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Effect of medium relaxation on the acidity constants of electronically excited states obtained by the Förster cycle method

Willem H. Mulder*

Department of Chemistry, The University of the West Indies, Mona Campus, Kingston 7, Jamaica, WI

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Abstract

The theoretical basis for the calculation of acid dissociation constants in the lowest excited singlet or triplet state of organic compounds has been reexamined in light of a recent study on solvatochromism. A mathematical analysis based on the Onsager cavity model reveals that the absorption or emission frequency of an acid and its conjugate base, as they appear in the Förster equation, should be replaced with the averages of absorption and emission frequencies corresponding to the 0–0 transition of acid and base, respectively, in order to account for Franck–Condon effects on the free energy balance. The free energy of spontaneous medium relaxation is found to be the same for absorption and emission, and proportional to one-half of the Stokes shift.

The main premise of the proposed method, besides the obvious requirement that both the acid and its conjugate base should fluoresce or phosphoresce, is that each excited state exists long enough for equilibrium with the medium to be established prior to emission.

Keywords: Acid–base equilibrium constants; Lowest excited singlet state; Förster cycle; Franck–Condon effect; Onsager cavity model; Excited-state dipole moments; Stokes shifts

1. Introduction

The evaluation of acidity or basicity constants of excited organic or inorganic compounds has been a topic of continued and growing interest among chemists and biologists since the early 1950s [1–3].

The reasons are obvious. For example, the information contained in the excited-state acidity constant K_a^* is very useful in acquiring some insight into the redistribution of electronic charge accompanying the transition.

In a more quantitative sense, knowledge of K_a^* is necessary in establishing Hammett correlations for different substituted compounds, with a view to verify the applicability of linear free energy relationships to excited states. Experimental studies by Favaro et al. [4] and by Baldry [5] on 4′-substituted 3-styrylpyridines, by Gnanasekaran and coworkers [6] on 2,4-dinitrophenylhydrazones of substituted acetylbiphenyls and acetylfluorenes, or by Aaron et al. [7] on substituted indoles, indeed seem to support the generalisation of such relationships to include excited states.

A knowledge of K_a^* is also prerequisite to determine rate constants of protonation in the excited state, once the deprotonation rate constant is known from quantum yield measurements in decay experiments performed at different pH [8].

Ground-state pK_a values can be easily obtained, e.g., spectrophotometrically or potentiometrically.

The pK_a^* value can only be determined indirectly, however, since in most cases its value does not correspond to a realistic, normally attainable state because the lifetimes of excited states are usually much shorter than the time necessary to establish acid–base equilibrium (the latter being typically on the order of 10^{-8} s), while quenching, especially of the protonated form, may proceed at a much faster rate, further hampering the equilibration process.

The most widely used method for obtaining pK_a^* is based on a simple thermodynamic device known as a Förster cycle [1] (see Fig. 1), which gives rise to the Förster equation (see Section 3, Eq. (19)). Other, more direct, methods are fluorescence titration [9] (which uses the pH dependence of the fluorescence intensities of both members of the conjugate acid/base pair) and triplet–triplet absorption [3] (where an acid or base in buffered solution is first promoted to the lowest-lying triplet state by flash photolysis).

Although of these three, the Förster method apparently is the easiest to apply, the literature exposes a persistent confusion regarding the choice of the frequencies ν_A

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* Fax: +1-876-977-1835.

E-mail address: wmulder@uwimona.edu.jm (W.H. Mulder).

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and ν_{B} that are to be substituted in the Förster equation [10].

Some authors prefer to use only the frequencies corresponding to the low-frequency maxima in the absorption bands of acid and base [6,11], while others use the high-frequency maxima in the fluorescence (or phosphorescence) bands [12]. Most commonly, however, an averaging of the frequencies of absorption and emission maxima of acid and base separately is believed to yield the most reliable approximation to ν_{A} and ν_{B}, respectively [13].

This latter procedure is based on the expectation that averaging will eliminate the solvent relaxation, or Franck–Condon, effects that inevitably accompany absorption and emission processes.

