# **936.** *Prototropic Equilibria of Electronically Excited Molecules. Part I. 3-Hydroxyquinoline.*

By J. C. Haylock, S. F. Mason, and B. E. Smith.

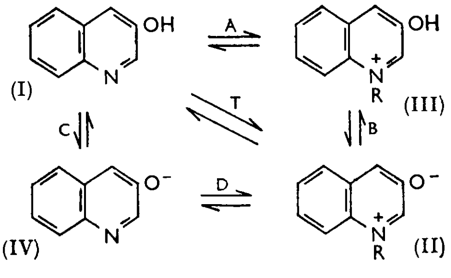
The absorption and the emission spectra of the four ionic species formed by 3-hydroxyquinoline in aqueous solution have been measured, and it is shown that a 2-naphthylmethyl anion model accounts for the observed band positions. The constants governing the prototropic equilibria between the four ionic species in the lowest electronically excited state are estimated from the transition energies, and, independently, from the change in the fluorescence spectrum with hydrogen-ion concentration. It is found that the hydroxy-group of 3-hydroxyquinoline is more acidic, and the ring-nitrogen atom more basic, in the excited than in the ground electronic state, as required by the 2-naphthylmethyl anion model, and that the difference between the free energy of ionic dissociation in the ground and the excited state is due primarily to a change in the heat, and not in the entropy, of ionisation.

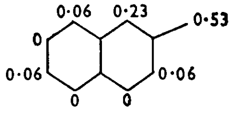
The study of the electronic absorption spectra of monocyclic heteroaromatic amines, and of hydroxy- and mercapto-compounds, has yielded a number of empirical generalisations relating the wavelength shifts observed to the ionic form of the compound, and to the position and the electronegativity of the heteroatoms.[1,2] Some of the same empirical spectroscopic generalisations are observed for the corresponding bicyclic compounds. Thus 3-hydroxyquinoline gives fluorescence maxima and long-wavelength absorption maxima (Table 1, Figs. 1 and 2) at wavelengths, dependent upon the ionic species, in the order, zwitterion (II) > anion (IV) > cation (III) > neutral form (I).

Table 1.

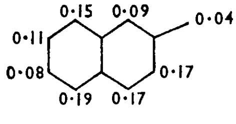
The long-wavelength absorption maxima and the fluorescence maxima of the various ionic species of 3-hydroxyquinoline in aqueous solution.

| Species | (I) | (II; R = H) | (II; R = Me) | (III; R = H) | (III; R = Me) | (IV) |
|---|---|---|---|---|---|---|
| $\lambda$ (abs.) (Å) | 3300 + 3215 | 3750 infl. | 3835 | 3410 | 3470 | 3490 |
| $\lambda$ (flu.) (Å) | — | 4650 | 4720 | 4100 | 4170 | 4240 |





(V)



(VI)

As in the monocyclic series,[2] the wavelength order is explained by a corresponding-carbanion model. The one-electron charge densities in the highest-occupied (V) and the lowest-unoccupied (VI) $\pi$-orbitals of the 2-naphthylmethyl anion give the change in orbital energy $\Delta E$, due to the replacement of carbon atoms by heteroatoms, through the expression,

$$\Delta E = \textstyle\sum_r c_r^2 \, . \, \Delta\alpha_r, \qquad (1)$$

where $c_r^2$ is the one-electron charge density at the position of the carbon atom r, replaced by a heteroatom with a Coulomb integral increment, $\Delta\alpha_r$, relative to the carbon atom.

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[1] Mason, *J.*, 1957, 5010.

[2] Mason, *J*, 1959, 1253; 1960, 219, 1282.

The Coulomb integral and the electronegativity of a conjugated atom are roughly proportional to one another, and the electronegativity orders, oxygen > nitrogen > carbon, and, positively charged atom > neutral atom > negatively charged atom, together with the one-electron charge densities in the highest-occupied (V) and lowest-unoccupied (VI) $\pi$-orbitals of the 2-naphthylmethyl anion, account qualitatively for the relative positions of the absorption and the emission maxima of the various ionic species formed by 3-hydroxyquinoline in aqueous solution.

