Protolytic Dissociation of Electronically Excited Organic Acids*

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Förster[1] and Weller[2] have shown that excitation by the absorption of ultraviolet light enhances the acidity of certain aromatic acids in aqueous solutions. Thus, the values of the acid dissociation constant for the excited singlets of molecules such as 1- or 2-naphthol are larger by a factor of 10^6–10^7 than the corresponding ground state values. In the present study the effects of electronic excitation on the dissociation of para-substituted phenols were studied. The values of pK_a^* for the excited state were estimated from spectroscopic data. In contrast with the ground state pK values of 10.02 for phenol, 10.27 for para-cresol and 9.38 for para-chlorophenol which follow the Hammett Equation, excited state values of 5.7, −0.6 and 3.6 were obtained for the above compounds. Apart from the large increases in acidity as a result of excitation, the dissociation constants of the excited phenols could not be correlated. From measurements in viscous glycerine solutions, an increase in acidity of about the same magnitude as in aqueous solutions was calculated for excited 2-naphthol, but the corresponding change appeared to be somewhat larger for glycerine solutions of phenol.

The acid dissociation constants for the electronically excited states of a number of organic acids and bases are known.[1-7] Förster[1] and Weller[2] have shown that excitation by ultraviolet light greatly enhances the protolytic dissociation of weak aromatic acids such as 1-naphthol and 2-naphthol in aqueous media. This is reflected both by the increased rate of the forward dissociation reaction, and since equilibrium appears to be established in the excited state, also by the values of the dissociation constant. For excited singlet states these values are 10^6–10^7 times larger than the corresponding ground state values. In contrast with such large shifts in acidity observed for excited singlet states, Jackson and Porter found that the dissociation constants for the lowest triplet levels hardly differed at all from the ground state values for molecules such as 1- or 2-naphthol, acridine and 2-naphthylamine.[7]

As outlined by Weller,[2] the value of pK^* for the excited state can be estimated from absorption and fluorescence spectra, if equilibrium is established in the excited state.

Referring to the schematic energy diagram of Fig. 1, it follows from the thermochemistry of the system where both the acid and its conjugate base can be raised to electronically excited levels that,

$$\Delta E + E_d^* = \Delta E' + E_d \qquad (1)$$

where ΔE and $\Delta E'$ are the energy changes for the transition from the ground state to the first singlet levels of an acid and its anion, respectively. Heats of dissociation in the ground and the excited states are, respectively, E_d and E_d^*. Their difference can be expressed as

$$E_d - E_d^* = (\Delta G + T\Delta S) - (\Delta G^* + T\Delta S^*) \qquad (2)$$

where the ΔG and ΔS terms are free energy and entropy changes (excited state values are denoted by asterisks). Assuming that the entropy changes should be about equal in the ground and the excited states, i.e., $\Delta S \doteq \Delta S^*$, it follows that

$$\Delta G - \Delta G^* = -RT (\ln K_a - \ln K_a^*) = \Delta E - \Delta E' \qquad (3)$$

and

$$pK_a - pK_a^* = \frac{\Delta E - \Delta E'}{2.303RT} \qquad (4)$$

where K_a and K_a^* are the dissociation constants for the ground and excited states. The energy changes ΔE and $\Delta E'$ can be estimated from the frequencies measured at the maxima of the long wave length absorption and short wave length fluorescence by means of the relations

$$\Delta E = h\nu = h \frac{\nu_{ab} + \nu_{fl}}{2} \qquad (5)$$

for the acid, and

$$\Delta E' = h\nu' = h \frac{\nu_{ab}' + \nu_{fl}'}{2} \qquad (6)$$

for the anion. Thus the value of pK_a^* can be calculated if the value of pK has been determined independently. The results obtained by this spectroscopic method are in good agreement with pK_a^* values determined from quantum yields of fluorescence measured as a function of the pH of the system.[2] The latter method is free of the assumptions used in the spectroscopic calculations.

In the present work the effects of electronic excitation on the dissociation constants of para-substituted phenols were studied. Absorption and fluorescence spectra of phenol, p-cresol and p-chlorophenol and of the corresponding anions were measured in aqueous solutions.

Measurements were also made using glycerol as a solvent for phenol and 2-naphthol in order to obtain information on the effect of increasing the viscosity of the solvent.

Experimental

The absorption and fluorescence spectra of phenol, para-cresol and para-chlorophenol and of the phenolate, para-cresolate and para-chlorophenolate anions were measured in neutral water and in 0.1 M aqueous sodium hydroxide solutions, respectively. Fluorescence spectra of the acid molecules were also obtained using 0.1 M aqueous hydrochloric acid solutions. In addition to the phenols, the absorption and fluorescence spectra of 2-naphthol and of phenol were also determined in neutral glycerol (Eastman Kodak spectro-grade) and in glycerol solutions of 0.1 M sodium methoxide.

