Estimation of pK_a* in the First Excited Singlet State

A Physicial Chemistry Experiment that Explores Acid–Base Properties in the Excited State

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The chemistry of an electronically excited species of a molecule may differ markedly from that of its counterpart ground-state state species. The lifetime of the former is very short, for example, 10^{-7}–10^{-9}s for the first excited singlet state of typical organic compounds; further, the geometry and electronic charge distribution can be quite different than in the ground state. For a chemist, however, the most interesting features of this state are the changes in chemical properties and the reactivity of these excited species. They can take part in various chemical reactions (photochemical reactions) different from those in the ground state; however, they can also take part in the same type of reactions as can molecules in the ground state. In this latter case the difference in their reactivity can be observed in the difference in the values of rate constants and equilibrium constants when the reactions are studied. Acid–base reactions are interesting example reactions that can occur both in the ground and excited states for the same compound.

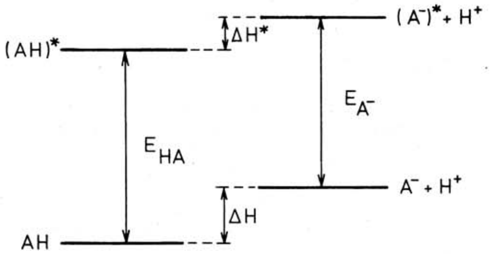

Figure 1. Electronic energy levels of an acid AH and its conjugate base A^- in the ground and excited states (the Förster cycle).

The acid–base reactions in excited states are some of the most elementary processes both in photochemistry and biochemistry and are, therefore, well-suited to form the basis for an undergraduate physical chemistry experiment. To acquaint our students with this phenomenon, we have chosen a simple experiment to illustrate the proton transfer reaction in the excited state.

Acid–Base Reactions in the Ground and Excited States

Let us discuss the following equilibrium in aqueous solutions in the ground state:

$$AH + H_2O \rightleftarrows A^- + H_3O^+ \qquad (1)$$

where AH and A^- symbolize acid and conjugated base, respectively. The equilibrium constant for eq 1 in dilute solution is given by

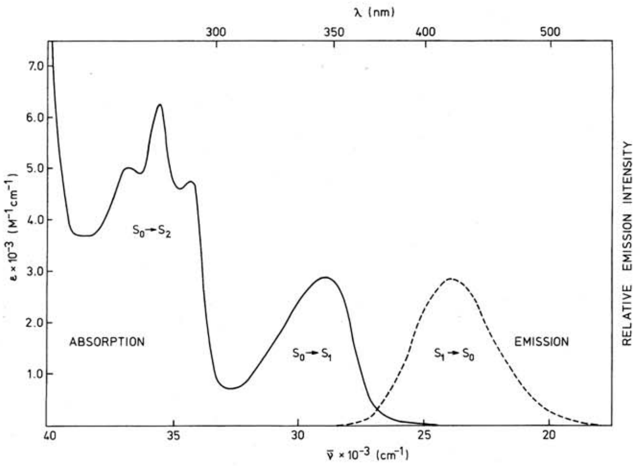

Figure 2. Absorption and fluorescence spectra of 2-naphthol in 0.1 M HCl.

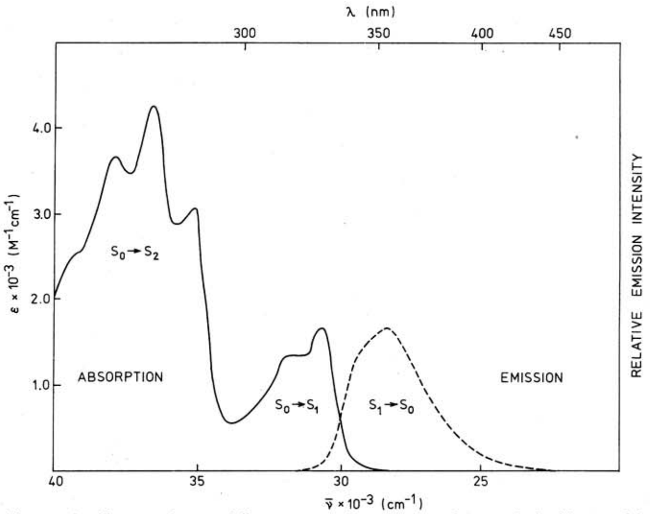

Figure 3. Absorption and fluorescence spectra of 2-naphthol in 0.1 M NaOH.

$$K_a = \frac{[A^-]\,[H_3O^+]}{[AH]}$$

and is expressed in terms of pK_a ($pK_a = -\log_{10} K_a$).