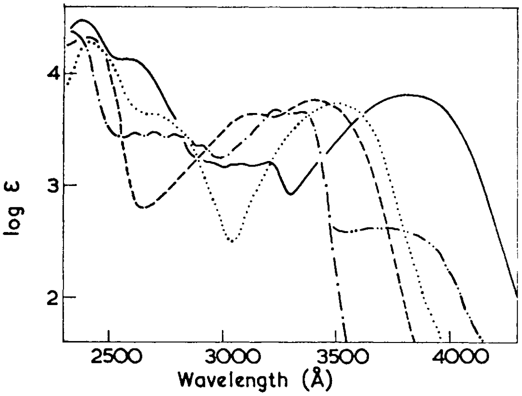

FIG. 1.

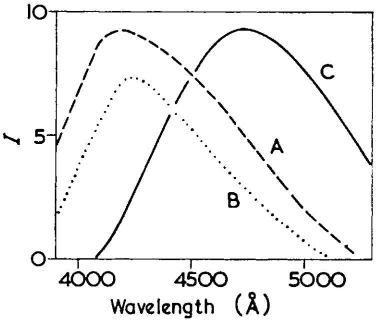

FIG. 2.

FIG. 1. The ultraviolet absorption spectra of 3-hydroxyquinoline in the cationic form (N/100-hydrochloric acid) (– – –), in the anionic form (pH 10·5) (· · ·), in the neutral form (ethanol) (· — · —), as the equilibrium mixture of neutral and zwitterionic forms (pH 6·15) (— · · —), and the 1-methyl derivative in the zwitterionic form (pH 10·5) (——).

FIG. 2. The emission spectra of 3-hydroxyquinoline (A) in the cationic form (10M-perchloric acid) and (B) in the anionic form (N/100-potassium hydroxide), and (C) of the 1-methyl derivative in the zwitterionic form (unbuffered aqueous solution).

Further, the 2-naphthylmethyl anion model indicates that on the promotion of an electron from the highest-occupied (V) to the lowest-unoccupied (VI) orbital, electronic charge migrates from the exocyclic atom to the atoms of the rings. If, as the spectroscopic evidence cited above suggests, similar charge shifts occur in the corresponding electronic transition of 3-hydroxyquinoline, the model requires that the hydroxyl group of this molecule should become more acidic, and the ring-nitrogen atom more basic, in the excited than in the ground electronic state.

In order to investigate the scope of the present molecular-orbital model, the constants governing the equilibria in aqueous solution between the four ionic forms (I)—(IV) of 3-hydroxyquinoline in the lowest electronically excited state have been estimated by two methods, both developed by Weller,[3] following earlier work by Forster[4] and by Weber.[5] In the first method, an approximate one, the equilibrium constants are obtained from the spectroscopically determined energy levels of the several ionic species (Fig. 3), and in the second, which depends upon a fast equilibration in the excited state, the constants are given by the variation of the fluorescence spectrum with the hydrogen-ion concentration of the solvent (Fig. 4).

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[3] Weller, " Progress in Reaction Kinetics," ed. Porter, Vol. I, Pergamon, London, 1961, p. 187.
[4] Forster, *Z. Elektrochem.*, 1950, **54**, 42.
[5] Weber, *Z. phys. Chem.*, 1931, *B*, **15**, 18.

The inter-level transition energies of an acid and its conjugate base, $\Delta E_{\mathrm{HA}}$ and $\Delta E_{\mathrm{A}}$, respectively, are related to the heat of ionisation, $\Delta H$, by

$$\Delta E_{\mathrm{HA}} + \Delta H^* = \Delta E_{\mathrm{A}} + \Delta H, \qquad (2)$$

where the starred and the unstarred quantity, $\Delta H$, refers to the excited and the ground electronic state, respectively (Fig. 3). If it is assumed that the entropy changes for corresponding prototropic equilibria in the ground and the excited state are the same, the reaction isotherm gives

$$\mathrm{p}K - \mathrm{p}K^* = (\Delta E_{\mathrm{HA}} - \Delta E_{\mathrm{A}})/\boldsymbol{R}T \log_e 10, \qquad (3)$$

where p$K$ and p$K^*$ refer to the negative logarithm of the acid dissociation constant in the ground and the excited state, respectively.

