between Roberts, Webb and McElhill's *pK* for *p*-nitrodimethylaniline and our value. The former figure was obtained by comparison with *p*-nitroaniline, for which a *pK* of 1.11[25] was adopted, and use of the more recent value for *p*-nitroaniline of 0.99[26] would reduce the figure for *p*-nitrodimethylaniline to 0.80. However, a similar correction should be applied to Roberts' value for *m*-nitrodimethylaniline and the difference for this substituent is thereby increased. It may be noted that most of the *pK*'s previously cited for substituted anilines and dimethylanilines were obtained at finite ionic strength using cells with liquid junction. Errors resulting from these factors could account for minor differences in Table IV.

In applying the Hammett equation to substituted phenols, use was made of the *pK* values of Biggs[19] and the substituent constants of McDaniel and Brown[27] for the substituents *m*-NO_2, *m*-Cl, *p*-Cl, *p*-Br, *m*-OMe, H, *m*-Me and *p*-Me. The reaction constant ρ = 2.183, the correlation coefficient r = 0.997 and the calculated pK_0 (for phenol) = 9.915. For substituted dimethylanilines similar data were taken for the substituents *m*-NO_2, *p*-Br, H, *m*-Me, *p*-Me and *m*-CN. In the case of the last substituent group, σ was taken as 0.615 (see below). Reaction constant ρ = 3.430, r = 1.000 and pK_0 (calcd.) = 5.065. These ρ-values for phenols and dimethylanilines should be among the most accurately known for any reaction series; in each case thermodynamic *pK*'s, determined by a single investigator, were used.

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(18) R. G. Bates and G. Schwarzenbach, *Helv. Chim. Acta*, **37**, 1069 (1954).

(19) A. I. Biggs, *Trans. Faraday Soc.*, **52**, 35 (1956).

(20) G. W. Wheland, R. M. Brownell and E. C. Mayo, This Journal, **70**, 2492 (1948).

(21) N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932).

(22) R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953).

(23) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1976 (1948).

(24) J. D. Roberts, R. L. Webb and E. A. McElhill, This Journal, **72**, 408 (1950).

(25) L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

(26) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

(27) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

Substituent Constants.—In deriving the substituent constants of Table V, use was made of the above values for ρ and pK_0, and of the measured dissociation constants, together with Jaffé's data,[28] for the dissociation of substituted anilinium ions, of $\rho = 2.767$ and pK_0 (calcd.) = 4.557.

TABLE V

SUBSTITUENT CONSTANTS FROM DISSOCIATION OF PHENOLS, ANILINIUM IONS AND DIMETHYLANILINIUM IONS

Substituent	*m*-CN	*p*-OMe	*p*-NO_2	*p*-CN	3,4-C_4H_4	*p*-NO
Phenols	0.598	−0.135[a]	1.267	0.891	0.046[c]	1.629
Anilines	.653	......	1.289[b]	1.018	.120[c]	...
Dimethylanilines	.611	−0.229	1.299	0.958	.144	0.153

[a] Taking pK for *p*-hydroxyanisole as 10.21.[19] [b] Taking pK for *p*-nitroaniline as 0.99.[26] [c] From ref. 3.

Two minor comments may be made on Table V. First, McDaniel and Brown give a value for $\sigma_{m\text{-CN}}$ of 0.56; this is an average of 0.615 and 0.520, both of these figures being derived from ionization of *m*-cyanobenzoic acid in water. The value of 0.520 was obtained from experiments using cells with liquid junction.[29] On the other hand, the value of 0.615 was derived from measurements on cells without liquid junction[30] and it is likely that this higher value is the more reliable. The mean of our own results is 0.621. Second, there is a surprising difference between the $\sigma_{p\text{-OMe}}$ value obtained from phenols and that from amines. However, both values indicate that, as one would expect, the *p*-methoxy substituent is less strongly electron-donating in these reactions than in the dissociation of benzoic acids ($\sigma_{p\text{-OMe}} = -0.268$),[27] in which conjugation exists between this substituent and the side-chain.

Values for $\sigma^-_{p\text{-}NO_2}$ agree within the limits of accuracy of the Hammett equation. For the *p*-CN and 3,4-benzo groups, σ^--values are spread over a considerably greater range. This spread of σ^--values does not necessarily indicate a variation in substituent–side-chain resonance interaction between one series and another. For the *p*-NO_2 group,[31] the resonance component (σ^-_R) of σ^- is 0.64, for *p*-CN[31] it is 0.41 and for 3,4-benzo, σ^-_R must be even smaller. It would be expected that a general variation in resonance interaction in these three reaction series would spread derived σ^--values for *p*-NO_2 more than for *p*-CN and even more than for 3,4-benzo. It seems therefore that the results cannot be explained on the above basis.

