

orbital is thus found to be in the range 0.7–0.3, which is all right as to magnitude even if somewhat high.

All this, we believe, tends to confirm the idea that the red shifts, especially going with 1- and 1,4-disubstitution, are caused principally by hyperconjugation.

Acknowledgment. We wish to thank Dr. Angelo Lamola for supplying us with pure *cis*- and pure *trans*-1,3-pentadiene; Dr. Carl Aufdermarsh for 1-chlorobutadiene, 2,3-dichlorobutadiene, and bis-2,2'-dibutadiene; and Dr. T. W. Koenig for helpful discussion.

Application of Linear Free Energy Relations to Electronically Excited States of Monosubstituted Phenols

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Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana. Received June 11, 1965

Protolytic dissociation of phenol and sixteen monosubstituted phenols in the lowest triplet and first excited singlet states has been investigated by means of fluorescence, phosphorescence, and ultraviolet absorption spectra. A treatment of the experimental data by means of the Hammett and Taft equations is presented. It is shown that excited-state acidities can be correlated well with ground-state substituent constants. Further evidence is provided for the concept that conjugative effects are much more important, relative to inductive effects, in electronically excited states than in the ground state. Direct resonance interactions between meta substituents are shown to be considerably more significant in excited singlet states than in the ground state; an approximate calculation of the magnitude of the effect is presented.

Introduction

The influence of substituent groups upon the rates and equilibria of reactions of aromatic compounds in their ground electronic states has received much study. Considerably less attention has been directed toward substituent effects on reactions of electronically excited molecules. Photochemical studies of Havinga² and Zimmerman³ indicated that substituent effects in electronically excited states may not always be predictable from ground-state chemical behavior.

Acidities of electronically excited molecules can be studied by fluorescence spectroscopy. In many cases, very striking changes in acidity are brought about by electronic excitation.⁴ Although acidities of many aromatic compounds have been determined in excited states, substituent effects upon excited-state acidities have received comparatively little attention. Bartok, Lucchesi, and Snider⁵ reported that the excited-state dissociation constants of phenol, *p*-chlorophenol, and *p*-cresol could not be correlated with Hammett sub-

stituent constants; more recently however, this conclusion has been rescinded.⁶ Jaffé and Jones⁷ have recently reported a treatment of excited-state acidities by means of the Hammett equation. Using data obtained solely from absorption spectra, these authors noted that, for a number of different types of compounds, excited-state acidities could be "correlated by the Hammett equation with moderate precision."⁷

The goal of the present study was to examine in detail the influence of substituents upon the excited-state dissociation of one class of compounds, monosubstituted phenols. We were particularly interested in ascertaining which factors improved (or decreased) a correlation of excited-state acidities with ground-state substituent parameters.

Experimental Section

The compound *p*-hydroxyphenyltrimethylammonium iodide was synthesized by the procedure of Hünig⁸ and then converted to the chloride, as described by Hepler.⁹ The synthesized compound was analyzed volumetrically for chloride; the experimental percentage chloride was 19.07%, compared with the theoretical value of 18.89%. All other phenols were commercial samples, purified by one or more of the following procedures: recrystallization, vacuum sublimation, vacuum distillation, column chromatography, or fractional freezing.

Water was purified by distillation from alkaline permanganate; absolute ethanol was distilled over reagent grade KOH which had been previously washed with ethanol to remove surface impurities.

Whenever feasible, ground-state dissociation constants for the phenols were taken from the literature. When this was not possible, pK_a values were determined spectrophotometrically,¹⁰ using carbonate and borate buffers described by Biggs.¹¹

Ultraviolet absorption spectra were measured using either a Bausch and Lomb Spectronic 505 or Cary

(1) (a) National Science Foundation Predoctoral Fellow, 1962–1965. Financial support from the Purdue Research Foundation is gratefully acknowledged. (b) Author to whom inquiries should be addressed at Indiana University, Bloomington, Ind.

(2) E. Havinga, R. O. de Jongh, and W. Dorst, *Rec. trav. chim.*, **75**, 378 (1956).

(3) H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915 (1963); H. E. Zimmerman and S. Somasekhara, *ibid.*, **85**, 922 (1963).

(4) For a review, see A. Weller, *Progr. Reaction Kinetics*, **1**, 189 (1961).