The ground-state p$K$ values governing the five prototropic equilibrium reactions between the four ionic forms (I)—(IV) of 3-hydroxyquinoline have been reported previously.[6] The wavelengths of the long-wavelength absorption maxima and of the emission maxima given by the four ionic species provide measures of the transition energies, $\Delta E_{\mathrm{HA}}$ and $\Delta E_{\mathrm{A}}$ (Fig. 3), and from the experimentally determined wavelengths (Table 1) the excited-state p$K^*$ values have been obtained (Table 2) by means of equation (3). The p$K^*$ values derived from the absorption and the emission wavelengths are in satisfactory agreement, and they show that in the lowest excited state the hydroxy-group of 3-hydroxyquinoline is more acidic, and the nuclear-nitrogen atom is more basic, than in the ground state, as required by the theoretical charge migrations due to the transition, (V) ⟶ (VI), given by the 2-naphthylmethyl anion model.

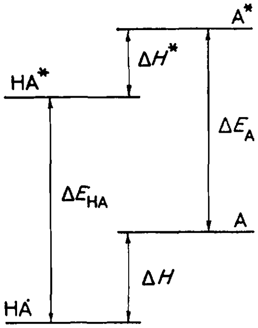

FIG. 3.

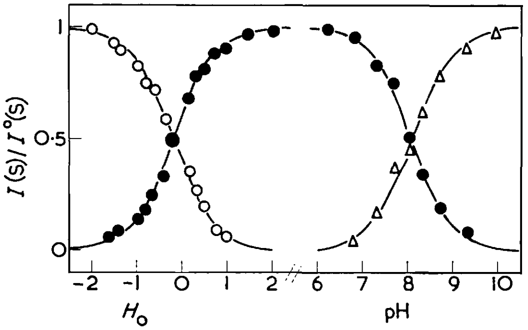

FIG. 4.

FIG. 3. The relation between the heats of ionisation ($\Delta H$) of an acid (HA) in the ground and the excited electronic state and the transition energies ($\Delta E$) of the acid and its conjugate base (A). Starred quantities refer to the excited electronic state.

FIG. 4. The relation between the corrected and normalised emission intensity $I(\mathrm{S})/I^{\circ}(\mathrm{S})$ of the ionic species (S) at the wavelength of the emission maximum and the acidity of the solvent expressed as pH or the Hammett acidity function, $H_0$. The ionic species of 3-hydroxyquinoline and the wavelengths used are (○) the cation (4100 Å), (●) the zwitterion (4700 Å), and (△) the anion (4200 Å). The theoretical curves refer to equilibria with p$K_{\mathrm{a}}$ values of $-0{\cdot}2$ and $8{\cdot}1$.

The assumption that the entropy changes are the same for corresponding prototropic equilibria in the ground and the excited state of a conjugated molecule may not be well founded, since the different charge distributions in the ground and the excited state give solvation entropies, due to the Born charging process,[7] which, in general, are not identical

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[6] Mason, *J.*, 1958, 674.

[7] Mason, *J.*, 1958, 808.

TABLE 2.

The p$K_a$ values of the equilibria in aqueous solution at 18° between the various ionic species of 3-hydroxyquinoline in the ground (p$K_a$) and the lowest excited (p$K_a^*$) electronic state. The methods used are calculation from the wavelength maxima of the absorption (abs.) and fluorescence (flu.), and from the variation of fluorescence spectrum with hydrogen-ion concentration (pH).

