butyrolactone could be detected. The only product identified was 1,3-diiodopropane which was formed in good yield. It was further shown that γ-butyrolactone was stable under the conditions of the experiments.

Preparation and Pyrolysis of 4-Bromobutyryl Peroxide.—**4-Bromobutyryl chloride** was prepared according to a general literature procedure[21] and was obtained as a colorless oil, b.p. 40° (0.6 mm.).

Anal. Calcd. for C_4H_6BrClO: C, 25.90; H, 3.26. Found: C, 26.38; H, 3.49.

The chloride was converted to the peroxide by a procedure similar to that described for the iodo derivative. 4-Bromobutyryl peroxide was obtained as a colorless oil that could not be induced to crystallize. Attempts at purification led to much decomposition; however, the infrared spectrum was very similar to that of the iodo peroxide and revealed only small impurities. The sample was used directly in pyrolysis experiments.

The vapor phase decomposition of the bromo peroxide was carried out analogously to that of the iodo compound. No cyclopropane was detected, and the only products that were identified by v.p.c. were γ-butyrolactone and 1,3-dibromopropane.

2-Bromomethylcyclohexanecarboxylic Acid Chloride.—Hexahydrophthalide (12.0 g., 0.086 mole) and anhydrous hydrogen bromide (27.0 g., 0.34 mole) were heated in a sealed tube for 1 hr. at 100°. The tube was cooled, and the excess hydrogen bromide was removed under reduced pressure. The residue was dissolved in thionyl chloride (30 ml.) and the solution was heated for 1 hr. on a steam bath. Distillation gave 18.4 g. (90%) of **2-bromomethylcyclohexanecarboxylic acid chloride**, b.p. 90–100° (0.5 mm.).

Anal. Calcd. for $C_8H_{12}BrClO$: C, 40.12; H, 5.05. Found: C, 40.30; H, 4.87.

The infrared spectrum showed a carbonyl stretching vibration at 5.60 μ.

Preliminary experiments showed that the acid chloride reacted very slowly with alkaline hydrogen peroxide. The acid chloride (4.78 g., 0.020 mole) in ether (15 ml.) was treated with 30% hydrogen peroxide (1.44 ml.) and sodium hydroxide (1.2 g.) in water (10 ml.). The mixture was stirred for 24 hr. at −5° and was then worked up as previously described for 4-iodobutyryl peroxide. 2-Bromomethylcyclohexanecarbonyl peroxide (0.50 g.) was obtained as a crystalline white solid at −70° from ether–petroleum ether. The peroxide was very sensitive to losses during purification, and acceptable analyses could not be obtained although the products had a clean infrared spectrum. On heating it decomposed violently at 65°. The recrystallized product was used in the pyrolysis experiments.

A solution of the peroxide (0.32 g., 0.00073 mole) in monoglyme (1 ml.) was heated at 60–70° until gas evolution ceased. No norcarane was detected in the residue by a v.p.c. technique sufficiently sensitive to detect 0.2%. Hexahydrophthalide (0.12 g.), identical with an authentic sample, and a liquid believed to be 2-bromomethylcyclohexyl bromide (*ca.* 0.05 g.) were also isolated. The former was determined by direct v.p.c. calibration, but the small amount of the bromide was only estimated.

Excited State pK Values. III. The Application of the Hammett Equation

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The possibility of application of the Hammett equation to the acid–base equilibrium constants in excited states of aromatic acids and bases was investigated. The excited state p*K* values are obtained by use of the Förster cycle, and the assumptions and approximations involved in its use are reviewed and carefully examined. The most important conclusion is that excited-state p*K* values conform, at least roughly to linear free-energy relations with ground-state parameters (σ). Universally, exalted substituent constants are required, probably because of the highly polar nature of excited states. The data presented suggest that *meta*- and *para*-substituted compounds may require different reaction constants (ρ). An attempt is made to interpret magnitudes of reaction constants for the p*K* values of different excited states in various reaction series.

The chemistry of excited states has recently become a focal point of wide interest. On the one hand, a large number of investigators are delving deeply into the mechanisms of reactions occurring in excited states. On the other hand, the pioneering work of Förster,[2] Weller,[3] and Porter[4] has paved the way to the measurement of chemical equilibria between molecules in their excited states; in particular, of acid–base equilibria.