(5) W. Bartok, P. J. Lucchesi, and N. S. Snider, *J. Am. Chem. Soc.*, **84**, 1842 (1962).

(6) W. Bartok, quoted by H. H. Jaffé, H. L. Jones, and M. Isaks, *ibid.*, **86**, 2934 (1964).

(7) H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965).

(8) S. Hünig, *Chem. Ber.*, **84**, 1056 (1952).

(9) H. C. Ko, W. F. O'Hara, T. Hu, and L. G. Hepler, *J. Am. Chem. Soc.*, **86**, 1003 (1964).

(10) R. A. Robinson in "Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 16.

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

Model 11 recording spectrophotometer. Fluorescence and phosphorescence spectra were obtained with an Aminco-Bowman spectrophotofluorometer. The 1-cm. quartz cells used for absorption and fluorescence measurements were capped with rubber stopples and purged of air by bubbling nitrogen into the cells by means of hypodermic needles. Purging was necessary owing to the sensitivity of phenolate anions to air oxidation and because of the quenching action of oxygen.

Emission spectra were corrected for variations in source intensity and detector response with wave length using the procedure of Melhuish.¹² The wave length scales of both the absorption spectrophotometers and the fluorometer were calibrated using a General Electric AH-4 mercury arc.

Fluorescence and absorption spectra of undissociated phenols were obtained in 1 *M* aqueous sulfuric acid; those for the anion were measured in 0.1 *M* aqueous KOH. Phosphorescence spectra of phenols and phenolate anions were obtained in rigid glasses (77°K.) of 0.1 *M* ethanolic H₂SO₄ and 0.1 *M* ethanolic KOH, respectively.

Excited-state dissociation constants were calculated by the Förster cycle¹³ (at 298°K.)

$$pK_a - pK_a^* = (2.10 \times 10^{-3})(\Delta\bar{\nu}) \quad (1)$$

In eq. 1, K_a and K_a^* are the protolytic dissociation constants in the ground and excited states, respectively, and $\Delta\bar{\nu}$ is the frequency difference (in cm.⁻¹) of the 0-0 bands of the electronic transition in the acid and conjugate base. The 0-0 frequency for the lowest triplet \rightarrow singlet transition can be measured directly from the high frequency limit of phosphorescence. However, in the case of the lowest singlet \rightarrow singlet transition, the 0-0 frequency cannot be obtained directly from room temperature absorption or fluorescence spectra owing to spectral overlap; the 0-0 frequency for a given species was therefore estimated by averaging the frequencies of absorption and fluorescence maxima of that species.¹³

Results

The spectroscopic results are summarized in Table I. The absorption frequencies are those of the ¹L_b band, the transition which excites fluorescence in substituted benzenes. Since the fluorescence maxima are rather broad, the tabulated frequencies are, in most cases, averages of several determinations.

The calculated excited-state dissociation constants are compared with the ground-state values in Table II. In our notation, pK_a refers to the ground state, pK_a^* to the first excited singlet, and pK_a^T to the lowest triplet state. The phenols are considerably more acidic in their first excited singlet states than in either the lowest triplets or the ground states, as noted by Jackson and Porter¹⁴ for 1- and 2-naphthol.

Discussion

Biggs and Robinson¹⁵ have shown that the ground-state pK_a values of monosubstituted phenols can be

(12) W. H. Melhuish, *J. Opt. Soc. Am.*, **52**, 1256 (1962).

(13) A. Weller, *Z. Elektrochem.*, **56**, 662 (1952).