Solutions of all compounds (obtained from the Matheson Company, Matheson, Coleman and Bell Division) were prepared in 0.001 molar concentrations for spectroscopic measurements. In the preparative work a dry box under a nitrogen atmosphere was used in order to insure freedom from contamination by oxygen or by moisture in the case of non-aqueous systems. The solutions were thoroughly purged with nitrogen before use.

* Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

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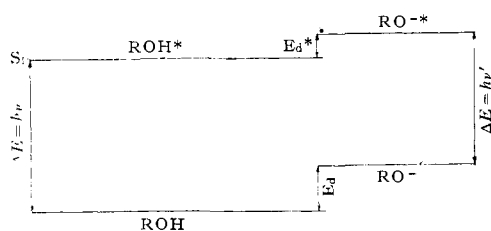
Fig. 1.—Schematic thermochemical diagram for the dissociation reactions: $ROH + H_2O \rightleftarrows RO^- + H_3O^+$ in the ground state; $ROH^* + H_2O \rightleftarrows RO^{-*} + H_2O$ in the excited state (after ref. 2).

Both absorption and fluorescence spectra were obtained using a Cary Model 11 Spectrophotometer. The instrument was converted for fluorescence studies by means of a special attachment. A mercury arc (Hanovia type "LO" burner) was used as the light source for excitation. The 2537Å mercury line was isolated using a 1.0 cm. path of 500 g./l. NiSO$_4$ solution in combination with a Corning 9863 red-purple Corex filter. Since the optical arrangement of the Cary attachment was such that the fluorescence was measured from the irradiated face of the solutions, the effects of self-quenching were kept to a minimum. The fluorescence spectra were obtained with corrections for background as required. Independent checks using the fluorescence modification of an Aminco-Keirs spectrophosphorimeter produced results in agreement with these measurements.

Results and Discussion

The data obtained on ultraviolet absorption by the compounds studied are summarized in Table I. As shown in the table, the results are in generally good agreement with the ultraviolet spectra of phenols published in the literature.[8-10]

TABLE I

ULTRAVIOLET ABSORPTION MEASUREMENTS

	Compound	Long wave length absorption maximum λ_{max}, mμ Literature	Present work
Aqueous	Phenol	270[a,b]	270
solution	Phenolate	288[a], 287[b]	288
	p-Cresol	277[b]	277
	p-Cresolate	295[b]	295
	p-Chlorophenol	279.5[a]	280
	p-Chlorophenolate	298[a]	298
	2-Naphthol	325[c], 328[d]	. .
	2-Naphtholate	345[c], 346[d]	. .
Glycerol	Phenol	. . . . . .	272
solution	Phenolate	. . . . . .	290
	2-Naphthol	. . . . . .	330
	2-Naphtholate	. . . . . .	349

[a] Ref. 9.   [b] Ref. 10.   [c] Ref. 2.   [d] Ref. 8 (in ethanol solution).

Table II presents a summary of the results obtained from the fluorescence spectra. For 2-naphthol and 2-naphtholate anions the agreement is satisfactory with previously published values.[2,8] In general, the fluorescence spectra were not sufficiently sharply defined to pinpoint the frequency at which the short wave length band had maximum intensity. This uncertainty was, of course, re-

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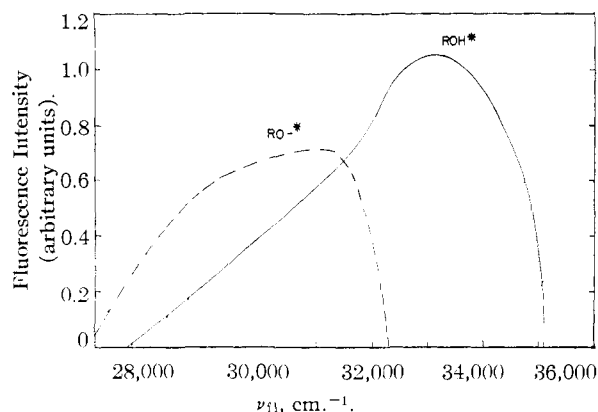

Fig. 2.—Fluorescence bands corresponding to the phenol molecule (ROH^*) and to the phenolate anion (RO^{-*}). The intensity values are normalized and do not represent the true relative intensities of the excited species involved. Curve --- is for RO^{-*} and — for ROH^*.

flected in all further calculations based on these spectroscopic measurements. The type of information obtained is illustrated in Fig. 2 by the fluorescence spectra of the phenol molecule and of the phenolate anion.