It is the aim of this paper to provide a more rigorous theoretical basis for this approach, and outline its limitations. The analysis of Franck–Condon corrections in the following sections closely follows that given in a recent treatment of solvatochromism [14] which, inter alia, takes into account the effect of electrolyte on Stokes shifts, an aspect that will prove equally pertinent to the present investigation.

2. Analysis of the Förster cycle: definition of standard state

The Förster cycle is shown in Fig. 1 for the case of a monoprotic acid ($\mathrm{A} \rightleftharpoons \mathrm{B} + \mathrm{H}^+$).

Since we are interested in the pK_{a} of the acid/base equilibrium in the excited state, the appropriate thermodynamic quantity in terms of which the cycle should be analysed is the standard Gibbs energy (and not the enthalpy, as is usually seen in the literature).

First of all, it needs to be understood exactly what is meant by "standard conditions" in the present context, as the definition slightly departs from the usual convention.

In the case of an ionic species i that is also endowed with a dipole moment, the standard state corresponds to a hypothetical solution in which the ion is present at standard concentration c^θ (e.g., $1\,\mathrm{mol\,dm^{-3}}$), while at the same time ion–ion interactions with other ions in solution are thought of as having been "switched off" (this could be brought about by an imaginary discharging process). Interaction between ions is explicitly accounted for in the usual manner via a term $kT \ln f_i$ in the chemical potential (where f_i is a single-ion activity coefficient), whereas deviations from standard concentration are contained in the term $kT \ln(c_i/c^\theta)$. The chemical potential can thus be written as

$$\mu_i = \mu_i^0 + kT \ln\left(\frac{f_i c_i}{c^\theta}\right) \tag{1}$$

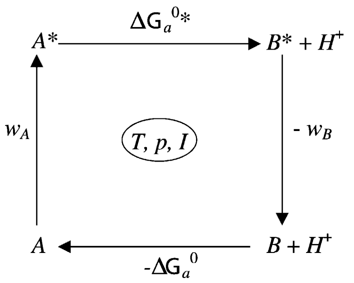

Fig. 1. The Förster cycle for a monoprotic acid at constant temperature, pressure and ionic strength. Standard free energy changes are indicated for the various stages of the cycle.

From the definition of f_i it follows that the standard chemical potential μ_i^0 must contain a contribution due to electrostatic interactions between the dipole on an ion of type i and the charges on the other ions (if dipole–dipole interactions among solutes are neglected). It is therefore to be regarded as a function, not only of temperature, but also of the ionic strength, I, of the solution. With the definitions

$$\Delta G_{\mathrm{a}}^0 = \mu_{\mathrm{B}}^0 + \mu_{\mathrm{H}^+}^\theta - \mu_{\mathrm{A}}^0 = 2.303kT\mathrm{p}K_{\mathrm{a}} \tag{2a}$$

$$\Delta G_{\mathrm{a}}^{0*} = \mu_{\mathrm{B}}^{0*} + \mu_{\mathrm{H}^+}^\theta - \mu_{\mathrm{A}}^{0*} = 2.303kT\mathrm{p}K_{\mathrm{a}}^* \tag{2b}$$

$$w_{\mathrm{A}} = \mu_{\mathrm{A}}^{0*} - \mu_{\mathrm{A}}^0 \tag{2c}$$

$$w_{\mathrm{B}} = \mu_{\mathrm{B}}^{0*} - \mu_{\mathrm{B}}^0 \tag{2d}$$

the standard free energy balance for the Förster cycle then reads

$$\Delta G_{\mathrm{a}}^{0*} = \Delta G_{\mathrm{a}}^0 + w_{\mathrm{B}} - w_{\mathrm{A}} \tag{3}$$

or, equivalently:

$$\mathrm{p}K_{\mathrm{a}}^* = \mathrm{p}K_{\mathrm{a}} - \frac{w_{\mathrm{A}} - w_{\mathrm{B}}}{2.303kT} \tag{4}$$

Since it may be safely assumed that activity coefficients f_i are independent of the electronic state of an ion, we can set $f_i^* = f_i$. As a consequence, the corresponding terms in Eq. (4) cancel, so that K_{a} and K_{a}^* can be taken to denote concentration products for the given solution (i.e., at the prevailing ionic strength, I). This is so because, in an actual experimental situation, both ground and excited-state acids and bases are present in the same electrolytic medium.