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

(15) A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

Table I. Absorption and Fluorescence Maxima for Phenols and Phenolate Anions^a

Substituent	Absorption		Fluorescence	
	$\bar{\nu}(\text{ArOH})$	$\bar{\nu}(\text{ArO}^-)$	$\bar{\nu}(\text{ArOH})$	$\bar{\nu}(\text{ArO}^-)$
H	37,000	34,950	33,450	29,750
<i>m</i> -F	37,300	35,600	33,300	29,850
<i>p</i> -F	36,100	34,000	33,000	29,900
<i>m</i> -Cl	36,500	34,250	32,800	29,950
<i>p</i> -Cl	35,700	33,550	32,200	28,400
<i>m</i> -Br	36,500	34,100	32,700	29,200
<i>p</i> -Br	35,700	33,450	32,050	28,100
<i>m</i> -CH ₃	36,750	34,550	33,000	29,400
<i>p</i> -CH ₃	36,100	33,900	32,250	28,700
<i>m</i> -C ₂ H ₅	36,750	34,500	33,100	29,650
<i>p</i> -C ₂ H ₅	36,000	33,900	32,350	28,850
<i>m</i> -OCH ₃	36,600	35,100	32,700	29,400
<i>p</i> -OCH ₃	34,700	32,800	30,200	27,700
<i>m</i> -OC ₂ H ₅	36,600	35,100	32,700	29,400
<i>p</i> -OC ₂ H ₅	34,950	32,900	30,100	27,550
<i>p</i> -SO ₃ ⁻	36,900	35,300	33,200	28,500
<i>p</i> -N(CH ₃) ₃ ⁺	37,000	34,850	33,450	29,200

^a All frequencies in cm.⁻¹.

Table II. pK_a Values for Phenols in the Ground and Excited States

Substituent	pK_a	Ref.	Log		Log		
			(K_x/K_0)	pK_a^* (K_x/K_0) [*]	pK_a^T (K_x/K_0) ^T	pK_a^T (K_x/K_0) ^T	
H	10.00	<i>a</i>	...	4.0	...	8.5	...
<i>m</i> -F	9.21	<i>a</i>	+0.79	3.8	+0.2	8.5	0.0
<i>p</i> -F	9.91	<i>a</i>	+0.09	4.4	-0.4	8.7	-0.2
<i>m</i> -Cl	9.13	<i>a</i>	+0.87	3.0	+1.0	7.6	+0.9
<i>p</i> -Cl	9.42	<i>a</i>	+0.58	3.2	+0.8	8.0	+0.5
<i>m</i> -Br	9.03	<i>a</i>	+0.97	2.8	+1.2	7.8	+0.7
<i>p</i> -Br	9.36	<i>a</i>	+0.64	3.1	+0.9	7.7	+0.8
<i>m</i> -CH ₃	10.09	<i>a</i>	-0.19	4.0	0.0	8.7	-0.2
<i>p</i> -CH ₃	10.26	<i>a</i>	-0.26	4.3	-0.3	8.6	-0.1
<i>m</i> -C ₂ H ₅	10.07	<i>b</i>	-0.07	4.1	-0.1
<i>p</i> -C ₂ H ₅	10.21	<i>b</i>	-0.21	4.3	-0.3
<i>m</i> -OCH ₃	9.65	<i>a</i>	+0.35	4.6	-0.6	8.4	+0.1
<i>p</i> -OCH ₃	10.21	<i>a</i>	-0.21	5.6	-1.6	8.6	-0.1
<i>m</i> -OC ₂ H ₅	9.54	<i>b</i>	+0.46	4.4	-0.4	8.5	0.0
<i>p</i> -OC ₂ H ₅	10.13	<i>b</i>	-0.13	5.3	-1.3	8.4	+0.1
<i>p</i> -SO ₃ ⁻	9.03	<i>c</i>	+0.97	2.4	+1.6	7.5	+1.0
<i>p</i> -N(CH ₃) ₃ ⁺	8.35	<i>d</i>	+1.65	1.7	+2.3

^a Reference 15. ^b This work. ^c E. E. Sager, M. R. Schooley, A. S. Carr, and S. F. Acree, *J. Res. Natl. Bur. Std.*, **35**, 521 (1945). ^d Reference 9.

correlated quite well by the Hammett equation

$$\log \left(\frac{K_x}{K_0} \right) = \sigma \rho \quad (2)$$

In a conventional Hammett plot, a best straight line described by the equation

$$\log \left(\frac{K_x}{K_0} \right) = 0.079 + 2.229\sigma \quad (3)$$

was obtained, and the value for the reaction constant ρ was 2.229.¹⁵ In the present work, eq. 3 has been used to calculate σ for the various substituents, which assures a "perfect" correlation of $\log(K_x/K_0)$ with σ in the ground state.

