

694. Dissociation of Benzylammonium Ions.

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The dissociation constants of benzylammonium and thirteen substituted benzylammonium ions have been measured. There is good agreement between the derived $\bar{\sigma}$ values and σ° values.

TAFT and his co-workers¹ and Wepster *et al.*² have independently derived sets of substituent constants (denoted σ° and σ_n , respectively) which were assumed to be measures of the inductive effects of substituted phenyl groups. For *para*-substituted groups the σ° values are based on closely similar reactivities (ionisation of phenylacetic and β -phenylpropionic acids, hydrolysis of ethyl phenylacetates and of benzyl acetates).

Clearly it is important to extend the range of reactivities for which *para*-substituted phenyl groups might be expected to exhibit σ° values. This is particularly so for *para*-(+*M*)-substituents. In the case of *para*-(-*M*)-substituents the actual σ° values are mean values derived from all reactivities not involving conjugation between reaction centre and *para* substituent. Furthermore, the reasonable assumption is made in evaluating the σ° values that the interposed methylene group inhibits resonance interaction between the ring and the functional centre. The reaction series we have chosen for study—dissociation of substituted benzylammonium ions—provides a test of this assumption. If any resonance occurs across a methylene group then *para*-(+*M*)-substituents should be better electron donors in Taft's phenylacetic acid reactivities, and *para*-(-*M*)-substituents should exert a more powerful electron-withdrawing effect on the benzylammonium ion dissociation.

EXPERIMENTAL

Benzylamines.—Benzylamine, b. p. 78°/16 mm., and 4-chloro-, b. p. 106°/15 mm., 4-methoxy-, b. p. 126°/16 mm., and 4-methyl-benzylamine, b. p. 96°/26 mm., were fractionated commercial products. The following substituted benzylamines were prepared by reduction³ of the corresponding substituted benzamides with lithium aluminium hydride: 3-bromo-, b. p. 91°/0.5 mm.; 3-chloro-, b. p. 85°/0.5 mm.; 3-methoxy-, b. p. 125°/19 mm. Reaction of the appropriate

¹ Taft and Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343; Taft, *J. Phys. Chem.*, 1960, **64**, 1805.

² Van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

³ Micovic and Mihailovic, *J. Org. Chem.*, 1953, **18**, 1190.

substituted benzyl bromide with hexamine and subsequent decomposition of the addition complex by Graymore's method⁴ gave 4-bromo-, b. p. 104°/1 mm., 3-fluoro-, b. p. 82°/16 mm., 4-fluoro- (from the chloride), b. p. 64°/0.5 mm., 3-methyl-, 62°/0.5 mm., 3-nitro-benzylamine, b. p. 116°/0.5 mm., and 4-nitro-benzylamine hydrochloride, m. p. 258°. Attempts were made to obtain the free base from 4-nitrobenzylamine hydrochloride. Although on one occasion colourless crystals were obtained, these rapidly turned brown and liquefied. 4-Cyanobenzylamine, b. p. 107°/0.5 mm., was obtained by reaction of 4-cyanobenzyl bromide with anhydrous ammonia in an autoclave. Purification of the amines was effected by recrystallisation of the hydrochlorides, followed by fractional distillation of the liberated amines, under vacuum, into ampoules (subsequently sealed). Absorption of carbon dioxide was prevented by soda-lime guard tubes. For all amines, calculated and found equivalent weights agreed to better than 0.5%.

Reagents.—Thymol Blue, m. p. 231°, was recrystallised (five times) from ethanol. De-ionised water (CO₂-free) was used for preparation of solutions.

Acid Dissociation Constants.—The spectrophotometric method was used. For each amine a stock solution of amine-amine hydrochloride buffer was prepared by weight. The amount of excess of amine was checked by potentiometric titration with standard hydrochloric acid. The calculated and found values agreed to within 0.5%. Buffer solutions of varied but known ionic strength (0.006—0.06), containing a known concentration of Thymol Blue indicator, were prepared from the stock buffer solution and a standard solution of indicator. Measurements of the optical density of the indicator (at $\lambda_{\text{max.}} = 595 \text{ m}\mu$, $\epsilon = 34,500$ for the bivalent anion) in the buffer solutions, in 0.1M-sodium hydroxide (alkaline form), and in phthalate buffer of pH = 5.3 (acid form, univalent anion) led to the ratio $m_{\text{In}}/m_{\text{HIn}}$. Values of $\text{p}K' (= \text{p}K - bI)$ were calculated from:

$$\text{p}K' = \text{p}K_{\text{HIn}} + \log m_{\text{In}}/m_{\text{HIn}} - \log m_{\text{B}}/m_{\text{HB}} - 2.05I^{1/2}/(1 + I)^{1/2}.$$

Plots of $\text{p}K'$ against I gave the values of b (slope) and $\text{p}K$ (intercept). Alternatively for each $\text{p}K'$ value a $\text{p}K$ value could be obtained ($\text{p}K = \text{p}K' + bI$). The variation of such $\text{p}K$ values

TABLE 1.