Since acid–base equilibria have been one of the original and most fruitful areas for the application of linear free-energy relations, the question arises naturally whether such relations will be equally applicable to electronically excited states. The only attempt to provide an answer to this question is contained in the investigations of Bartok and co-workers.[5] Before we deal with these papers, we must briefly discuss the experimental techniques used to obtain excited-state equilibrium data.

The determination of the p*K* of a compound in the electronic ground state is readily achieved if it is possible to estimate the ratio of the concentrations of a conjugate acid–base pair as a function of pH. An analogous procedure is, of course, applicable to excited states. The entire field of excited-state equilibrium measurements was therefore opened when Förster showed that the fluorescence spectra of a few acids depended on pH. When it was shown that this pH dependence of fluorescence in the excited state was vastly different from the pH dependence of the absorption of the ground-state species, it was demonstrated that equilibrium had been established in the excited state. Careful fluorescence measurements in buffered solutions then permit determination of the p*K* in the excited singlet state (p*K**). This technique, however, is extremely exacting, very time consuming, and applicable only to compounds in which at least one of the pair of conjugate acid–base fluoresces. The last factor produces some extreme limitations.

The measurement of the p*K* values of the lowest triplet state is achieved by a method of Porter.[4] It involves excitation of the substrate in buffered solution to the triplet state by flash photolysis, followed by triplet–triplet absorption measurements, which are

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(1) Procter and Gamble Fellow, 1963–1964.

(2) T. Förster, *Z. Elektrochem.*, **54**, 42 (1950).

(3) A. Weller in "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Pergamon Press, New York, N. Y., p. 187, and references cited therein.

(4) G. Jackson and G. Porter, *Proc. Roy. Soc.* (London), **A260**, 13 (1961).

(5) (a) W. Bartok, P. J. Lucchesi, and N. S. Snider, *J. Am. Chem. Soc.*, **84**, 1842 (1962); (b) W. Bartok, P. J. Lucchesi, and R. B. Hartman, *ibid.*, in press.

evaluated exactly as ground-state absorption data in the spectrophotometric method of pK determination.

An alternate method of obtaining the pK values of excited singlet states (but not of triplets) is also due to Förster. It depends on the Förster cycle,[3,6] which is shown in Figure 1. In this cycle, which is applicable either to absorption or fluorescence spectra, ΔE_B and ΔE_{BH} are the energy differences between ground and excited state for conjugate base (B) and acid (BH), respectively, and ΔH and ΔH^* are the heats of ionization in the ground and excited state, respectively. To use this cycle for the evaluation of pK^*, a number of rather drastic assumptions are necessary.

(1) It must be assumed that ΔS is the same in the two electronic states. This seems to be a rather reasonable assumption. It seems probable that the most important contribution to such a difference would come from differences in solvation. Although solvation for ground and excited state is likely to be rather different, the difference may be expected to be very much alike in the conjugate pair of compounds, provided the charge distribution is similar in both. This will in general be the case, if the excited states are similar in nature (*cf.* the third assumption, below).

(2) The Förster cycle is *a priori* applicable only to the O–O vibrational bands of either absorption or emission spectra. Unfortunately, the position of the O–O band is generally unknown. In order to overcome this difficulty, some authors have used the average of absorption and fluorescence spectra as a measure of the O–O band.[5] This still presupposes that the energy distribution between vibrational subbands are the same in absorption and fluorescence spectra, and that the vibrational spacing is the same in ground and excited states. Neither of these suppositions is necessarily valid.

On the other hand, if we presume that the maximum of the absorption bands of the acid and base occur an equal amount above the O–O level, absorption spectra alone can be used in a Förster cycle. This last assumption is valid if the vibrational spacings of the excited states of the conjugate pair are alike, and if the energy distribution between vibrational subbands is alike. Although no proof for the validity of these assumptions exists, they appear quite reasonable, particularly in rigid aromatic systems where the vibrational structure involves mostly ring deformations and in comparison of absorption bands of similar electronic origin.

(3) Both the previous assumptions appeared reasonable only if the nature of the absorption bands of the conjugate acid–base pair were similar. This requirement is even more important for another reason. A chemical reaction is not normally accompanied by an electronic transition. Unless the excited states of the conjugate acid–base pair belong the same electronic configuration, the equilibrium reaction would have to be accompanied by an electronic transition, a process which is very unlikely. Similarly, even if the configurations of the pair are the same, but if they belong to different irreducible representations of the point group to which they belong (or of the highest common subgroup of their respective point groups), the process is again unlikely. This low probability most likely may be expressed in terms of a large entropy effect, and thus the first assumption requires that the transitions be corresponding, *i.e.*, that they belong to the same configuration and to the same irreducible representation of the highest common subgroup.