In Figure 1, a plot of the calculated ground-state σ values against $\log[K_x^*/K_0^*]$ is shown. The least-squares line is

$$\log \left(\frac{K_x^*}{K_0^*} \right) = 3.62\sigma - 0.27 \quad (4)$$

The reaction constant is 3.62 and the correlation coef-

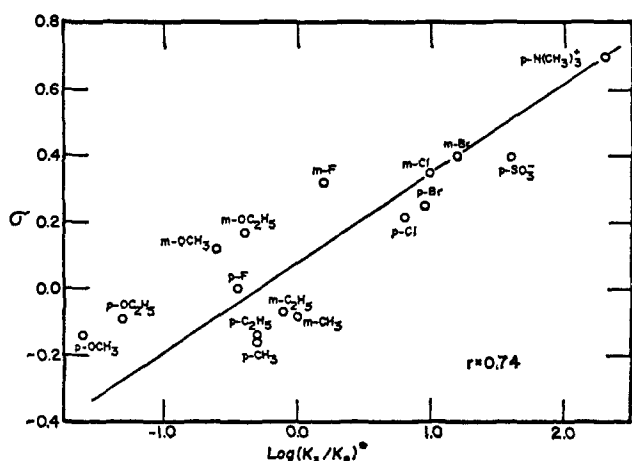


Figure 1. Hammett plot for the excited-singlet-state dissociation of phenols, using ground-state σ values calculated from eq. 3.

ficient r is 0.74.¹⁶ Earlier, Jaffe and Jones⁵ reported a correlation of excited-state acidity with ground-state substituent constants for the 1L_b transition of thirteen (unspecified) phenols. They found $r = 0.50$ and $\rho = 1.8$. In accounting for the relatively large difference in the correlation coefficients obtained by Jaffé and Jones⁷ and in the present study, at least three factors may be significant. First, it is likely that different compounds have been investigated in the present work. Second, Jaffé and Jones appear to have used σ^- , rather than σ , values for their correlation. Third, and most important, the excited-state pK_a values were calculated by different methods in the two studies. Jaffé and Jones utilized pK_a^* values calculated *only* from absorption maxima,⁷ whereas we have utilized *both* absorption and fluorescence spectra. To show that this is indeed a significant factor, we have used the frequencies of the absorption maxima in Table I to calculate pK_a^* values, which were then correlated with the same ground-state σ constants used to obtain the correlation in Figure 1. When only the absorption maxima are considered, the correlation coefficient obtained is 0.43, compared to the value of 0.74 obtained when both absorption and fluorescence frequencies are used. The correlation coefficient thus depends upon the method by which the excited-state pK_a values are calculated. For reasons discussed elsewhere,¹⁷ we believe the use of both absorption and fluorescence maxima is essential to the calculation of meaningful excited-state acidities.

The present work confirms the observation of Jaffé and Jones⁷ that there exists a statistically significant correlation between ground-state substituent constants and excited-singlet-state pK_a values. In light of the earlier work of Havinga² and Zimmerman,³ this result is very interesting; apparently the rules of ground-state chemistry may often be of considerable utility in semiquantitatively predicting the behavior of electronically excited molecules. It is also evident that the large increase in acidity produced by excitation is the primary effect, and the substituent perturbation in

(16) Correlation coefficients were calculated by the method of H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

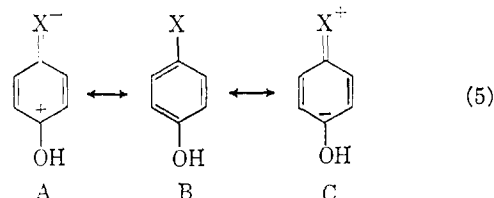
(17) E. L. Wehry and L. B. Rogers, *Spectrochim. Acta*, to be published.

the excited state behaves essentially as a second-order effect.

The Hammett correlation in Figure 1 can be improved if σ^+ , rather than ordinary σ , values are used, particularly for ethoxy- and methoxyphenols.¹⁸ The $\log(K_x/K_0)$ values for these compounds *decrease* in passing from the ground to first excited singlet state (Table II). Although the alkoxy groups exhibit electron-withdrawing inductive effects, they also exert electron-donating (acid-weakening) resonance effects. The above data can, therefore, be rationalized only by assuming that resonance effects become relatively more important in the first excited singlet state. In fact, this effect has been predicted theoretically.¹⁹

The excited-state Hammett correlation is also enhanced by using σ^+ for *p*-methyl- and *p*-ethylphenols. This may indicate increased electron-donating hyperconjugation in the first excited singlet states of these compounds.