$\text{p}K$ Value for the second dissociation of Thymol Blue.

$\text{p}K$ (borax buffer) = 9.234		$m_{\text{B}}/m_{\text{HB}} = 1.000$			
$m_{\text{In}} + m_{\text{HIn}} = 3 \times 10^{-5}\text{M.} \quad \epsilon_{\text{HIn}} = 16. \quad 10^{-4}\epsilon_{\text{In}} = 3.454.$					
I	$10^{-4}\epsilon$	$\log (m_{\text{In}}/m_{\text{HIn}})$	$1.02I^{1/2}/(1 + I^{1/2})$	$\text{p}K'$	$\text{p}K$
0.100	2.215	0.252	0.246	9.228	9.188
0.050	2.147	0.215	0.187	9.206	9.186
0.010	2.007	0.142	0.093	9.185	9.181
0.005	1.948	0.111	0.068	9.190	9.190
Mean $\text{p}K = 9.186.$					

TABLE 2.

$\text{p}K$ Value of benzylammonium ion.

$m_{\text{B}}/m_{\text{HB}} = 0.666$		$\log (m_{\text{B}}/m_{\text{HB}}) = -0.177$			
$m_{\text{In}} + m_{\text{HIn}} = 3 \times 10^{-5}\text{M.} \quad \epsilon_{\text{HIn}} = 0. \quad 10^{-4}\epsilon_{\text{In}} = 3.478.$					
$10^{-2}I$	$10^{-4}\epsilon$	$\log (m_{\text{In}}/m_{\text{HIn}})$	$2.05I^{1/2}/(1 + I^{1/2})$	$\text{p}K'$	$\text{p}K$
3.97	2.322	0.303	0.340	9.325	9.385
2.98	2.270	0.274	0.301	9.335	9.380
2.39	2.222	0.248	0.274	9.337	9.373
1.99	2.198	0.235	0.253	9.355	9.385
1.49	2.154	0.211	0.223	9.351	9.373
1.19	2.141	0.205	0.202	9.366	9.384
0.85	2.091	0.178	0.173	9.368	9.381
0.66	2.062	0.163	0.154	9.372	9.382
Mean $\text{p}K = 9.380.$					

is a good measure of the consistency of a set of results. Detailed results for Thymol Blue and for benzylamine are given in Tables 1 and 2, respectively. No correction (to the stoichiometric buffer ratio) for indicator ionisation was necessary because the indicator was in such low concentration. Similarly no correction was required for the "buffering effect" of water.

⁴ Galat and Elion, *J. Amer. Chem. Soc.*, 1939, **61**, 3585; Graymore, *J.*, 1947, 1116.

No significance should be attached to the difference between the ϵ_{HIn} and ϵ_{In} values listed in Tables 1 and 2. Relative ϵ values within either Table are precise since in each case a single (but different) stock solution of indicator was used. Slight errors in absolute ϵ values might also arise from errors in wavelength setting. The wavelength drum of the spectrophotometer (Hilger "Uvispek") was left untouched throughout the complete set of measurements for each pK determination.

Mean pK values for dissociation of benzylamines are presented in Table 3. Values of pK are estimated accurate to ± 0.02 units, except for *p*-cyanobenzylammonium ion, when it was necessary to warm the mixture to ensure complete dissolution. This treatment could conceivably result in partial hydrolysis of the cyanide group.

TABLE 3.
Dissociation of X-benzylammonium ions in water at 25°.

X	H	3-Br	4-Br	3-Cl	4-Cl	4-CN	3-F
pK	9.38	8.98	9.13	9.01	9.14	(8.52)	9.04
pK (ref. 5)	9.38	—	—	—	—	—	—
X	4-F	3-Me	4-Me	3-MeO	4-MeO	3-NO ₂	4-NO ₂
pK	9.30	9.45	9.54	9.29	9.51	8.65	8.50
pK (ref. 5)	—	9.38	9.41	9.19	9.51	—	—

DISCUSSION

There is good agreement between our value for the second dissociation constant of Thymol Blue and that quoted by Kolthoff and Laitinen⁶ (9.20).