The large difference between σ^--values, for the *p*-nitroso substituent, derived from phenol and dimethylaniline reactions is readily explained in terms of tautomerism of *p*-nitrosophenol and of the *p*-nitrosodimethylanilinium ion. In each case we have the equilibria

$$HB_1 \overset{K_1}{\rightleftarrows} H + B \overset{K_2}{\rightleftarrows} HB_2$$

where HB_1 represents the "nitroso" form and HB_2 the "quinonoid" form. Now

$$K_{\text{exptl}} = a_Ha_B/(a_{HB_1} + a_{HB_2}) = f(a_Ha_B/a_{HB_1}) = fK_1$$

where f is the fraction of the tautomeric mixture which is in the nitroso form. Hence

$$pK_{\text{exptl}} \not< pK_1$$

and

$$pK_0 - pK_{\text{exptl}} \not> pK_0 - pK_1$$

Since ρ is positive, $\sigma^-_{\text{exptl}} \not> \sigma^-_{p\text{-NO}}$. The ratio a_{HB_1}/a_{HB_2} will determine the difference between σ^-_{exptl} and $\sigma^-_{p\text{-NO}}$. It thus would be surprising if both the phenol and amine experiments led to the same value for σ^-_{exptl}. In addition, the higher of our two measured σ^--values must be a lower limit for $\sigma^-_{p\text{-NO}}$; hence $\sigma^-_{p\text{-NO}} \not< 1.625$. Miller and Parker[32] have obtained a figure of 1.46 from the methanolysis of 4-substituted-1-chloro-2-nitrobenzenes. For this reaction ρ is not known with accuracy, which makes it possible that Miller's value does not differ significantly from the limit now suggested.

These considerations also lead to further information on the position of tautomeric equilibrium in the conjugate acid of *p*-nitrosodimethylaniline. The following argument shows that at equilibrium the fraction of anilinium form must be less than 10^{-5}.

$$pK_{\text{exptl}} = -\log f + pK_1$$

We characterize the phenol case by pK_1', etc., and the amine case by pK_1'', etc. Then

$$\begin{aligned} pK_0' - pK'_{\text{exptl}} &= \log f' + pK_0' - pK' \\ &= \log f' + \rho'\sigma^-_{p\text{-NO}} \end{aligned}$$

Similarly

$$pK_0'' - pK''_{\text{exptl}} = \log f'' + \rho''\sigma^-_{p\text{-NO}}$$

Thus

$$\log f'' = -\rho''(pK_0' - pK'_{\text{exptl}} - \log f')/\rho' + pK_0'' - pK''_{\text{exptl}}$$

Since $\log f'$ is negative

$$\begin{aligned} \log f'' &< -\rho''(pK_0' - pK'_{\text{exptl}})/\rho' + pK_0'' - pK_0'' - pK''_{\text{exptl}} \\ &< -5.06 \end{aligned}$$

and $f'' < 8.7 \times 10^{-6}$

Thus the fraction of the conjugate acid of *p*-nitrosodimethylaniline present in nitroso form is completely insignificant. On general chemical grounds, Taylor and Baker[33] have qualitatively reached a similar conclusion. The measured pK is therefore that of the tautomer.

Relative Basicities in the Two Amine Series.—It will be noted that, whereas dimethylaniline is a stronger base than aniline, *p*-nitrodimethylaniline is a weaker base than *p*-nitroaniline. This is contrary to what one would expect on purely electronic grounds. Thus a substituent group, constant for a Hammett reaction series, should exert a constant base strengthening or weakening effect. If this were the only pertinent factor, it would be expected that ρ would be the same for the aniline and dimethylaniline series in the same way as ρ for some reactions is found to be unaffected by the introduction of a constant *ortho* group.[28] But

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(28) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(29) M. Kilpatrick and R. D. Eanes, THIS JOURNAL, **65**, 589 (1943).

(30) G. Briegleb and A. Bieber, *Z. Elektrochem.*, **55**, 250 (1951).

(31) R. W. Taft, Jr., THIS JOURNAL, **79**, 1045 (1957).

(32) J. Miller and A. J. Parker, *Australian J. Chem.*, **11**, 302 (1958).

(33) T. W. J. Taylor and W. Baker, "Sidgwick's Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1937, pp. 219–220.

our results lead to a value of ρ for dimethylanilinium ion dissociation which is considerably larger than that for anilinium ion dissociation, a fact which is reflected in the specific case of relative basicities quoted above.