The results for the halophenols also indicate enhanced conjugative interactions in excited states. Note in Table II that $\log(K_x/K_0)$ *increases* upon excitation for the bromo- and chlorophenols, but *decreases* for both *m*- and *p*-fluorophenols. Such behavior may be rationalized on the basis of enhanced conjugative interactions in the excited state. Chloro and bromo groups substituted onto an aromatic nucleus can engage in two types of resonance, either electron-attracting ($B \leftrightarrow A$) or electron-repelling ($B \leftrightarrow C$).



The former involves acceptance of π electrons by halogen d_π orbitals, while, in the latter, p_π orbitals of the halogen donate π electrons to the ring. In the ground state, both types of resonance are possible for $X = \text{Cl}$ or Br , but only the *acid-weakening* form is significant for $X = \text{F}$, because the fluorine d orbitals are too energetic to participate effectively in resonance with ring electrons.²⁰ The observed trend in excited halophenol acidities suggests that this statement is also true in the excited state, and that the resonance effects of the halogens far outweigh the inductive effects in the excited singlet state.

As Leffler and Grunwald²¹ have shown, the Hammett ρ - σ relationship involves more than one interaction mechanism; in fact, two interaction mechanisms (the inductive and conjugative effects) are usually assumed to apply. A linear Hammett plot for any given reaction should be obtained, *provided that the*

(18) σ^+ values were taken from H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(19) W. F. Hammer and F. A. Matsen, *ibid.*, **70**, 2482 (1948); H. Sponer, *J. Chem. Phys.*, **22**, 234 (1954); L. Goodman and H. Shull, *ibid.*, **27**, 1388 (1957).

(20) For a discussion of conjugative effects in halobenzenes, see L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963, pp. 393-401; V. Baliah and M. Uma, *Naturwissenschaften*, **21**, 512 (1958); L. Goodman and L. J. Frolen, *J. Chem. Phys.*, **30**, 1361 (1959).

(21) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York N. Y., 1963, pp. 192-194.

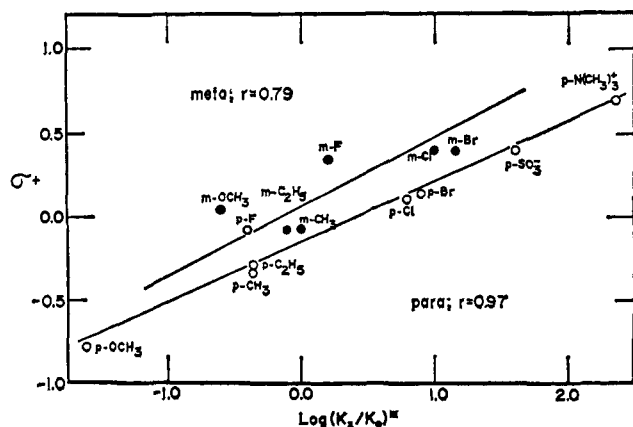


Figure 2. Hammett plot for the excited-singlet-state dissociation of phenols, using ground-state σ^+ values (except for $p\text{-SO}_3^-$ and $p\text{-N}(\text{CH}_3)_3^+$).

relative importance of the inductive and resonance effects remains relatively constant in the series of compounds under investigation. The fact that a satisfactory Hammett correlation is found for excited phenols indicates that the ratio of resonance to inductive effects is relatively constant for the excited phenols, but evidence indicates that the ratio is larger than in the ground state.