The value of pK_a depends on the electronic charge distribution. Since electronic excitation can modify charge densities, variations in acidity between the ground and excited states can be observed. The acid–base equilibrium in the electronically excited state is expressed as follows:

$$(AH)^* + H_2O \rightleftarrows (A^-)^* + H_3O^+ \qquad (2)$$

with the equilibrium constant K_a^* ($pKa^* = -\log_{10} K_a^*$). Since proton exchange can be a very fast process, an acid–base equilibrium between excited $(AH)^*$ and $(A^-)^*$ molecules can be established, in spite of the short lifetime of the excited species.

Several methods based on fluorescence intensity and lifetime measurements have been employed to determine the pK_a^* values of the lowest excited singlet state (*1–3*). We suggest applying a simple and less time-consuming method based on determination of the energy gap between the ground and excited singlet states of the conjugated acid and base. The thermodynamic cycle employed in this case is known as the "Förster cycle" (*4*). This method has been successfully used by various authors for many years (see refs *1–3*). Let us consider a diagram of the electronic states for equilibria 1 and 2 (see Fig. 1).

The difference in excited-state energies of the the HA and A^- forms can be expressed as the difference in enthalpy changes for reactions 1 and 2:

$$E_{HA} - E_{A^-} = \Delta H - \Delta H^* \qquad (3)$$

Using the relation $\Delta G = \Delta H - T\Delta S$, one can obtain:

$$E_{HA} - E_{A^-} = (\Delta G + T\Delta S) - (\Delta G^* + T\Delta S^*) \qquad (4)$$

where ΔG and ΔG^* are free energy changes of reaction in the ground and excited states and ΔS and ΔS^* are entropy changes of reaction in the ground and excited states.

Assuming that the entropy of dissociation is the same in both the ground and excited states (ΔS does not change appreciably upon excitation, see ref. *5*), approximating the changes of ΔG, ΔH, and ΔS to the standard values, and using the relation $\Delta G = -RT \ln K_a$, the following equation can be obtained:

$$E_{HA} - E_{A^-} = \Delta G - \Delta G^* = -RT(\ln K_a - \ln K_a^*) \qquad (5)$$

And finally:

$$pK_a - pK_a^* = \frac{E_{HA} - E_{A^-}}{2.3RT} \qquad (6)$$

where R is the gas constant (8.31 J $mol^{-1} K^{-1}$), T is temperature (K), and E_{HA} and E_{A^-} are the energies of the electronic transitions for the conjugated acid and base determined as the O–O transition energies.

In the majority of absorption and fluorescence spectra in solutions it is not so simple to determine the O–O transition precisely. An estimate may be made by taking the value from the region where the absorption and fluorescence spectra of both acid and base overlap. These values can be estimated, for example, by averaging the frequencies of absorption and fluorescence maxima of both acid and base forms:

$$E_{HA} = Nhc\frac{\bar{\nu}^a_{HA} + \bar{\nu}^f_{HA}}{2}$$

$$E_{A^-} = Nhc\frac{\bar{\nu}^a_{A^-} + \bar{\nu}^f_{A^-}}{2} \qquad (7)$$

where $\bar{\nu}^a$ and $\bar{\nu}^f$ are wavenumbers (cm^{-1}) for the maxima of absorption and fluorescence spectra, respectively; N is the Avogadro constant (6.022×10^{23} mol^{-1}); h is the Planck constant (6.625×10^{-34} Js); and c is the speed of light in vacuum (3×10^8 ms^{-1}).

This method is usually employed for the spectra with well-resolved vibrational structure and, in this case, $\bar{\nu}^a$ and $\bar{\nu}^f$ represent O–O transitions in absorption and fluorescence, respectively. When vibrational structure is not observed in the absorption and fluorescence spectra, the O–O transition can be estimated as the wavenumber corresponding to the intersection point of mutually normalized absorption and emission spectra. Spectroscopic determination of O–O transitions in solutions for HA and A^- forms has been recently discussed in reference *5*.

In the following experiment, the value of pK_a^* for the lowest excited singlet state of 2-naphthol is determined using, a Förster cycle. This experiment illustrates, in a simple way, the change of acid–base properties in the excited state as well as provides some basic knowledge about absorption and luminescence spectroscopies. It has been performed for more than five years in our laboratory (undergraduate course in physical chemistry) and has shown a high degree of reliability in student hands.

Excited Singlet State pK_a* Values for 2-Napthol in H_2O

Förster cycle	Fluorescence titration[a]	Kinetic analysis[b]
3.1 ± 0.3 (this work[c])	–	–
3.0 ± 0.1 (this work[d])	–	–
2.5–3.1 (*2,3*)	2.8–3.0 (*2,3*)	–
2.8 ± 0.1 (*8*)	2.6 ± 0.1 (*8*)	2.7 ± 0.2 (**8**)

[a] From the midpoint of fluorescence titration curves.

[b] On the basis of dynamic analysis involving proton-induced fluorescence quenching processes, rate constants of proton dissociation (k_1) and association (k_2) were determined ($K_a^* = k_1/k_2$).