Now it is often found that (in water) tertiary amines are weaker bases than the corresponding primary amines, *e.g.*, methylamine and trimethylamine. Two explanations have been offered. Brown[34] suggests that on proton addition, there is a contraction in bond angles resulting in a steric strain which destabilizes the conjugate acid. An alternative view[35] is that, in the tertiary amine case, relief of electrostatic energy by solvation is sterically hindered. Our present findings appear to be explicable in terms of the second of these suggestions. When comparing dimethylanilines with anilines, the presence of the methyl groups should lead to a constant base-strengthening electronic effect and also to a base-weakening steric hindrance to solvation, the extent of which should depend upon the electronic charge on the amine nitrogen; this charge would in turn depend upon the nature of any substituent present in the aromatic ring. For dimethylaniline itself the electronic effect outweighs the steric effect but in a series in which this amine possesses a progressively more electron-withdrawing substituent in the ring, the net positive charge on the amine nitrogen is similarly increased. There should therefore be a concomitant increase in the "desire" for solvation; in other words, the "steric inhibition of solvation" term becomes larger and it is suggested that for the *p*-NO_2 substituent, this term is so large that, when one compares *p*-nitroaniline and *p*-nitrodimethylaniline, this term outweighs the electronic base-strengthening effect of the methyl groups. Thus *p*-nitrodimethylaniline is a weaker base than *p*-nitroaniline.

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[34] H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

[35] (a) D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A177**, 499 (1941); (b) R. G. Pearson, THIS JOURNAL, **70**, 204 (1948); (c) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).

[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Reactions of Grignard Reagents with Peroxy Compounds[1,2]

BY SVEN-OLOV LAWESSON[3] AND N. C. YANG

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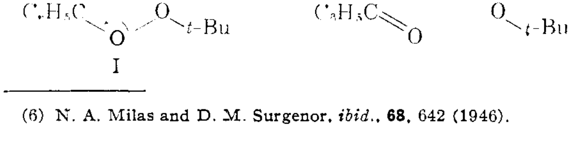
In contrast to the reactions with esters, Grignard reagents react with *t*-butyl perbenzoate at 0° to give *t*-butyl ethers and benzoic acid. The reaction may be used as a convenient laboratory method for the preparation of *t*-butyl ethers. Aryl and alkyl Grignard reagents react with *t*-butyl hydroperoxide to give in excellent yields the corresponding phenols and alcohols. The reaction constitutes a two-step displacement of a halogen atom by a hydroxyl group. This observation supports Ivanoff's mechanism for oxidation of mixed Grignard reagents by molecular oxygen. Benzoyl peroxide reacts with Grignard reagent to give an abnormally high yield of benzoic acid together with lesser amounts of the ester and the halide. The possible mechanism of this reaction is discussed. Di-*t*-butyl peroxide fails to react with phenylmagnesium bromide even at elevated temperatures.

The reaction of Grignard reagents with diacyl peroxides and dialkyl peroxides had been reported in the literature, but the extent of these investigations is primarily exploratory. Gilman and Adams[4] found that Grignard reagents reacted with benzoyl peroxide to form benzoates or tertiary carbinols and phenylmagnesium bromide reacted with diethyl peroxide to give phenetole and biphenyl. Campbell and co-workers[5] later observed that alkyl Grignard reagents reacted with di-*t*-butyl peroxide to give a mixture of products containing some *t*-butyl ether, while phenylmagnesium bromide failed to react under identical conditions. In connection with our current interest in the chemistry of peroxy compounds, the reactions of organometallic compounds with various peroxy compounds were investigated.

(a) The Reaction of *t*-Butyl Perbenzoates with Grignard Reagents.

—*t*-Butyl perbenzoate (I) reacts with sodium methoxide in methanol to give methyl benzoate and the sodium salt of *t*-butyl hydroperoxide[6]; the reaction of *t*-butyl perbenzoate with different types of nucleophilic reagents, otherwise, receives little attention. Contrary to the reaction of esters with Grignard reagents, *t*-butyl perbenzoate was found to react with a variety of Grignard reagents to give good yields of *t*-butyl ethers and benzoic acid. The Grignard reagents employed were phenyl, α-naphthyl-, *p*-tolyl-, *p*-anisyl-, ethyl-, 1-octyl-, cyclohexyl- and 2-propylmagnesium halides, and the reaction may be formulated as



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[2] Presented in part at the 134th Meeting of the American Chemical Society in Chicago, Ill., September, 1958.

[3] Institute of Chemistry, University of Uppsala, Uppsala, Sweden.

[4] H. Gilman and C. E. Adams, THIS JOURNAL, **47**, 2816 (1925).

[5] T. W. Campbell, W. Burney and T. L. Jacobs, *ibid.*, **72**, 2735 (1950).

[6] N. A. Milas and D. M. Surgenor, *ibid.*, **68**, 642 (1946).