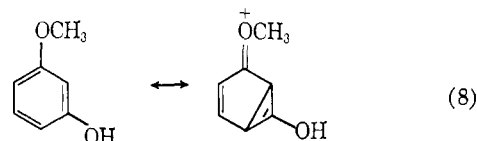
Despite the fact that $\log(K_x/K_0)$ increases upon excitation for the chloro- and bromophenols, a better Hammett correlation is obtained if σ^+ is used, instead of σ , for these compounds. The "improved" Hammett correlation is depicted in Figure 2. The least-squares line for the eight *para* substituents is

$$\log\left(\frac{K_x}{K_0}\right)^* = 0.41 + 2.68\sigma^+ \quad (6)$$

with $\rho = 2.68$. The correlation coefficient has the remarkably high value of 0.97. The correlation for *para*-substituted phenols is considerably better than that for the *meta*-substituted compounds. The least-squares line for the latter is

$$\log\left(\frac{K_x}{K_0}\right)^* = 2.37\sigma^+ - 0.14 \quad (7)$$

with $\rho = 2.37$ and $r = 0.79$. If, as discussed above, enhanced conjugative interactions occur in the excited state, this result may initially appear anomalous, since it is considered that resonance effects are considerably less important at *meta*, than at *para*, positions. Perhaps, as indicated by earlier studies,^{2,3,7} this statement is vitiated in excited states. For example, Table II shows that *m*-fluorophenol, *m*-methoxyphenol, and *m*-ethoxyphenol experience a decrease in $\log(K_x/K_0)$ upon excitation, even though the inductive effects alone are acid strengthening. Since the $-\text{F}$, $-\text{OCH}_3$, and $-\text{OC}_2\text{H}_5$ substituents can engage in electron-donating resonance, the present results provide additional evidence for the importance of direct resonance interactions between two functional groups situated *meta* to one another in electronically excited states. We may crudely pictorialize this statement by using Dewar structures



If Dewar structures indeed contribute significantly to the charge distributions of electronically excited phenols, one would not expect a good correlation between pK_a^* and σ (or even σ^+) for *meta*-substituted phenols, because the ground-state σ and σ^+ values do not allow sufficiently for the enhanced resonance interaction at *meta* positions in excited phenols.

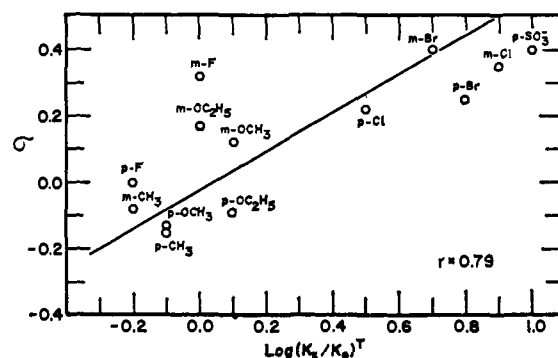


Figure 3. Hammett plot for the lowest triplet-state dissociation of phenols, using σ values calculated from eq. 3.

A semiquantitative evaluation of resonance effects at *meta* positions in excited state was carried out by use of the Taft equation²²

$$\log\left(\frac{K_x}{K_0}\right) = \sigma_I\rho_I + \sigma_R\rho_R \quad (9)$$

where the subscripts I and R denote inductive and resonance, respectively. Taft and Lewis²² have shown that

$$\sigma_I\rho_I = \left[\frac{1}{1-\alpha}\right] \left[\log\left(\frac{K_x^m}{K_0}\right) - \alpha \log\left(\frac{K_x^p}{K_0}\right)\right] \quad (10)$$

where α denotes the magnitude of the resonance effect at a *meta* position, compared to that of the same substituent at a *para* position. Rearranging eq. 10, we obtain

$$\alpha = \frac{\sigma_I\rho_I - \log(K_x^m/K_0)}{\sigma_I\rho_I - \log(K_x^p/K_0)} \quad (11)$$

To calculate α in the excited state, the various K values are replaced by the corresponding K^* values. We assume that the ground-state $\rho_I\rho_I$ values apply to the lowest excited singlet state. This assumption is reasonable on the basis of evidence which indicates that the transition from the ground to first excited singlet state of a benzene derivative is accompanied by enhanced conjugative interaction in the excited state, without any appreciable inductive effect on the transition energy.¹⁹ Table III lists α values calculated from ground- and excited-state K_x^m and K_x^p values for five substituents. These calculations indicate that, in the first excited singlet state, direct resonance inter-

(22) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958); *Tetrahedron*, **5**, 210 (1959).