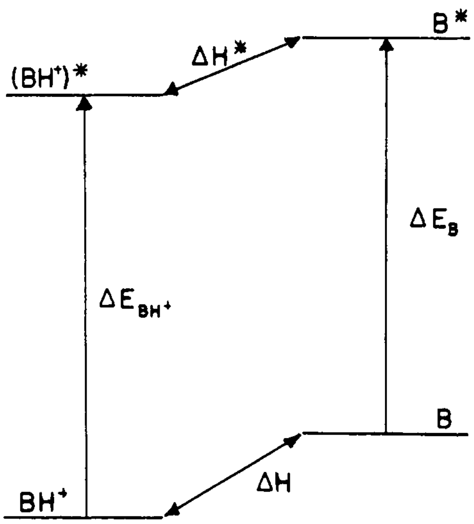

Figure 1.—The Förster cycle.

Thus we have now available three methods for the determination of the pK^* of a singlet excited states: (1) measurement of fluorescence intensity as a function of pH; (2) measurement of fluorescence frequency of acid and base; and (3) measurement of absorption frequency of both compounds; alternately, use of the average of absorption and fluorescence frequency. Of these methods, 1 and 2 are restricted to compounds which show fluorescence and to reactions which attain equilibrium during the lifetime of the fluorescing state; for the application of method 2, actually both the acid and base must fluoresce. Also, since almost all fluorescence occurs only from lowest singlet states, both methods 1 and 2 can be applied only to these excited states. Method 3, on the other hand, is rather general and can be applied to any higher excited states, provided pairs of corresponding states can be found.[6] This method, though in principle applicable, cannot readily be applied to triplet excited states, since singlet–triplet absorption in solution has never been observed. In a critical examination of these methods, Mason[7] has shown that all three methods give substantially identical results. On the other hand, Bartok[5] has used an average of fluorescence and absorption frequencies. Separation into two determinations, one by fluorescence, the other by absorption alone, leads to substantially diverging results. It appears likely that the divergence is fortuitous, since high accuracy is difficult to attain with fluorescence measurements.

The first attempt to correlate excited-state pK values of a series of substituted phenols[5a] using only three compounds failed. Subsequent work by the same authors,[5b] however, shows that this was mostly due to the most common difficulty of work in luminescence spectra—contamination—and that the pK^* values of the phenols actually show a reasonably good correlation with sub-

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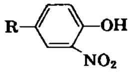
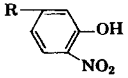
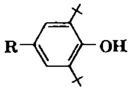
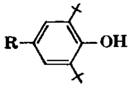
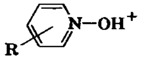
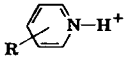
[6] H. H. Jaffé, D. L. Beveridge, and H. L. Jones, *J. Am. Chem. Soc.*, **86**, 2932 (1964); see also R. E. Ballard and J. W. Edwards, *Spectrochim. Acta*, **20**, 1275 (1964).

[7] J. C. Haylock, S. F. Mason, and B. E. Smith, *J. Chem. Soc.*, 4897 (1963).

