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Solvent Effects on the Photochemical Behaviour of 4-Phenylazo-1-naphthol: A Flash Photolysis Study

Patrice Jacques

Laboratoire de Photochimie Générale Associé au CNRS No. 431,
Ecole Nationale Supérieure de Chimie, 3 rue A. Werner, 68093 Mulhouse, France

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SUMMARY

A detailed kinetic scheme is presented which accounts for the complicated photochemical behaviour of 4-phenylazo-1-naphthol. The scheme underlines the interdependence between the photochromism and tautomerism exhibited by this model dye. A study of the solvent effects on the kinetic parameters additionally emphasizes that the tautomerism occurs on a large time scale.

INTRODUCTION

Tautomerism is a widely encountered topic in organic chemistry. Most textbooks (for example Ref. 1) convey the statement that: 'organic molecules may undergo proton shifts (tautomerism) *rapidly* and easily, and the chemical reactivity of the two isomers may be quite different'. Although this definition is quite rigorous, it should be noted that the term 'rapidly' is too loose, since tautomerism occurs on a time scale ranging from microseconds to days depending on the compound and the medium.

Hydroxyazo dyes exhibit this phenomenon and 4-phenylazo-1-naphthol (**I**) is a typical representative.

The equilibrium constant K_e is strongly solvent-dependent, as Fig. 1 demonstrates. In non-protic solvents, K_e increases with dielectric constant whereas hydrogen-bond-acceptor (HBA) solvents favour the A tautomer and hydrogen-bond-donor (HBD) solvents the H tautomer. In non-protic solvents, the H configuration is favoured by decreasing temperature.[2]

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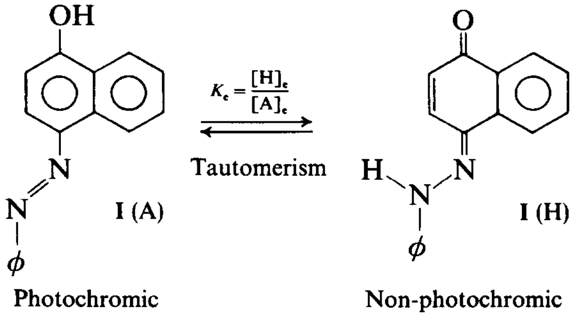


Since the electronic structures of the tautomers are quite different, their photochemical behaviour can reasonably be expected to be different also. In fact, upon absorption of a photon, I(A) undergoes *trans–cis* isomerization, whereas I(H) does not show any detectable transient signal.[3] Moreover the *cis* azo isomer does not obey the classical relaxation (direct *cis–trans* conversion), being initially converted to the hydrazone tautomer and then to the corresponding azo form in order to restore the initial concentration.

This phenomenon was observed in 1959 by Fischer, using UV spectroscopy at low temperature.[4] More recently a flash photolysis study on the *p*-methyl derivative of I dissolved in methanol led to the same conclusion.[3] However, a kinetic scheme was not proposed nor was the influence of the solvent studied. This lack of information provided the impetus for this present study, in which we observed a significant influence of the solvent on the transient signal nature. We also report a scheme which accounts for all the experimental observations and which clearly