The quantity w_{A} should be interpreted as a free energy change, equal to the work of forming an excited-state acid molecule or ion, characterised by a permanent dipole moment of magnitude $\mu_{\mathrm{p,A}}^*$ (not to be confused with the symbol for chemical potential!), from its ground state which has dipole moment $\mu_{\mathrm{p,A}}$. The term w_{B} is defined similarly.

It would certainly be incorrect to identify w with the quantum of energy $h\nu$ absorbed from the light source, because the latter corresponds to a transition from the ground state to an excited (Franck–Condon) state to which the medium only responds via an instantaneous change in its electronic polarisation. This is followed by a relatively slow relaxation of solvent dipole moments and rearrangement of ions as the medium adapts to the new dipole moment, leading to a new equilibrium (provided the excited state survives long enough). This process is accompanied by a negative free energy change, ΔG_{FC}, that has to be added to $h\nu$. Hence:

$$w = h\nu + \Delta G_{\mathrm{FC}} \tag{5}$$

In the next section, the different terms in Eq. (5) will be calculated separately, based on results obtained in a previous study on solvatochromism in the presence of electrolyte.

3. Calculation of pK_a^*: connection with solvatochromic shifts

Based on the definitions given in the preceding section, w can be written as the resultant of three contributions (see Fig. 2):

(i) The photon energy $h\nu_0$, absorbed by the molecule or ion if present in a vacuum. This transition is accompanied by a change in dipole moment from μ_{p} to μ_{p}^*.

(ii) The electrostatic stabilisation energy of the excited-state dipole in solution:

$$w_{\mathrm{el}}^* = \frac{1}{2}\alpha^* E_{\mathrm{r}}^2(\vec{\mu}^*) - \int_0^{\vec{\mu}^*} \vec{E}_{\mathrm{r}}(\vec{\mu}')\cdot \mathrm{d}\vec{\mu}' \tag{6}$$

where α^* is the (supposedly isotropic) polarisability of the excited molecule, while $\vec{E}_{\mathrm{r}}(\vec{\mu}')$ denotes the reaction field of the medium acting on the dipole $\vec{\mu}'$ in response to its presence.

The first term on the right-hand side equals the work of polarisation, the second term is the free energy of the interaction between the dipole and its polarised environment.

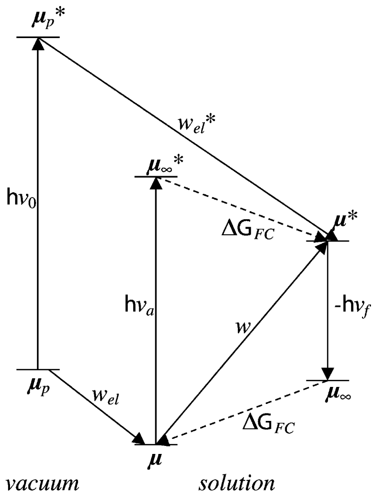

Fig. 2. Relationships among free energies for an absorption, emission, relaxation cycle between the lowest vibrational levels of the electronic ground state and first excited state (0–0 transition) of a single acid or base molecule or ion. Dipole moments in the different states are also shown (see text for an explanation of the symbols).

In Ref. [14] it was shown that if, in accordance with the classical Onsager model [15], the molecule is represented as a point dipole (possibly superimposed on a charge) located at the centre of a spherical cavity of constant radius a [16], the reaction field is equal to

$$\vec{E}_{\mathrm{r}}(\vec{\mu}) = \frac{2\vec{\mu}}{4\pi\varepsilon_0 a^3}\,\frac{\varepsilon'-1}{2\varepsilon'+1} \tag{7}$$

where ε' is an apparent dielectric constant that effectively takes into account the contribution to $\vec{E}_{\mathrm{r}}$ due to the average redistribution of ions about the dipole:

$$\varepsilon' = \varepsilon\left(1 + \frac{(\kappa a)^2/2}{1+\kappa a}\right) \tag{8}$$

where ε is the dielectric constant of the solvent and κ the reciprocal Debye length:

$$\kappa = \sqrt{\frac{2F^2 I}{\varepsilon\varepsilon_0 RT}} \tag{9}$$

where F is the Faraday constant.