TABLE I

REACTION CONSTANTS FOR EXCITED-STATE ACID–BASE EQUILIBRIA

Reaction	Ground state^a			Excited state										
					λ_{max}, mμ^b									
	Solvent	ρ	pK_0	Band	Acid	Base	Solvent	ρ^c	$S\rho^{*d}$	n^e	R^f	σ type	p$K_0{}^{*g}$	Ref.
ArCOOH	H_2O	1.00	4.20	^1L_b	273.0	268.0	H_2O	2.4	1.3	4^h	0.80	Any	6.17	*i*
				^1L_a	230.0	224.0	H_2O	4.4	0.3	19	0.95	σ^-	6.85	*i*
				^1B	210.0^j	202.0^j	H_2O	−1.8	0.2	4^k	0.98	σ^+	. . .	*i*
$ArNH_3{}^+$	H_2O	2.78	4.56	^1L_b	254.0	280.0	H_2O	2.9	0.2	$7^{k,l}$	0.98	σ^+	−2.93	*i*
				^1L_a	203.0	230.0	H_2O	14.5	1.4	14^l	0.95	σ^-	−4.23	*i*
ArOH	50% EtOH	2.67	11.16	^1L_b	271.0	288.0	50% EtOH	3.8	0.9	10	0.82	σ^-	6.85	*m*
				^1L_b	271.0	288.0	50% EtOH	1.6	0.3	6^l	0.95	σ^+	6.35	*m*
	H_2O	2.11	9.85	^1L_b	270.0	285.0	H_2O	1.8	1.0	13	0.50	σ^-	5.28	*n*
	H_2O	2.16	6.89	^1L_b	350.0	414.0	H_2O	2.6	0.1	10^l	0.99	$\sigma^\pm$	−2.19	*o*
	H_2O	3.01	7.22	^1L_b	350.0	418.0	H_2O	3.6	1.0	10^h	0.79	Any	−2.41	*p*
	50% EtOH	4.62	14.22	^1L_b	271.0	295.0	50% EtOH	3.8	0.7	5^l	0.97	σ^+	7.32	*m*
ArOH	H_2O	2.11	9.85	^1L_a	210.5	235.0	H_2O	5.6	1.7	13	0.71	$\sigma^\pm$	3.01	*i*
				^1L_a	210.5	235.0	H_2O	5.5	0.9	8^l	0.92	$\sigma^\pm$	1.35	*i*
ArOH	50% EtOH	2.67	11.16	^1L_a	211.0	232.0	50% EtOH	5.2	0.6	11^l	0.97	$\sigma^\pm$	2.13	*m*
	50% EtOH	4.62	14.22	^1L_a	214.0	244.0	50% EtOH	8.4	0.7	10^l	0.97	$\sigma^\pm$	2.09	*m*
ArSH	95% EtOH	2.85	9.21	^1L_a	237.0	270.0	100% EtOH	9.6^q	1.2	6	0.96	$\sigma^\pm$	−0.37	*r*
ArOH	H_2O	2.11	9.85	^1B	210.0^s	221.0^s	H_2O	10.0	4.6	7^t	0.71	σ^-	. . .	*i*
	H_2O	1.89	0.79	^1L_b	257.0	254.0	H_2O	8.0	1.7	6	0.92	σ^-	2.07	*u*
				^1L_a	217.0	205.0	H_2O	−2.8	2.6	8	0.40	σ^+	4.10	*u*
	H_2O	5.71	5.29	^1L_b	256.0	257.0	H_2O	5.0	2.4	19	0.45	$\sigma^\pm$	6.94	*v*
				^1L_b	256.0	257.0	H_2O	18.3	4.8	7^l	0.86	$\sigma^\pm$	1.50	*v*
				^1L_a	224.0^w	216.0^w	H_2O	9.7	1.1	5	0.98	σ^-	. . .	*v*
$ArC(OH)_2{}^+$	Aq. H_2SO_4	1.09	−7.26		260.0	235.0	Aq. H_2SO_4	5.4	1.0	23	0.75	σ^-	1.62	*x*
$ArCHOH^+$	Aq. H_2SO_4	1.85	−7.10		296.0	251.0	Aq. H_2SO_4	6.9	1.5	7	0.90	σ^-	5.46	*y*
$ArC(Me)OH^+$	Aq. H_2SO_4	2.17	−6.15		290.0	251.0	Aq. H_2SO_4	4.9	1.3	17	0.71	σ^-	7.02	*z*

