The Protolysis of Singlet Excited beta-Naphtol A Two-Day Laboratory Experiment to Introduce Photophysics

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The Protolysis of Singlet Excited β-Naphtol

A Two-Day Laboratory Experiment to Introduce Photophysics

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Ever since the classical work by Weller[1] on β-naphtol and its fluorescence intensity dependence on pH, this system, and similar systems, have served as models for excited state reactions in general. Without any exaggeration it may be claimed that an understanding of these kinds of reactions forms an indispensible building block for future successful photophysical work.

In this report we present a two-day laboratory experiment to estimate the pK for the protolysis of β-naphtol in its ground state and the first singlet excited state. The results are compared to results obtained from the integrated rate equations in which the values of the rate constants were taken from a time-resolved study.

The experiment has been included as part of a 10-week full-time course in spectroscopy during the third year for university students in chemistry. The students' background is a two-year course in chemistry that contains about 30% of physical chemistry corresponding to Alberty and Daniels "Physical Chemistry" where they have met the concepts of absorption, emission, and rate equations of kinetics, and are also familiar with enthalpy, entropy, and free energy concepts. The aim of the experiment is to familiarize students with excited state reactions and with absorption and emission intensity measurements.

Experimental

Stock solutions of 2×10^{-2} M β-naphtol in ethanol (99%), 1 M HCl (aq), and 0.1 M NaOH(aq) were used to prepare fresh solutions of 1×10^{-4} M β-naphtol in HCl and NaOH. **Warning:** β-naphtol is a potential carcinogen. The solutions were kept in the dark as much as possible during the following experiments to avoid degradation effects.

Absorption spectra were recorded at room temperature (21 °C) from 270 nm to 400 nm on a Beckman ACTA III spectrophotometer. Different pH's of the solutions were obtained by titrating with the acid solution directly in the cuvette, the pH being measured with a Scott micro pH combination electrode (N6O) in combination with a Radiometer pH meter (±0.05 pH units). Six spectra were recorded at values mainly around pH = 9.5 (∼pK).

Fluorescence intensity measurements were made on solutions with a pH mainly around 9.5 and 2.8 (∼pK for the excited state reaction). Excitation of the fluorescence was at 311 nm or 365 nm, according to the discussion below. The emission was recorded from 330 nm to 480 nm with an Aminco SPF 500, corrected spectra version.

Results and Discussion

The absorption spectra obtained at different pH values are illustrated in Figure 1. Two isosbestic points were clearly

shown at 321 nm and at 302 nm, and indicated a ground state reaction. Its reversibility could have been proven if the spectra also had been recorded when the solution was titrated with the base. It was found that the spectrum of the base form (B) of β-naphtol was redshifted to the acid form (A) spectrum, which means that the following scheme was applicable to describe the energetics.
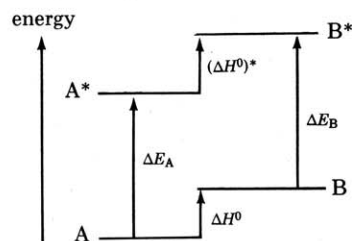
where $\Delta H^0 > (\Delta H^0)^*$ and $\Delta E_A > \Delta E_B$.

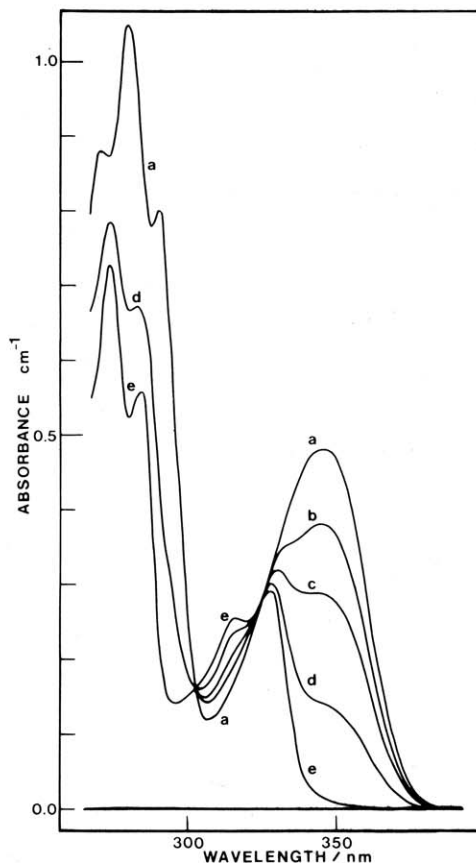Since the total concentration of β-naphtol was kept constant during the titrations we could write

Figure 1. Absorption spectra of β-naphtol at different pH values. Curve (a), pH = 13.3; (b), pH = 10.0; (c), pH = 9.6; (d), pH = 9.0; (e), pH = 0.0.