[c] A typical value obtained by students using wavenumbers for maxima of absorption and fluorescence (eq 7), to estimate E_{A^-}, and E_{HA}.

[d] A typical value obtained by students using the intersection point of mutually normalized absorption and fluorescence spectra to determine E_{A^-} and E_{HA}.

Experimental

In this experiment, the absorption and fluorescence spectra of 2-naphtol solutions can be measured using any available absorption spectrophotometer and spectrofluorimeter. The results presented here have been performed using a Specord UV–VIS spectrophotometer (Zeiss) and a Perkin–Elmer MPF 44A spectrofluorimeter.

Materials

2-Naphthol (Merck) was purified by repeated crystallization from water and sublimation. HCl (38%, POCh) and NaOH (POCh) were used as obtained. Double-distilled water was used to prepare 0.1 M HCl and 0.1 M NaOH solutions.

Solutions

Two solutions of 2-naphthol are prepared in the concentration range of 1×10^{-4} M: one in 0.1 M HCl and the other in 0.1 M NaOH. They are used for the measurement of absorption spectra in 1-cm cells. However, to avoid inner filter and concentration quenching effects (*6*) (see also ref *7*) the solutions should be diluted for fluorescence measurements. Thus, 1×10^{-5} M 2-naphthol in 0.1 M NaOH is recommended for fluorescence studies.

Procedure

1. Record the absorption spectra in turn for the two 2-naphthol solutions ($c \sim 1 \times 10^{-4}$ M in 0.1 M HCl and 0.1 M NaOH, respectively), using a 1-cm cell in the range of 240–400 nm (0.1 M HCl or 0.1 M NaOH must be used in the reference cell, respectively).

2. Record the fluorescence spectra of 2-naphthol solutions ($c \sim 1 \times 10^{-5}$ M in 0.1 M NaOH) using a 1-cm cell in the range of 320–560 nm (excitation wavelength 282 nm).

3. Record the fluorescence spectra of solvents in the same experimental conditions as in point 2.

4. Calculate the maxima of the long wavelength absorption bands (wavenumbers $\bar{\nu}^a_{HA}$ and $\bar{\nu}^a_{A^-}$ in cm^{-1}) and the maxima of fluorescence (wavenumbers $\bar{\nu}^f_{HA}$ and $\bar{\nu}^f_{A^-}$ in cm^{-1}).

5. Using eq 7, determine E_{HA} and E_{A^-}

6. Using eq 6, calculate the value of pK_a* (for 2-naphthol pK_a = 9.5 (*3*)).

Results and Discussion

The absorption and fluorescence spectra of 2-naphthol are measured in 0.1 M HCl and 0.1 M NaOH, where only acid or only base forms were observed. The measured absorption and corrected (for apparatus response) fluorescence spectra are presented in Figures 2 and 3. The solvents used do not show any emission under the experimental conditions used.

Following the procedure described in the experimental section, the value of pK_a* for the excited singlet state of 2-naphthol was estimated as pK_a* = 3.1 ± 0.3. This value shows that for 2-naphthol the increase in acidity with excitation is very large, ~ 6 pK_a units (in the ground state pK_a = 9.5).

If the student's time is not limited, he or she can estimate O–O transitions for acid and base forms at the intersection point of mutually normalized absorption and emission spectra (Figs. 2 and 3). In this case, however, the fluorescence spectra must be corrected for apparatus response, which can be done automatically (MPF 44A) or by the "point by point" method (see *6*). As is described in reference *5*, this is a better approximation to the O–O transition for 2-naphthol than the average of the corresponding absorption and luminescence maxima. The pK_a* values obtained by students in our laboratory as well as those taken from the literature are summarized in the table. The pK_a* values obtained for 2-naphthol in the first excited singlet state using the Förster cycle are in good agreement with those measured by different more time-consuming methods.

Even the results obtained by the approximation of O–O transition as the average value of wavenumbers for the maxima of absorption and fluorescence spectra (eq 7) are comparable with the data taken from the literature (see table).

This experiment can be extended by the determination of fluorescence spectra of 2-naphthol as a function of pH to see if the resultant "titration curves" give the same excited state pK_a* value as from the Forster cycle method. The detailed description of pK_a* determination by the fluorescence titration and kinetic analysis methods including the case of 2-naphthol, can be found in references *2*, *3*, and *8*.

Finally, a student can also measure the fluorescence spectra for different excitation wavelengths (e.g., 282 nm gives excitation to the S_2 state; 315 nm and 340 nm give excitation to the S_1 state for the HA and A^- forms, respectively) and prove that the fluorescence bandshape of 2-naphthol and 2-naptholate in solution and its position do not depend on the excitation wavelength.

Acknowledgment

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