$ArC(NH_2)OH^+$	Aq. H_2SO_4	1.30	−2.16		245.0	225.0	Aq. H_2SO_4	6.4	0.5	11	0.97	σ^-	5.05	[aa]
Ar_2COH^+	Aq. H_2SO_4				344.0	258.0	Aq. H_2SO_4	8.5	2.4	7	0.85	σ^-	12.87	[bb]
$ArCH{=}CHC(Ph)OH^+$	Aq. H_2SO_4	1.26	−5.17		415.0	308.0	Aq. H_2SO_4	3.8	0.5	5	0.97	σ^-	12.17	[cc]
$ArN{=}NPh$[dd]	20% EtOH	2.20	−3.00	^1B	419.0	322.0	20% EtOH	2.6	0.3	10	0.97	$\sigma^\pm$	13.62	[ee]
$ArN{=}NC_6H_4{-}NO_2$-*m*[dd]	20% EtOH	2.75	−4.61	^1B	412.0	316.0	20% EtOH	2.6	0.5	10	0.89	σ^-	11.24	[ff]
$ArN{=}NC_6H_4{-}OMe$-*p*[dd]	20% EtOH	1.80	−1.31	^1B	469.0	348.0	20% EtOH	2.2	0.4	7	0.94	σ^+	14.05	[gg]
$ArN{=}N(O)Ph$[dd]	20% EtOH	2.51	−6.57	^1B	395.0	322.0	20% EtOH	6.6	0.9	7	0.96	σ^-	3.23	[hh]
$ArCH{=}N{-}NHR$[ii]	50% dioxane	0.441	10.90	^1B	387.0	473.0	50% dioxane	3.1	0.1	12	0.99	$\sigma^\pm$	89	[jj]
$ArC(Me){=}N{-}NHR$[ii]	50% dioxane	0.511	11.18	^1B	385.0	468.0	50% dioxane	3.8	0.3	10	0.98	$\sigma^\pm$	.91	[jj]

[a] The values for ρ and pK_0 are from the same source as the excited-state constants; otherwise they are from H. H. Jaffé, *Chem. Rev.*, **53,** 191 (1953). [b] The values given are for the parent compound unless otherwise noted. [c] ρ^* is the exited-state reaction constant. [d] The standard deviation of experimental measurements from the regression line. [e] The number of compounds involved in the calculation of ρ. [f] The correlation coefficient. [g] The intercept of the regression line with ordinate ($\sigma = 0$). [h] *meta* substituents only. [i] J. M. Vandenbelt, private communication. [j] Value for *p*-methoxybenzoic acid. [k] Electron-repelling substituents only. [l] *para* substituents only. [m] L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85,** 3397, 3402 (1963). [n] W. Bartok, P. J. Lucchesi, and R. B. Hartman, *ibid.*, **87,** 0000 (1965). [o] M. Rapoport, C. K. Hancock, and E. A. Meyers, *ibid.*, **83,** 3489 (1961). [p] C. K. Hancock and A. D. H. Clague, *ibid.*, **86,** 4942 (1964). [q] The ground-state pK value of *m*-CO_2Me was used for the *m*-CO_2Et substituent. [r] S. I. Miller and G. S. Krishnamurthy, *J. Org. Chem.*, **27,** 645 (1962). [s] Value for *p*-carbomethoxythiophenol. [t] Electron-withdrawing substituents only. [u] H. H. Jaffé, *J. Am. Chem. Soc.*, **77,** 4451 (1955). [v] H. C. Brown and X. Mihm, *ibid.*, **77,** 1725 (1955); H. C. Brown and D. H. McDaniel, *ibid.*, **77,** 3752 (1955); S. F. Mason, *J. Chem. Soc.*, 219, 1282 (1960); S. F. Mason, *ibid.*, 1253 (1959). [w] Value for *m*-methoxypyridine. [x] R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **82,** 4059 (1960). [y] K. Yates and R. Stewart, *Can. J. Chem.*, **37,** 664 (1959). [z] R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **80,** 6355 (1958). [aa] J. T. Edward, H. S. Chang, K. Yates, and R. Stewart, *Can. J. Chem.*, **38,** 1518 (1960). [bb] R. Stewart, M. R. Granger, R. B. Moodie, and L. J. Munster, *ibid.*, **41,** 1065 (1963). [cc] D. S. Noyce and M. J. Jorgeson, *J. Am. Chem. Soc.*, **84,** 4312 (1962). [dd] Refers to the acid dissociation of the conjugate acids of the base. [ee] R. W. Gardner, M.S. Thesis, University of Cincinnati, 1957. [ff] S.J. Yeh, Ph.D. Thesis, University of Cincinnati, 1958. [gg] C.S. Hahn, Ph.D. Thesis, University of Cincinnati, 1961. [ii] R = $-C_6H_3$-2,4-$(NO_2)_2$. [jj] L. A. Jones and N. L. Mueller, *J. Org. Chem.*, **27,** 2356 (1962).

stituent constants. The next indication that Hammett correlations in excited states could be obtained came out of the recognition that Hancock's[8] correlations between $\Delta\nu$, the difference in absorption frequency between acid and base, and substituent constants implied a similar correlation for ΔpK = pK^* − pK, the difference between excited- and ground-state pK values.[9] These encouraging results led us to search for another series in which such correlations might be found, and to examine their generality. Since the only data required are the aborption spectra of acid and base, it appeared that data should be available for all series of compounds for which ground-state pK values had been determined by spectrophotometric methods.