[1] Weller, A. *Z. Elektochem. Ber. Bunsenges. Physik. Chem.* **1952,** *56,* 662.

Table 1. Absorbances at 337.5 nm

pH	12.87	11.20	10.72	10.07	9.69	9.22	8.61	6.94	0.00
Abs.	0.301	0.296	0.283	0.240	0.192	0.126	0.059	0.032	0.026

$$\text{pH} - \text{p}K = \log \frac{Abs_{\text{tot}} - Abs_{A^0}}{Abs_{B^0} - Abs_{\text{tot}}} = \alpha \tag{1}$$

where Abs_{A^0} and Abs_{B^0} refer to the observed absorbances of pure A and B, respectively, i.e., the observed total absorbances at low and high pH, respectively. Equation (1) predicted a linear relation between α and pH. From the observed absorbances at 337.5 nm, Table 1, we found that

$$\alpha = 0.983 \,(\text{pH}) - 9.332 \tag{2}$$

which gave $\text{p}K = 9.332$ (the intercept) and $\text{p}K = 9.493$ (with $\alpha = 0$). The latter value was expected to be more accurate since no extrapolation was needed in its calculation. This was in excellent agreement with the value 9.49 at 25 °C reported by Weller[1].

Before discussing the emission spectra it is in place to introduce the rate equations describing the excited state reactions given by the following reaction cycle.

$$A^* \underset{k_4}{\overset{k_3}{\rightleftarrows}} B^* + H^+$$

$$I_A \updownarrow k_1 \qquad I_B \updownarrow k_2$$

$$A \rightleftarrows B + H^+$$
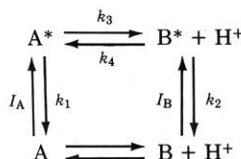
The rate constants k_1 and k_2 include deactivation by fluorescence, internal conversions and quenching by oxygen, while $k_4 = k'_4 c_{H^+}$, where k'_4 is the second-order rate constant for the reaction $B^* + H^+ \rightarrow A^*$. I_A and I_B are the excitation rates, which for continuous light illumination and with low absorption, can be written $I_A = W\epsilon_A c_A$ and $I_B = W\epsilon_B c_B$, where W is a constant including all instrumental constants. c_A and c_B can then be taken as constants, independent of time.

For the reaction cycle we obtain

$$-\frac{d}{dt}(c_{A^*}) = (k_1 + k_3)c_{A^*} - k_4 c_{B^*} - I_A$$

$$-\frac{d}{dt}(c_{B^*}) = (k_2 + k_4)c_{B^*} - k_3 c_{A^*} - I_B$$

If we assume steady-state conditions for A^* and B^* and introduce the following notation

$$\sigma = \frac{I_B}{I_A} = \frac{\epsilon_B}{\epsilon_A} 10^\alpha \tag{3}$$

where α is given by eq. (1) it is straightforward to show that the fluorescence intensities from A^* and B^* can be written

$$F_{A^*} = D_A \frac{1}{1 + 10^\alpha} \frac{1 + k_4/k_2(1 + \sigma)}{1 + k_4/k_2 + k_3/k_1} \tag{4}$$

$$F_{B^*} = D_B \frac{10^\alpha}{1 + 10^\alpha} \frac{1 + k_3/k_1(1 + 1/\sigma)}{1 + k_4/k_2 + k_3/k_1} \tag{5}$$

where D_A and D_B are constants which do not depend on pH.

It is seen that if only A or B is excited, i.e., by choosing an appropriate excitation wavelength and/or an appropriate pH, the relative magnitudes of k_1, k_2, k_3, and k'_4 determine whether both B^* and A^* emissions can be detected. The values of the rate constants were determined and reported by Brand[2] in a time-resolved study at 24 °C and are given in Table 2.

Table 2. Values of Rate Constants Used in Eqs (4 and 5)[a]

$$k_1 = 1.38 \times 10^8 \text{ s}^{-1}$$

$$k_2 = 1.06 \times 10^8 \text{ s}^{-1}$$

$$k_3 = 7.0 \times 10^7 \text{ s}^{-1}$$

$$k'_4 = 4.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$
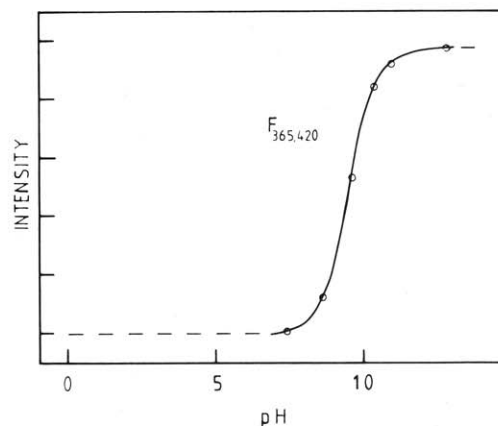
[a] From reference in footnote 2.