Table III. Calculation of α in the Ground and First Excited Singlet States^a

Substituent	σ_1^b	α	α^*
F	+0.50	0.31	0.8
Cl	+0.47	0.37	0.8
Br	+0.45	0.25	0.6
OCH ₃	+0.23	0.28	0.6
CH ₃	-0.05	0.26	0.5

^a Using $\rho_1 = 2.229^{16}$; $\rho_1^* = 3.62$ from eq. 4. ^b Reference 22.

actions at *meta* positions are nearly as important as those at *para* positions.

A correlation between triplet-state acidities and ground-state σ values has also been made. Table II lists the $\text{p}K_a^T$ values obtained from phosphorescence spectra. The least-squares line for a plot of $\text{p}K_a^T$ vs. σ

(Figure 3) is

$$\log \left(\frac{K_x}{K_0} \right)^T = 1.72\sigma + 0.04 \quad (12)$$

with $\rho = 1.72$ and $r = 0.79$. However, the difference between the triplet- and ground-state acidity constants is so small that uncertainties in the determination of spectroscopic frequencies are much more significant in this case than for the lowest singlet state. Hence, other than demonstrating a statistically significant Hammett correlation in the lowest triplet state, no further treatment of the triplet-state data was attempted.

Acknowledgment. The authors wish to thank L. P. Hammett for helpful discussions.

Successive One-Electron Reduction Potentials of Porphins and Metal Porphins in Dimethylformamide

D. W. Clack and N. S. Hush

Contribution from the Department of Inorganic Chemistry, University of Bristol, Bristol 8, England. Received May 26, 1965

The reduction of a number of porphins, including tetra-benz- and tetraazaporphins, and their metal complexes, has been studied at a dropping mercury electrode in dimethylformamide. Either three or four one-electron steps are found, corresponding to the formation of mono-, di-, tri-, and tetranegative porphin ions. The disproportionation free energies of the ions are positive and (for a given ion charge) remarkably constant. Some aspects of the electronic structures of the porphins and of the metal complexes are discussed in the light of these results.

Introduction

The negative ions of a number of porphin, tetra-benzporphin, azaporphin, and phthalocyanine molecules and metal complexes have been prepared in 2-methyltetrahydrofuran solution by reduction with sodium metal.¹ The formation of the negative ions of zinc $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin by reduction with sodium benzophenone ketyl and sodium anthracene has also been studied in tetrahydrofuran solution.² Quantitative experiments showed that both mono-negative and dinegative ions were formed.

These ions—and perhaps ions in still more negative oxidation states—should also be formed by reduction of the porphins at a cathode in an aprotic solvent. In order to investigate this, we have examined the reduction steps of a number of porphins at a mercury electrode in dimethylformamide solution. Closs and Closs² have reported a two-step reduction of zinc $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin. Apart from this and some recent work³ using aqueous solutions (yielding tetrahydrophins as final reduction products), porphin reduction does not seem to have been much studied at

electrodes. This work forms part of a general investigation of the formation and properties of porphin ions.

Experimental Section

Current-potential measurements were made using a three-electrode cell at $20 \pm 1^\circ$. The dropping mercury electrode had a flow rate of 1.50 mg. sec.⁻¹ and a drop time of 4.0 sec. on open circuit. The anode was a mercury pool, and a saturated aqueous calomel electrode was used as a reference. The junction of the reference electrode and the solution was made through a ground-glass sleeve fitting the tapered end of the side arm of the calomel half-cell. No diffusion of water through this junction could be detected in the reduction experiments over periods of at least 2 hr.

The potential of the cathode was measured to ± 1 mv. using a Pye precision potentiometer. The current was determined by a null method, by backing off the potential drop resulting from the current flow across a precision resistor with an accuracy of $\pm 0.01 \mu\text{a}$. "White spot" nitrogen, which had previously been passed through a liquid nitrogen trap and a presaturator containing dimethylformamide and 0.1 M $\text{N}(n\text{-Pr})_4\text{-ClO}_4$, was bubbled through the solution for 15 min. before each experiment to remove oxygen and was passed continuously over the surface of the solution during the run. Each set of current-potential measurements was rechecked after 2 hr. Good agreement was found for the half-wave potentials. For some molecules, the wave heights were larger after the solutions had been left for this time. This was due to a concentration increase, as some of the porphins were very slow to dissolve at room temperature. The solvent used in all experiments was dimethylformamide containing $\text{N}(n\text{-Pr})_4\text{-ClO}_4$ (0.1 M).

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