The results of the literature search were disappointing. Data, obtained with reasonable care and reported in sufficient detail, were available only for a quite limited number of series. In a previous paper[9] we have reported a few of these which seemed encouraging. We hoped, by careful scrutiny of the available experimental material and by trial and error using different types of σ-values, to gain information concerning the types of resonance effects operating in the excited state and their importance.

Before proceeding further, it is worthwhile to inquire into the uncertainty of the pK^* values obtained in the manner used here. Some uncertainty arises, of course, from the failure of assumptions 1–3, discussed above; another, from an error in measurement, or more important, from determination of λ_{max} in absorption bands, which are frequently broad. This error is large. An error of 1 mμ at a wave length of 250 mμ translates into 0.33 pK units, *i.e.*, a factor of 2 in the equilibrium constant. Even at 350 mμ, 1 mμ corresponds to 0.17 in pK, *i.e.*, a factor of 1.5 in K. Errors of this magnitude are obviously serious; however, as will be seen below, the pK^* values in some series range over 10 or more pK units; consequently these spectroscopic errors may be tolerable. The error in the ground-state pK, which also enters the calculation, is probably negligible in comparison. Lack of correspondence of the electronic transitions examined may be another difficulty encountered when comparing series of excited-state pK value obtained by the method under discussion. A determined effort was made, and was probably successful, to compare only bands classified in any *formal* classification system as equivalent. However, this may not be sufficient, since spectra, as observed, never correspond completely to any classification system, but through configuration interaction are generally complex mixtures of different types of transitions; the make-up of these mixtures is sensitive to the nature of the substituents. Thus, while it is probably quite appropriate to characterize the benzoic acid spectrum in terms of ^1L_b and ^1L_a, and ^1B,[10] with only moderate amounts of intramolecular charge-transfer character, it is probable that for the spectrum of the nitrobenzoic acids this classification has largely broken down, and classification into local-

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(8) L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25,** 226 (1960); L. A. Jones and N. L. Mueller, *ibid.*, **27,** 2356 (1962).

(9) H. H. Jaffé, H. L. Jones, and M. Isaks, *J. Am. Chem. Soc.*, **86,** 2934 (1964).

(10) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962.

excited and charge-transfer states[11] becomes more appropriate. Consequently, it is not surprising that, frequently, the nitro compounds deviate most seriously from the correlation.

All series of reactions for which we have been able to find data are summarized in Table I. It is readily noted that few extremely good correlations are obtained. This is undoubtedly due to the large uncertainty in the pK^* values, discussed above. On the other hand, most of the series show moderately good correlations. A single glance at the ρ-values obtained shows that they are almost uniformly larger than the corresponding ground-state values.

Data have been obtained for several transitions in several series of compounds. Uniformly, where the assignment can readily be made, the ρ-values for the ^1L_a transitions are substantially larger than those for ^1L_b or ground states. The ρ-values for ^1L_b range from slightly smaller than ground state to about 2.5 times this value. The ^1B states, for which very little experimental material exists, are difficult to interpret; in the benzoic acids they give a *negative* ρ, the first case of a negative ρ for an acid dissociation on record. In the phenol series, on the other hand, they give a very large ρ (7.0).

Next, let us examine the type of substituent constant which gives the best correlation. It must be recognized, of course, that the separation into three types of substituent constants (σ, σ^-, and σ^+) is only a gross approximation[11]; however, the data available at this time is insufficient to apply the more refined breakdown of effects which have been proposed. In several of the series reported, the number of compounds is insufficient to make a clear distinction between the different constants; also, some of the correlations are too inexact to draw valid conclusions. Even in some of the best correlated and longest series, the determination cannot unambiguously be made. Thus, in the ^1L_b bands of the anilines, σ or σ^- (there are no electron-withdrawing substituents) gives $\rho = 5.1$, $r = 0.97$; σ^+ gives $\rho = 5.1$, $r = 0.97$. In the ^1L_a band, σ^+ gives $\rho = 14.5$, $r = 0.95$; σ^+ and σ^- (for electron-repelling and -withdrawing substituents, respectively) give $\rho = 10.7$, $r = 0.94$. Similarly, for the benzoic acids, for ^1L_a, σ^- gives $\rho = 4.4$, $r = 0.95$; σ^+ and σ^- give $\rho = 2.9$, $r = 0.92$. Thus, no definite conclusions can yet be reached.