In deriving Eq. (7), it had to be assumed that I is not too high, such as to keep the value of κa well below 1.

(iii) The third contribution to w is the negative of the electrostatic stabilisation energy of the ground-state dipole:

$$w_{\mathrm{el}} = \frac{1}{2}\alpha E_{\mathrm{r}}^2(\vec{\mu}) - \int_0^{\vec{\mu}} \vec{E}_{\mathrm{r}}(\vec{\mu}')\cdot \mathrm{d}\vec{\mu}' \tag{10}$$

with symbols defined analogously to those in Eq. (6).

Thus

$$w = h\nu_0 + \frac{1}{2}\alpha^* E_{\mathrm{r}}^2(\vec{\mu}^*) - \frac{1}{2}\alpha E_{\mathrm{r}}^2(\vec{\mu}) - \int_{\vec{\mu}}^{\vec{\mu}^*} \vec{E}_{\mathrm{r}}(\vec{\mu}')\cdot \mathrm{d}\vec{\mu}' \tag{11}$$

In Eqs. (6), (10) and (11) and Fig. 2, $\vec{\mu}$ and $\vec{\mu}^*$ are the total dipole moments in the ground state and excited state, respectively, in equilibrium with their surroundings, whereas in Fig. 2, $\vec{\mu}_\infty^*$ and $\vec{\mu}_\infty$ represent the dipole moments immediately after absorption or emission of a photon with energy $h\nu_{\mathrm{a}}$ or $h\nu_{\mathrm{f}}$, respectively.

Using the relationship

$$\vec{\mu} = \vec{\mu}_{\mathrm{p}} + \alpha \vec{E}_{\mathrm{r}}(\vec{\mu}) \tag{12}$$

which is valid for the equilibrium ground state, and introducing the scaled polarisability $\alpha' = \alpha/4\pi\varepsilon_0 a^3$, it follows, together with Eq. (7), that

$$\vec{\mu} = \frac{2\varepsilon'+1}{2\varepsilon'+1-2\alpha'(\varepsilon'-1)}\vec{\mu}_{\mathrm{p}} \tag{13}$$

and

$$\vec{E}_{\mathrm{r}}(\vec{\mu}) = \frac{2(\varepsilon'-1)}{2\varepsilon'+1-2\alpha'(\varepsilon'-1)}\,\frac{\vec{\mu}_{\mathrm{p}}}{4\pi\varepsilon_0 a^3} \tag{14}$$

If it can be assumed that α^* and α are approximately equal, substitution of Eqs. (13) and (14) and the corresponding expressions for the excited-state dipole into Eq. (11) yields

$$w = h\nu_0 - \frac{\mu_{\mathrm{p}}^{*2} - \mu_{\mathrm{p}}^2}{4\pi\varepsilon_0 a^3}\,\frac{\varepsilon'-1}{2\varepsilon'+1-2\alpha'(\varepsilon'-1)} \tag{15}$$

Note that this result is valid whether or not the acid is ionic, provided that dielectric saturation effects are negligible in which case ionic and dipolar fields are independent and simply superimposed.

From the treatment of solvatochromic shifts in the presence of electrolyte [14], the following expression was obtained for the energy difference between the ground state and the lowest excited Franck–Condon state corresponding to the 0–0 transition (see Fig. 2):

$$\begin{aligned} h\nu_{\mathrm{a}} = h\nu_0 - \frac{\vec{\mu}_{\mathrm{p}}^{*} - \vec{\mu}_{\mathrm{p}}}{4\pi\varepsilon_0 a^3} \cdot \Bigg\{ & \frac{2(\varepsilon' - 1)}{2\varepsilon' + 1 - 2\alpha'(\varepsilon' - 1)}\vec{\mu}_{\mathrm{p}} \\ & + \frac{(n^2 - 1)(\vec{\mu}_{\mathrm{p}}^{*} - \vec{\mu}_{\mathrm{p}})}{2n^2 + 1 - 2\alpha'(n^2 - 1)} \Bigg\} \end{aligned} \tag{16}$$

where n is the refractive index of the solution. In the case of an emitting compound with a sufficiently long-lived excited singlet or triplet state, the fluorescence or phosphorescence energy is given by a similar equation:

$$\begin{aligned} h\nu_{\mathrm{f}} = h\nu_0 - \frac{\vec{\mu}_{p}^{*} - \vec{\mu}_{\mathrm{p}}}{4\pi\varepsilon_0 a^3} \cdot \Bigg\{ & \frac{2(\varepsilon' - 1)}{2\varepsilon' + 1 - 2\alpha'(\varepsilon' - 1)}\vec{\mu}_{\mathrm{p}}^{*} \\ & - \frac{(n^2 - 1)(\vec{\mu}_{\mathrm{p}}^{*} - \vec{\mu}_{\mathrm{p}})}{2n^2 + 1 - 2\alpha'(n^2 - 1)} \Bigg\} \end{aligned} \tag{17}$$

Comparing Eqs. (16) and (17) with Eq. (15) immediately leads to the interesting result

$$w = h(\nu_{\mathrm{a}} + \nu_{\mathrm{f}})/2 \equiv hc\bar{\tilde{\nu}} \tag{18}$$

introducing the symbol $\bar{\tilde{\nu}}$ to denote the average of the absorption and emission wavenumbers.

Substitution of Eq. (18) into Eq. (4) produces the following important relationship:

$$\mathrm{p}K_{\mathrm{a}}^{*} = \mathrm{p}K_{\mathrm{a}} - \frac{hc}{2.303kT}(\bar{\tilde{\nu}}_{\mathrm{A}} - \bar{\tilde{\nu}}_{\mathrm{B}}) \tag{19}$$

This formula can of course only be used if the requirements for its applicability are fulfilled. First of all, both the acid and its conjugate base should emit upon return to their respective ground states from excited states that persist long enough for equilibrium to have been established prior to fluorescence or phosphorescence. Secondly, ground-state and excited-state polarisabilities should at least be approximately equal.

Another interesting corollary to the theory developed so far follows after substitution of Eqs. (16)–(18) into Eq. (5), leading to

$$\begin{aligned} \Delta G_{\mathrm{FC}} & = -h\frac{\nu_{\mathrm{a}} - \nu_{\mathrm{f}}}{2} \\ & = -\frac{(\vec{\mu}_{\mathrm{p}}^{*} - \vec{\mu}_{\mathrm{p}})^2}{4\pi\varepsilon_0 a^3} \\ & \quad \times \left(\frac{\varepsilon' - 1}{2\varepsilon' + 1 - 2\alpha'(\varepsilon' - 1)} - \frac{n^2 - 1}{2n^2 + 1 - 2\alpha'(n^2 - 1)} \right) \end{aligned} \tag{20}$$

which is obviously negative, as it should be, and applies to both absorption and emission, as also indicated in Fig. 2. Hence, under the stated conditions and assumptions, the Gibbs energy liberated during the spontaneous relaxation of the solute–medium system from a Franck–Condon state is simply proportional to the Stokes shift $(\tilde{\nu}_{\mathrm{a}} - \tilde{\nu}_{\mathrm{f}})$ for the 0–0 transition under consideration.

To conclude this section, a comment concerning the consequences of incomplete medium relaxation for the value of $\mathrm{p}K_{\mathrm{a}}^{*}$, as obtained with Eq. (19), is in order.

It must be remembered that premature fluorescence will only invalidate Eq. (17). In the most extreme case where no medium reorganisation occurs at all, $\tilde{\nu}_{\mathrm{f}}$ coincides with $\tilde{\nu}_{\mathrm{a}}$. For intermediate cases, $\tilde{\nu}_{\mathrm{f}}$ is always less than $\tilde{\nu}_{\mathrm{a}}$, but higher than the value predicted by Eq. (17). Consequently, $hc\bar{\tilde{\nu}}$ will always tend to overestimate w.

The errors introduced by substituting the experimentally obtained values for $\bar{\tilde{\nu}}_{\mathrm{A}}$ and $\bar{\tilde{\nu}}_{\mathrm{B}}$ into Eq. (19) will therefore partially compensate each other, thereby mitigating the effect on $\mathrm{p}K_{\mathrm{a}}^{*}$ to some extent.