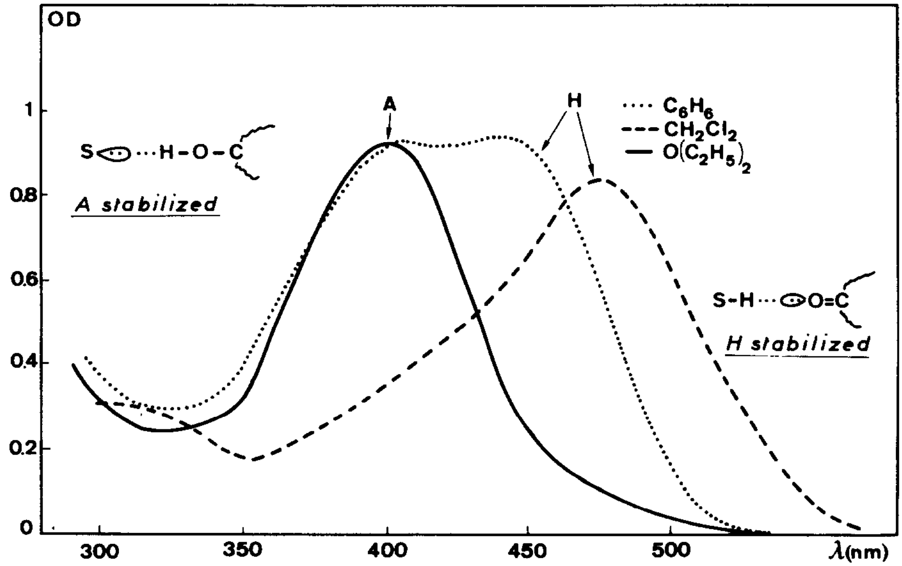


Fig. 1. Influence of the solvent on K_e. Role of the specific interactions.

demonstrates the relationship between photochromism and tautomerism, both of which phenomena are of prime importance in studies of the lightfastness of hydroxy azo dyes.[5-8]

EXPERIMENTAL

A conventional flash photolysis equipment was used (power 800 J; half duration pulse $<10\,\mu$s). In the case of slow relaxation rates the analysing light was attenuated sufficiently to prevent photo-induced $A_{cis} \rightarrow A_{trans}$ conversion.

Compound **I** m.p. 201°C, was synthesized by standard methods.

Concentrations used were 10^{-5} mol litre^{-1} unless specified otherwise.

THEORY

Let us first consider the general situation, viz. both tautomers are present. Following light excitation, a small portion ($<10\%$) of the A_{trans} molecules ($[A_t]_0$) are converted (time $<10^{-9}$ s) into A_{cis} isomers ($[A_c]_0$) and consequently the tautomeric equilibrium is broken (the hydrazone tautomer is not light-sensitive). The concentrations immediately after the flash ($t=0$) and after complete relaxation ($t=\infty$) are respectively:

$$t=0\begin{cases}[A_c]=[A_c]_0\\ [A_t]=[A_t]_e-[A_c]_0\\ [H]=[H]_e\end{cases}\qquad\qquad t=\infty\begin{cases}[A_c]=0\\ [A_t]=[A_t]_e=[A]_e\\ [H]=[H]_e\end{cases}$$

From Fig. 2 it is apparent that two processes occur simultaneously viz.,

(i) The A_{cis} molecules are unstable and relax to H according to a first-order kinetics with a rate constant $k_1 = k_{\mathrm{I}}$.

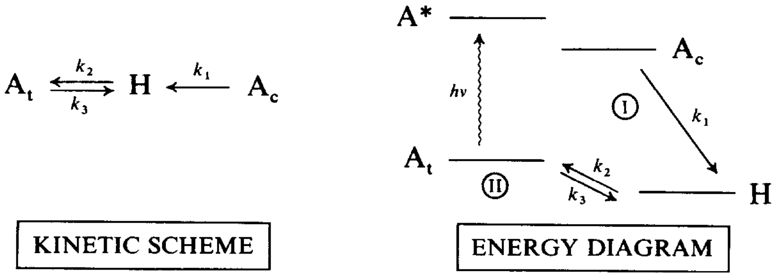
(ii) The initial concentrations of the tautomers at time $t=0$ adjust concertedly according to a first-order kinetics with a rate constant $k_{\mathrm{II}} = k_2 + k_3$,[9] so as to be in accord with the relationship which binds together the concentrations of the reactants: $K_e = [H]/[A]$.

From the boundary conditions and since the tautomeric equilibrium is only slightly shifted, the solutions of the kinetic scheme[9] can be written as

$$[A_t] = [A_t]_e - [A_c]_0\frac{k_2}{(k_2+k_3)-k_1}e^{-k_1 t} - [A_c]_0\frac{k_3-k_1}{(k_2+k_3)-k_1}e^{-(k_2+k_3)t}$$

$$[H] = [H]_e + [A_c]_0\frac{k_1-k_3}{(k_2+k_3)-k_1}e^{-k_1 t} + [A_c]_0\frac{k_3-k_1}{(k_2+k_3)-k_1}e^{-(k_2+k_3)t}$$

The interplay between k_{I} and k_{II} is clearly evident.