TABLE II

FLUORESCENCE MEASUREMENTS

	Compound	Short-wave length fluorescence maximum λ_{max}, mμ Literature	Present work
Aqueous	Phenol	. . . . . .	302
solutions	Phenolate	. . . . . .	320
	p-Cresol	. . . . . .	310
	p-Cresolate	. . . . . .	417
	p-Chlorophenol	. . . . . .	313
	p-Chlorophenolate	. . . . . .	351
	2-Naphthol	350[a], 358[b]	356
	2-Naphtholate	425[a], 429[b]	421
Glycerol	Phenol	. . . . . .	298
solutions	Phenolate	. . . . . .	341
	2-Naphthol	. . . . . .	357
	2-Naphtholate	. . . . . .	423

[a] Ref. 2.   [b] Ref. 8.

As expected, the fluorescence bands of the anions were located at lower frequencies than those corresponding to the undissociated molecules. Since the shift of the absorption bands of the phenol molecules and of the anions are of about the same magnitude for all these systems, the fluorescence shift is a measure of the change in acidity between ground and excited states. As discussed later, the unusually large change from 310 mμ for para-cresol to 417 mμ for the anion leads to a very large increase of acidity in the excited state.

In addition to the fluorescence spectra of phenols listed in Table II, the determination of the value of pK^* by this method was also attempted for para-nitrophenol. However, no fluorescence could be detected with solutions of this compound at any pH value, probably because of the quenching effect of the nitro-group.

The values of pK_a^* were calculated by combining Equations 4, 5 and 6, using the known pK_a values

for ground state dissociation reactions. These results are presented in Table III. The values indicate that the acidity of the compounds studied is greatly increased by excitation. However, while the Hammett equation holds very well for ground state acid dissociation constants,[11] it does not appear to be obeyed by the fluctuating pK_a^* values obtained for the excited species. In the case of para-cresol the very large change from pK_a = 10.27 to pK^* = −0.6 is unexpected in the light of the relatively small inductive effects of para-substituents compared with the influence of electronic excitation. This change in the pK values is several orders of magnitude larger than the estimated accuracy of the spectroscopic calculations. Furthermore, the same trend was qualitatively confirmed for para-cresol and para-chlorophenol by estimating energy changes for the electronic transitions from the short wave length limits of fluorescence.

TABLE III

AQUEOUS DISSOCIATION OF PHENOLS

Compound	Ground state $pK_a{}^a$	Hammett $\sigma{}^b$	Excited singlet state pK_a^*
Phenol	10.02	0	5.7 ± 0.7
p-Cresol	10.27	−0.170	-0.6 ± 0.5
p-Chlorophenol	9.38	0.227	3.6 ± 0.8

^{a} Ref. 11. ^{b} Ref. 10.

As shown in Tables I and II, the absorption and fluorescence spectra of 2-naphthol and of phenol were also obtained in neutral and basic glycerol solutions. In all cases, fluorescence was observed with higher intensities than measured from aqueous solutions of the same species. The location of the frequencies of maximum absorption and fluorescence intensities permitted the calculation of $(pK - pK^*)$ for these acids. Thus $(pK - pK^*)$ = 6.3 for 2-naphthol, a value which is in good agreement with the $(pK - pK^*)$ in aqueous solu-

(11) H. H. Jaffé, Chem. Revs., **53**, 199 (1953).

tion. However, for phenol a value of $(pK - pK^*)$ = 6.8 was calculated, i.e., about the "usual" increase due to excitation instead of $(pK - pK^*)$ = 4.3 determined for aqueous solutions of phenol.

The reason for the exceptionally large increase in the acidity of excited para-cresol is not understood. Since the ease of protolytic dissociation should be enhanced by an increased positive charge density at the phenolic oxygen atom, it may be argued tentatively on the grounds of resonance and induction effects that the methyl group of para-cresol could accommodate a positive change more easily than the chlorine atom of para-chlorophenol, and therefore para-cresol would be significantly more acidic than para-chlorophenol in the excited state. It is worth noting that para-cresol can undergo hyperconjugation, a factor which may in turn affect the ease of proton detachment from this molecule.

Quantum-chemical calculations carried out by Sandorfy[12] indicate that the increased acidity of the naphthols and of phenol due to excitation could be predicted from changes in charge-distributions. It may be worthwhile to see whether such calculations could also predict the exceptionally large increase in acidity of excited para-cresol. The effect of substitution on pK^* could also arise from differences in the reverse reaction rates for the recombination of protons with anions, rather than differences in the rates of proton detachment. Such a change caused by steric factors was suggested by Weller,[13] who found the value of the recombination rate constant reduced from 4.8×10^{10} l./(mole $\times$ sec.) for 2-naphthol to 2.1×10^{10} l./(mole $\times$ sec.) for 8-cyano-2-naphthol (excited state values). It is intended to extend the findings of the present work to other substituent groups and series of compounds.

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