4. Discussion

The theory of excited-state acidity constants presented in this paper hinges on a description of medium relaxation, consequent upon electronic transitions, in terms of a classical continuum model for the solvent. This treatment is in line with that of solvatochromism, as it has been applied, with varying success, to the determination of excited-state dipole moments [17].

Other factors that, no doubt, contribute to the values of absorption and emission frequencies are a dynamic red shift [18], dispersion forces between solute and solvent [19], and, sometimes, hydrogen bonding. These are usually considered small with respect to electrostatic effects. In the present application, which depends on the difference between two average frequencies, one pertaining to an acid, the other to its conjugate base, such contributions are likely to cancel out for the most part anyway.

The averaging of frequencies in the Förster equation (19) had been advocated previously by some authors, but only on semi-quantitative or intuitive grounds. The choice of frequencies to be substituted in this equation (absorption-only, emission-only, or averages) is rather critical, as the individual Stokes shifts and acid–base frequency gaps are often of the same order of magnitude.

In Sections 2 and 3, a more rigorous quantitative approach is taken, which also highlights the conditions under which this procedure can be expected to give reasonable results. First of all, acid and base should both be emitters with lifetimes of the excited states exceeding the typical medium relaxation time. Whenever the latter requirement is not met, a dynamic analysis based on, e.g., the Debye model for solvent relaxation becomes necessary. Here, no attempt has been made to allow for incomplete relaxation but in this case, again, some cancellation of errors can be anticipated, as pointed out at the end of Section 3. Secondly, it is essential for the applicability of Eq. (18) that polarisabilities of ground and excited-state molecules or ions are practically equal. If this is not the case, extra terms arise in Eqs. (16) and (17) that depend on the difference $(\alpha^* - \alpha)$, but which do not appear in the corrected version of Eq. (15) [20].

An important feature of Eq. (19) is that it automatically makes allowance for the fact that the acid–base pair is present in an electrolyte solution at finite ionic strength, I.

To the lowest order, the electrolyte effect on the free energy of excitation, w, is proportional to $(\kappa a)^2$, and hence, varies linearly with I, as may be verified by substituting ε' from Eq. (8) into Eq. (15), and expanding the resulting expression in terms of the small parameter κa.

Although the electrolyte-induced shifts in wavelength are usually very small (on the order of a few nanometers), the effect on $\mathrm{p}K_\mathrm{a}^*$ can be substantial. For example, at a (gas-phase) wavelength of 300 nm, a 4 nm shift already amounts to a change by one log unit.

Yet another advantage of the present approach, compared to most of the earlier treatments, is that the Förster cycle is analysed directly in terms of free energy, rather than enthalpy. In this way, one avoids the kind of needless speculation regarding the values of standard molar dissociation entropies ($\Delta\bar{S}_\mathrm{a}^0$ and $\Delta\bar{S}_\mathrm{a}^{0*}$) that seems to pervade the literature on this topic [10].

As a matter of fact, the difference in standard entropy of acid dissociation between ground and excited state is obtained simply by taking the temperature derivative of Eq. (3), after substitution of Eq. (18), as follows:

$$\Delta\bar{S}_\mathrm{a}^{0*} - \Delta\bar{S}_\mathrm{a}^{0} = Lhc\left(\frac{\partial(\bar{\tilde{\nu}}_\mathrm{A} - \bar{\tilde{\nu}}_\mathrm{B})}{\partial T}\right)_{\mathrm{p},I} \qquad (21)$$

where L is Avogadro's constant.

An explicit assumption in the derivation of the Förster equation, as it is usually presented in the literature, is that this difference can be taken to be equal to zero. According to Eq. (21), the correctness of this assertion can be tested by measuring the temperature dependence of $\bar{\tilde{\nu}}_\mathrm{A}$ and $\bar{\tilde{\nu}}_\mathrm{B}$. However, we are really dealing with a non-problem here, for, in case Eq. (19) does not produce the correct $\mathrm{p}K_\mathrm{a}^*$, this should be attributed to factors unrelated to this issue, as has been argued in this contribution.

Finally, it should be noted that the theory expounded in this paper could also be applied, with minor modification, to other types of excited-state dissociation processes or rearrangement reactions such as intramolecular proton transfer [21].

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