Figure 2. Fluorescence intensity of β-naphtol at different pH values. Excitation 365 nm, emission measured at 420 nm. Circles = experimental points. Full drawn curve = eq (5).

The first emission spectra obtained in the present study were excited at 365 nm. According to the absorption spectra, excitation at wavelengths above 360 nm for all pH values created only direct excited B^* and not B^* produced via the route $A \rightarrow A^* \rightarrow B^*$. Also, emission at all wavelengths emanated with this choice of excitation wavelength only from B^* since for $\text{pH} > \text{p}K^*$ $(= -\log(k_3/k'_4) = 2.83)$, the channel k_4 $(=k'_4 c_{H^+})$ was negligible compared with k_3, while $\text{p}K > \text{p}K^*$. (A first approximative value of $\text{p}K^*$ should be estimated with the Förster cycle as described, for example, by Parker.[3]) The fluorescence intensities, $F_{365,420}$, excited at 365 nm and measured at 420 nm, are presented in a plot versus pH in Figure 2, (circles). The full drawn curve is eq (5) with $1/\sigma = 0$ $(I_B \gg I_A)$, values of the rate constants according to Table 2, and D_B set equal to the largest value of observed F_{B^*} at high pH. The agreement between experimental data from this study and eq (5) was excellent. From eq (5) it was concluded that, when $\alpha = 0$, $F_{B^*} = 1/2 \, D_B$, which gave $\text{p}K = 9.4$. It is noteworthy that studies of the *excited* state give information about the *ground* state.

The choice of excitation wavelength for the first emission study of this work made it possible to study exclusively the emission from B^*. For wavelengths below 360 nm it was also

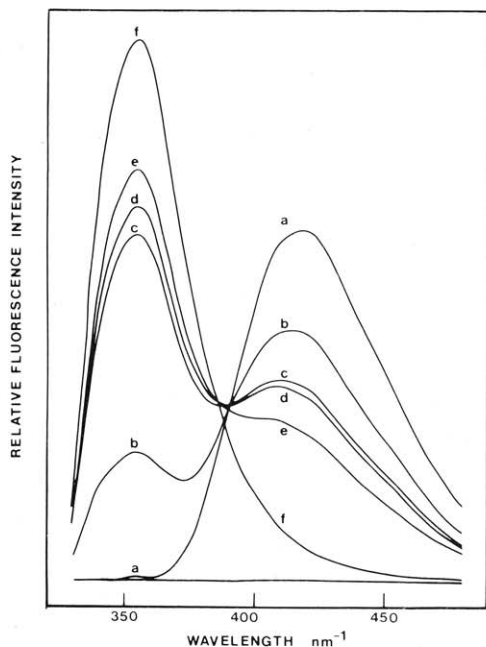[2] Laws, W. R.; Brand, L. *J. Phys. Chem.* **1979**, *83*, 795.

Figure 3. Emission spectra of β-naphtol at different pH values. Excitation at 311 nm. Curve (a), pH = 13.6; (b), pH = 9.2; (c), pH = 8.3; (d), pH = 7.8; (e), pH = 2.8; (f), pH = 1.0.
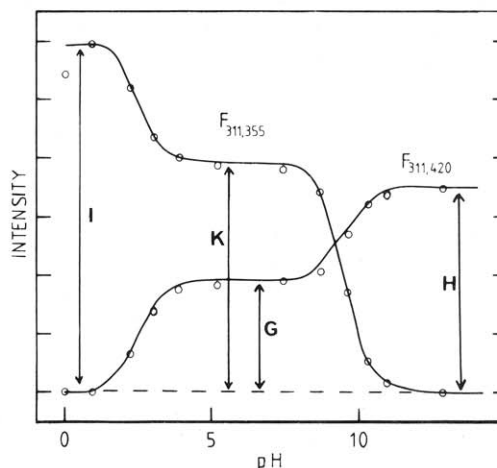

Figure 4. Fluorescence intensity of β-naphtol at different pH. Excitation at 311 nm, emission measured at 355 nm and 420 nm. Circles = experimental points. Full drawn curves = eqs (4 and 5). The meaning of G,H,I, and K are discussed in Parker[3]: $G = X\epsilon_{A,311}\phi_B\cdot^0$; $H = \epsilon_{B,311}\phi_B\cdot^0$; $I = \epsilon_{A,311}\phi_A\cdot^0$; $K = (1 - X)\epsilon_{A,311}\phi_A\cdot^0$. X is the degree of dissociation of A^* before emission takes place from A^*. ϕ^0 is the fluorescence quantum yield of the indicated species. ϵ is the molar extinction coefficient of the indicated species at the indicated wavelength.

possible to excite A if the pH < pK. Thus, when the pH was lowered from pH = 13, we expected the emission to show two species, with complicated relative intensities for different pH values.