The reaction constant for dissociation of benzylammonium ion was obtained by fitting a regression line to the pK against σ° data for the seven *meta*-substituents (including hydrogen): slope (ρ), 1.047; correlation coefficient (r) 0.997; intercept with the ordinate (pK_0), 9.39. Using the pK values for the *para* substituents, effective sigma values ($\bar{\sigma}'$) were calculated from the relation: $\bar{\sigma}' = (9.39 - pK)/1.047$. These, together with σ° values, are shown in Table 4.

TABLE 4.
Values of $\bar{\sigma}$ and σ° for X-phenyl groups.

X	H	3-Br	4-Br	3-Cl	4-Cl	4-CN	3-F
$\bar{\sigma}'$	+0.01	+0.39	+0.25	+0.36	+0.24	+0.83	+0.33
σ°	+0.00	+0.38	+0.26	+0.37	+0.27	+0.69	+0.35
$\bar{\sigma}$	+0.01	+0.39	+0.25	+0.36	+0.24	+0.82	+0.33
X	4-F	3-Me	4-Me	3-MeO	4-MeO	3-NO ₂	4-NO ₂
$\bar{\sigma}'$	+0.09	-0.06	-0.14	+0.10	-0.12	+0.71	+0.85
σ°	+0.17	-0.07	-0.15	+0.13	-0.12	+0.70	+0.82
$\bar{\sigma}$	+0.09	-0.06	-0.14	+0.10	-0.11	+0.70	+0.84

Within the limit of precision of σ° values, there is good agreement between the σ' and σ° values except for *p*-cyanophenyl and *p*-fluorophenyl. Following Taft and Lewis's procedure¹ a regression line was fitted to the pK against σ° data for all benzylamines except *p*-cyano- and *p*-fluoro-benzylamine: slope, 1.056; r , 0.996; standard deviation, s , 0.03; pK_0 9.39.

Effective values, calculated from the relation: $\bar{\sigma} = (9.39 - pK)/1.056$, are also shown in Table 4. These of course do not differ significantly from the $\bar{\sigma}'$ values.

Experimental difficulties met in the determination of the dissociation constant of *p*-cyanobenzylamine have already been mentioned, and the close agreement between $\bar{\sigma}$ and σ° for *p*-nitrophenyl suggests that the resonance interaction between the amino and *para*-(- M)-groups, present in substituted anilines, is completely inhibited by the methylene group in benzylamines. Similarly the general agreement between $\bar{\sigma}$ and σ° for the *para*-(+ M)-substituted phenyl groups implies that the resonance interaction between such

⁵ Carothers, Bickford, and Hurwitz, *J. Amer. Chem. Soc.*, 1927, **49**, 2908; Bredig, *Z. phys. Chem.*, 1894, **13**, 306.

⁶ Kolthoff and Laitinen, "pH and Electrotitrations," John Wiley and Sons, Inc., New York, 2nd ed., p. 41.

substituted benzoic acids (and esters) is absent in the substituted phenylacetic acids (and esters). The $\bar{\sigma}$ value for *p*-fluorophenyl falls in the range of values derived from reactions of phenols and anilines. Taft¹ has offered an explanation of the apparently greater $+M$ effect exhibited by *p*-fluoro in phenol dissociation as compared with phenylacetic acid dissociation and related (σ°) reactivities in terms of a concept of Mulliken. Taft suggests that in the *p*-fluorophenoxide anion the negative charge relayed through σ bonds to the *p*-fluoro-substituent allows more extensive $+M$ interaction of the latter with the ring than in *p*-fluorophenol. However, this explanation cannot be applied to aniline reactivities, which give $\bar{\sigma}$ values for *p*-fluorophenyl of similar magnitude to those derived from phenol reactivities. Furthermore, it may be re-emphasised that, while comparable $\bar{\sigma}$ values are obtained from phenol reactivities, aniline reactivities, and benzylamine dissociation, these values are different from those obtained from phenylacetic acid and related reactivities; it seems unlikely that a single explanation can encompass these findings.

The value of ρ (1.056) is substantially larger than that derived by Jaffé⁷ from the pK values of Carothers⁵ *et al.* (0.732). As already indicated, we believe that our pK values are more accurate than those. More important, the range of substituents investigated by Carothers was rather small (σ° values from +0.13 to -0.12). Clearly our ρ -value should be more reliable than Jaffé's, and this is reflected in the correlation coefficients (0.996 and 0.942, respectively) and standard deviations (0.030 and 0.044). Our value of ρ conforms to Taft's relationship: $\rho = (2.8 \pm 0.5)^{1-i}$, where i is the number of "saturated" links intervening between the benzene ring and the atom at which there is unit decrease in positive charge or ionisation of a proton.

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⁷ Jaffé, *Chem. Rev.*, 1953, **53**, 191.