| Equilibrium | p$K_a$ § | p$K_a^*$ (abs.) | p$K_a^*$ (flu.) | p$K_a^*$ (pH) | Equilibrium | p$K_a$ § | p$K_a^*$ (abs.) | p$K_a^*$ (flu.) |
|---|---|---|---|---|---|---|---|---|
| A (III $\rightleftharpoons$ I) | 4·33 | 7·3 | | | D (II $\rightleftharpoons$ IV) | 6·84 | 11·1 | 11·3 |
| B (III $\rightleftharpoons$ II) | 5·52 | −0·3 | −0·5 | −0·2 | T (I $\rightleftharpoons$ II) | 1·19 | −7·6 | |
| C (I $\rightleftharpoons$ IV) | 8·03 | 3·6 | | | | | | |

§ Values quoted from Mason, *J.*, 1958, 674.

for the two states. However, the relative contributions of the heat and the entropy term to the difference between the p$K$ values in the ground and the excited state may be evaluated by determining the free energy of ionisation in the excited state from the variation in the fluorescence spectra of the ionic species in equilibrium with the hydrogen-ion concentration of the solvent.

In acid solution, over the acidity function range, $-H_0$ 2—5, 3-hydroxyquinoline and its 1-methyl derivative give a fluorescence band with a maximum intensity near to 4100 Å, due to the cation (III), whilst the parent compound over the pH range 2—6, and the 1-methyl derivative over the pH range 2—12, give an emission band, due to the zwitterion (II), with an intensity maximum near 4700 Å (Table 1, Fig. 2). In the pH range 10—13, 3-hydroxyquinoline gives a fluorescence band, which may be ascribed to the anion (IV), with an intensity maximum at 4240 Å (Table 1, Fig. 2). Fluorescence due to the neutral species (I) could not be detected, owing either to the dominance of the emission due to the 6% of zwitterion (II) present [1,6] in the ground state at neutral pH values, or to the rapid tautomerism of the excited neutral form (I) to the zwitterion (II), which is thermodynamically the more stable by some 10 kcal. mole$^{-1}$ in the excited state (Table 2).

As the acid concentration is increased from pH 2 to $-H_0$ 2, the intensity of the emission at 4700 Å falls whilst the fluorescence intensity at 4100 Å rises, and an approximate p$K$ value for the equilibrium between the cation (III) and the zwitterion (II) in the excited state is given by the pH or $H_0$ at which the emission intensity change attains one-half of its terminal value. The contributions of the cation (C) and the zwitterion (Z) to the total emission intensity at a given wavelength, $I_\lambda$, may be separated by using the approximate p$K$ value for the equilibrium between the ions, since

$$I_\lambda = I_\lambda(\mathrm{Z}) + I_\lambda(\mathrm{C}), \qquad (4)$$

and

$$I_\lambda(\mathrm{Z}) = [\mathrm{Z}]I_\lambda{}^\circ(\mathrm{Z}),\ I_\lambda(\mathrm{C}) = [\mathrm{C}]I_\lambda{}^\circ(\mathrm{C}), \qquad (5)$$

where [Z] and [C] are the fractional concentrations of the zwitterion and the cation, respectively, and $I_\lambda{}^\circ(\mathrm{Z})$ and $I_\lambda{}^\circ(\mathrm{C})$ are the emission intensities at the wavelength considered for the pH range 2—6 and the $-H_0$ range 2—5, respectively.

The observed emission intensity at 4100 Å, corrected by equations (4) and (5) for the small contribution (Fig. 2) from excited zwitterionic species at this wavelength, gives, when normalised as the quotient $I(\mathrm{C})/I^\circ(\mathrm{C})$, the fractional concentration of the cation [C] in the equilibrium mixture of excited species. Similarly, the emission intensity at 4700 Å, corrected for the contribution from the excited cations (Fig. 2), gives the fractional concentration of the zwitterion in the mixture of excited species as the quotient $I(\mathrm{Z})/I^\circ(\mathrm{Z})$.