One thing, however, is striking: throughout Table I, exalted σ-values, either σ^+, σ^-, or both, give the best correlation; in only a few cases would normal σ-values have served equally well. This fact appears to emphasize the tremendous importance of resonance effects in excited states, which are, of course, expected, since ionic resonance structures make much larger contributions to the excited states than to ground states.

Based on the recognition of the much larger importance of resonance effects in excited states, one might postulate that *meta*-substituted compounds alone would give good correlations, and that the exalted resonance effects of *para* substituents would show up as deviations of the *para*-substituted compounds from the *meta*-compound correlation.[12] This is definitely not the case. In a few series, sufficient data are available to obtain separate correlations for *meta* and *para* compounds. In most cases, the correlation of the *para* compounds alone is about equal or better than that for the *meta* compounds alone. In some cases, the *meta* compounds are almost completely uncorrelated (the ^1L_a bands of anilines give a ρ of 0.12 with an r of 0.02, although the pK^* values have a range of over 4 pK units); in other cases, both series are about equally well correlated, but with vastly different ρ-values (^1L_b of phenols, *para*, $\rho = 1.6$, $r = 0.86$; *meta*, $\rho = 8.3$, $r = 0.89$; pK values of the conjugate acids of benzamides, *para*, $\rho = 2.6$, $r = 0.88$; *meta*, $\rho = 4.8, r = 0.91$).

This different behavior of the *meta*-substituted compounds may be related to the completely different electron distribution in the excited state, as evidenced, *e.g.*, in the directive effects.[13] Consequently one may expect direct resonance effects to be transmitted from a substituent to a side chain attached in a *meta* position.

A few of the reaction series reported in Table I require special comment. In the ground state, it has previously been noted that the conjugate acids of the pyridine N-oxides behave very much like the phenols, with which they are isoelectronic.[14] No such correspondence is observed in the excited states; although the correlation for the heterocyclic series is poor, there seems no doubt that ρ is very large; the pK^* values vary over 22 pK units! The reason for this discrepancy probably lies in the high polarizability of the pyridine oxides[15] and the large amount of charge-transfer character in the excited state.

In the pyridine series the observations largely parallel those in the benzene series. The correlation for the basicities of the first excited state (^1L_b) of a long series of 3- and 4-substituted pyridines is poor; the 4-substituted compounds alone, however, give a much better correlation with a very large ρ (18), reflecting a very large range of pK^* values (5–15). Interestingly enough, a good correlation is encountered for a short series of pK^* values of the next higher state (^1L_a).

The pK_a values of several series of aromatic carbonyl compounds have recently been measured in aqueous sulfuric acid. The excited-state pK values of these compounds are more or less well correlated by σ^--values, in distinct contrast to the ground-state values, which require, as expected, σ^+-values. The reason for this discrepancy is not immediately obvious. That these correlations are at all successful seems somewhat surprising, since there seems little reason to believe that the absorption bands of the conjugate acid–base pair are corresponding.

It may be concluded, then, that excited-state pK values may be correlated by the Hammett equation with moderate precision. Such correlations appear equally successful for different excited states of the same series of compounds. The ρ-values for different states, however, vary widely. Resonance effects are

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(11) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen and Co. Ltd., London, 1963.

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(13) H. E. Zimmermann, *Tetrahedron Suppl.*, **2**, 393 (1963); *cf.* also R. Grinter and E. Heibronner, *Helv. Chim. Acta*, **45**, 2496 (1962).

(14) H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 4441 (1955); H. H. Jaffé, *J. Org. Chem.*, **23**, 1790 (1958).

(15) H. H. Jaffé, *J. Am. Chem. Soc.*, **76**, 3527 (1954).

of substantial importance, such that exalted σ-values (σ^+, σ^-, or both) are always required.

There is a strong suggestion, however, that *meta* and *para* compounds do not fall on the same correlation lines. It is suggested that, in excited states, *meta* substituents enter into direct resonance interaction with a side chain and that consequently ground-state σ_m-values do not apply.