The experiments were made by exciting at 311 nm, where both A (at low pH) and B (at high pH) could absorb the light. The recorded spectra are shown in Figure 3. In this case an isoemissive point indicated an excited state reaction, whose reversibility could have been proved in the same way as in the case of the ground state reaction. The recorded curves at high and low pH did not interesect at the isoemissive point. This was also observed by Weller[1] and attributed to the high ionic strengths at these pH values (transient effects). The observed emission at 355 nm was attributed to A^*, while the emission at 420 nm was corrected for the contribution from F_{A^*} at this wavelength. The correction was obtained from the spectra at low pH as $F_{A^*420}/F_{A^*355} = 0.055$, which was then subtracted from the observed F_{420}. The emission intensities $F_{311,355}$ and $F_{311,420}$ at different pH values are shown in Figure 4 (circles). The full drawn curves were obtained from eqs (4 and 5) with D_A and D_B set equal to the observed intensities at low and high pH, respectively. Further, σ was calculated from eq (3) with $\epsilon_B/\epsilon_A = 0.611$ as calculated from the absorption spectra at 311 nm at high and low pH, and α as given by eq (2). The values of the rate constants were again taken from the work by Brand,[2] Table 2.

The behavior of the fluorescence intensities of A^* and B^* has been discussed by Parker.[3] The meaning of the symbols G,H,I, and K are given in the caption to Figure 4. From the measured values of these constants we calculated X to be 0.323 and 0.395 (from G/H and K/I, respectively) which gave an average of 0.338. This value could be compared to $k_3/(k_1 + k_3) = 0.337$, which again confirmed the reliability of this study.

It is noteworthy that the finding that $X = 0.338$ indicated that we were studying a reversible reaction that was not at equilibrium. If k_3 had been much larger than k_1 and the pH kept low then $k_3/(k_1 + k_3)$ and $k_4/(k_2 + k_4)$ both had been nearly equal to one, and the equilibrium would have had time to establish more or less before emission had taken place from either A^* or B^*. ($k_3/(k_1 + k_3)$ is the probability that A^* disappears via k_3 instead of via k_1 and similar $k_4/(k_2 + k_4)$ is the probability for the back reaction in the excited state.) Thus, this conclusion gave rise to the question of how to determine pK^*.

Weller[1] has shown an elegant way to determine pK^* if k_2 and k_1 are known. From eq (4) it is found that

1) *if* the pH is chosen so that $k_3/k_1 = k_4/k_2$, or equivalently if the pH is chosen so that p$K^* = $ pH $ + \log(k_2/k_1)$, then we will have pH $\approx$ pK^* since $\log(k_2/k_1) \approx 0$. This means that $10^\alpha \ll 1$ and $\sigma \ll 1$ which gives

$$\frac{F_{A^*}}{D_A} = \frac{1 + k_3/k_1}{1 + 2k_3/k_1}$$

which we call ratio R_a.

2) for a pH, such that $k_4/k_2 \ll 1$, e.g., for p$K^* < $ pH $ < $ pK we have

$$\frac{F_{A^*}}{D_A} = \frac{1}{1 + k_3/k_1} = R_p$$

From (1) and (2) above we get

$$R_a = \frac{1}{2 - R_p}$$

R_p is well defined by the plateau value of F_{A^*} and from Figure 4 was estimated to be 0.647, which then gives $R_a = 0.739$. This value of R_a was experimentally found at pH = 3.0. Thus p$K^* = 3.0 + \log(k_2/k_1) = 2.9$.

With the same discussion for F_{B^*}/D_B it can be shown that $R_a = R_p/(1 + R_p)$, where now R_a and R_p refer to B^* fluorescence. pK^* estimated with this relation gave a value of 2.6. For the average of these two estimations we had p$K^* = 2.75$, which could be compared to $p(k_3/k'_4) = 2.83$. The values were in acceptable agreement.

[3] Parker, C. A. "Photoluminescence of Solutions"; Elsevier: Amsterdam, 1968.

Conclusions

We have shown that the protolysis of singlet excited β-naphtol was described by a reversible reaction, which was possible to study with a simple titration method, avoiding the more complicated influence from added buffer to the system. Aspects concerning the reversibility of the reaction and its equilibrium were given as well as quantitative results that were well in accordance with other reports. The study was well suited to incorporate as a laboratory experiment as part of an introductory course in photophysics for university chemistry students. In discussions with students it was worthwhile to comment on the temperature influence on the rate constants and pK and pK^*. However, according to Weller[1], the variation of pK and pK^* with temperature is not more than 0.5 to 0.4 pH units over the temperature range 15 °C to 60 °C. Extension of the study to include the temperature effects was therefore not done, and should not be done, unless very well-controlled experimental conditions can be achieved.