The estimates of the fractional concentrations of excited-zwitterion and excited-cation species are independent, and they sum to unity in the acidity range, pH 2 to $-H_0$ 2, indicating that pH-dependent quenching effects are not important in this range (Fig. 4). Further, the fractional concentrations plotted as a function of the acidity of the solvent follow the theoretical curves required by a p$K^*$ value of −0·2 for the constant governing the equilibrium between the zwitterionic and the cationic forms of 3-hydroxyquinoline in the excited state (Fig. 4). This $pK^*$ value measures directly the free energy of the acid dissociation of the cation to the zwitterionic form in the electronically excited state, and it does not differ greatly from the corresponding values derived by means of equation (3) from the wavelengths of the absorption and the fluorescence maxima (Table 2) on the assumption that the entropy changes are the same for analogous prototropic equilibria in the ground and the excited state of a given molecule. Thus the assumption is well founded in the present case, and it is concluded that the difference between the free energies of ionic dissociation in the ground and the lowest-excited electronic state of the cation (III) is due primarily to a change in the heat and not in the entropy of ionisation.

A similar treatment of the emission intensity changes at 4200 Å and 4700 Å with hydrogen-ion concentration over the pH range 6—10 yields an acid dissociation constant with the $pK$ value of 8·1 (Fig. 4). The second acid dissociation constant of 3-hydroxyquinoline, determined potentiometrically,[8] has the value, $pK_a$ 8·06, so that the changes in the fluorescence spectrum observed near to pH 8 reflect the ground-state ionisation process. The reaction between the hydrogen ion and the anion of 3-hydroxyquinoline is probably diffusion-controlled, having a rate constant of the order of $10^{10}$ l. mole$^{-1}$ sec.$^{-1}$, but at pH 8 the fluorescent emission, with a rate constant of $\sim 10^8$ sec.$^{-1}$, is faster than the protonation by a factor of $\sim 10^6$, so that equilibrium between the anion (IV) and either the zwitterion (II) or the neutral form (I) is not established within the lifetime of the excited states of these species.

On the other hand, the equilibrium between the cation (III) and the zwitterion (II) of 3-hydroxyquinoline is established within the lifetime ($\sim 10^{-8}$ sec.) of the excited species, since the reaction between the hydrogen ion and the zwitterion is also probably diffusion-controlled, so that in M-acid the pseudo-first-order rate constant for the protonation of the excited zwitterion, and the first-order constant for the acid dissociation of the excited cation, are of the order of $10^{10}$ sec.$^{-1}$.

## EXPERIMENTAL

*Materials.*—These were as in ref. 1.

*Absorption Spectra.*—These were measured with a Hilger Uvispek quartz spectrophotometer. The solvents were N/100-hydrochloric acid for the cations (III; R = H and Me), ethanol for the neutral form (I), and 0·01M-phosphate buffers with pH 6·15 for the mixture of neutral (I) and zwitterionic (II; R = H) forms, and pH 10·5 for the anion (IV) and the zwitterion (II; R = Me).

*Fluorescence Spectra.*—These were measured with a Hilger glass, constant-deviation wavelength spectrometer, fitted with a IP28 photomultiplier in place of the eyepiece. The fluorescence was excited by the 3650 Å lines of a 125 w high-pressure mercury lamp by the frontal irradiation of a rectangular glass cell containing a boiled-out aqueous $10^{-4}$M-solution of 3-hydroxyquinoline or its 1-methyl derivative. The cell was fitted with a nitrogen bubbler, a mechanical stirrer, and a glass and a calomel electrode connected to a pH-meter for the measurement of the change in fluorescence intensity at selected wavelengths with hydrogen-ion concentration. The fluorescence spectra (Fig. 2) were measured in 10M-perchloric acid, unbuffered aqueous solution, and N/100-potassium hydroxide, for the cationic (III; R = H and Me), zwitterionic (II; R = Me), and the anionic (IV) species. Hydroxide ions weakly quench the fluorescence of the anion (IV), and chloride ions have a similar effect upon the fluorescence of the cation (III). The fluorescence spectra (Fig. 2) were corrected for spectrometer and photomultiplier response by means of a calibration curve based upon the established [9] quantum emission spectrum of quinine hydrogen sulphate.

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[8] Albert and Phillips, *J.*, 1956, 1294.

[9] Melhuish, *J. Phys. Chem.*, 1960, **64**, 762.