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The Application of the Hammett Equation to Amidines

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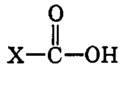
Ionization constants of C-substituted and of N-phenyl-C-substituted amidinium ions, of substituted guanidinium ions, and of 1-substituted 3-nitroguanidines were correlated with the Hammett equation using the σ_I, σ_m, and σ_p constants. The amidinium sets gave best results with σ_m, the guanidinium and nitroguanidine sets with σ_I. Correlation of the ionization constants of substituted ammonium, methylammonium, dimethylammonium, and diethylammonium ions were made, best results being obtained with σ_I. The results indicate that in guanidinium ions and guanidines which bear electron-acceptor substituents, proton transfer involves the nitrogen atom bearing the substituent. The electrical effect in C-substituted amidinium ions is believed to be due to a short-range localized effect. The major component of the localized electrical effect in substituted ammonium ions appears to be the inductive rather than the field effect.

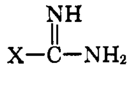
In the course of a previous investigation[1] we have studied the correlation of ionization constants of substituted carboxylic acids (I) with the Hammett equation.[2] As amides (II) are structural analogs of carboxylic acids, and are in fact iselectronic with them, it seemed of interest to study the correlation of their ionization constants with the Hammett equation. No previous correlation of simple amidines with the Hammett equation is extant in the literature. Jaffé[2] has correlated data of Lorz and Baltzly[3] on the ionization constants of 3- or 4-substituted N,N-dibutylbenzamidines (III).

$$Q_X = \rho\sigma_X + Q_H \qquad (1)$$



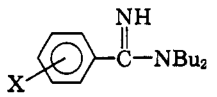
$$X-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

I



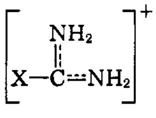
$$X-\overset{\overset{\displaystyle NH}{\|}}{C}-NH_2$$

II



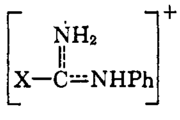
III

We have correlated ionization constants (pK_a values), obtained from the literature, for C-substituted amidinium ions (IV), C-substituted N-phenylamidinium ions (V), and 1-substituted guanidinium ions (VI), and for 1-substituted 3-nitroguanidines (VII), with the Hammett equation using the σ_I, σ_m, and σ_p constants. The correlations were made as described by Jaffé.[2] The data used are given in Table I. The σ_m and σ_p constants used were taken from the compilation of McDaniel and Brown,[4] and the σ_I constants used were from those given by Lewis and Taft,[5] whenever possible. Constants obtained from other sources are given in Table II. The results of the correlations are presented in Table III.



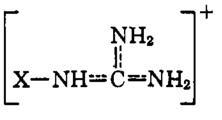
$$\left[X-\overset{\overset{\displaystyle NH_2}{\|}}{C}=NH_2\right]^+$$

IV



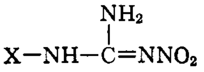
$$\left[X-\overset{\overset{\displaystyle NH_2}{\|}}{C}=NHPh\right]^+$$

V



$$\left[X-NH=\overset{\overset{\displaystyle NH_2}{\|}}{C}=NH_2\right]^+$$

VI



$$X-NH-\overset{\overset{\displaystyle NH_2}{|}}{C}=NNO_2$$

VII

In some cases statistical factors were necessary to provide a common basis for correlation. A statistical factor of $^2/_3$ was used for X = NH_2 in the C-substituted amidinium set as in the following reaction (i) and

$$[X-C(NH_2)_2]^+ + H_2O = X-C(NH)NH_2 + H_3O^+ \qquad (i)$$

guanidinium (X = NH_2) is $^3/_2$ times as likely to react as are the other members of the series. When X = PhNH in the C-substituted N-phenylamidinium set, a statistical factor of $^1/_2$ was used, as the ionizable proton is assumed to be that which is attached to the nitrogen bearing the phenyl group,[6] and there are two such ionizable protons in this member of the set. When X = H in the 1-substituted guanidinium ions, a statistical factor of $^1/_6$ was used since the ionizable proton in this set is assumed to be attached to the nitrogen atom bearing the strongest electron-acceptor substituent[6]; and when X = H there are six equivalent protons. In the 3-nitro-1-substituted guanidines when X = H, a statistical factor of $^1/_4$ was used since there are four equivalent protons.

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

[5] R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

[6] See discussion below.