The A_{cis} molecules are unstable → Ⓘ $k_{\mathrm{I}} = k_1$
The tautomeric equilibrium is broken → Ⓘⓘ $k_{\mathrm{II}} = k_2 + k_3$

Fig. 2. The interplay between photochromism and tautomerism.

The hydrazone and the azo UV spectra can more or less overlap. It is therefore more convenient to focus the discussion on oscillograms recorded at a wavelength (λ_a) located in the hydrazone absorption spectrum ($\lambda_a > 460$ nm). It should be noted that the coefficients before the exponential terms are equal except for the sign. Thus, depending on the relative values of k_1, k_2, k_3, an accumulation ($[\mathrm{H}] > [\mathrm{H}]_e$) or a depletion ($[\mathrm{H}] < [\mathrm{H}]_e$) will be observed, as illustrated in Fig. 3.

(i) $k_1 > k_3$ with $k_1 > k_2 + k_3$:

$$[\mathrm{H}] = [\mathrm{H}]_e - \underset{\text{fast}}{\lambda e^{-k_1 t}} + \underset{\text{slow}}{\lambda e^{-(k_2+k_3)t}}$$

(An accumulation must be observed.)

(ii) $k_1 < k_3$ with $k_1 < k_2 + k_3$:

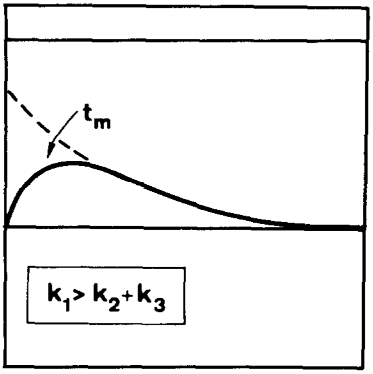
$$[\mathrm{H}] = [\mathrm{H}]_e - \underset{\text{slow}}{\lambda e^{-k_1 t}} + \underset{\text{fast}}{\lambda e^{-(k_2+k_3)t}}$$

(A depletion must be observed.)

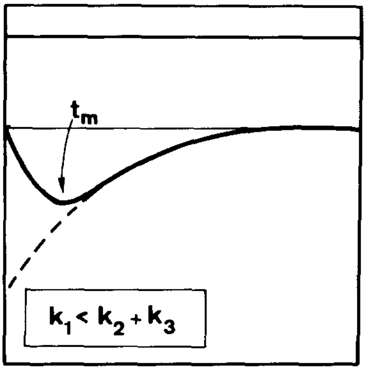
The kinetic constant of the slower process can readily be deduced from the final part of the oscillogram. Moreover, simple subtraction of the slow component from the observed decay, and replotting the differences, would give a rate constant for the faster first-order process. However, it is more elegant to take advantage of the following relationship for the time at which [H] reaches its extremum:[8]

$$t_m = \frac{\ln k_1 - \ln(k_2 + k_3)}{k_1 - (k_2 + k_3)}$$

Moreover, if the equilibrium constant $K_e = [\mathrm{H}]_e/[\mathrm{A}]_e$ can be estimated, then k_2, k_3 can be calculated and the kinetic scheme can thus be entirely parameterized.



a) Accumulation (Methanol)



b) Depletion (Benzene)

Fig. 3. The possible oscillograms at an analysis wavelength λ_a located in the hydrazone absorption spectrum.

RESULTS AND DISCUSSION

We can now show that this kinetic scheme can account for all the observed transient signals. For the sake of clarity let us consider successively the three possible cases, viz., $K_e \simeq 1$; $K_e \gg 1$; $K_e \ll 1$.

$K_e \simeq 1$: both tautomers are observed

This is the most interesting situation since it illustrates the interdependence of tautomerism and photochromism. Using methanol as solvent we observed an oscillogram of type a (Fig. 3) with the following rate constants:

$$k_2 + k_3 = 180\,\mathrm{s}^{-1}; \qquad k_1 = 410\,\mathrm{s}^{-1}; \qquad t_{\max} = 3{\cdot}6 \times 10^{-3}\,\mathrm{s}$$

These rate constants do not depend on the total concentration of compound **I** and follow an Arrhenius law as the temperature changes:

$$k_2 + k_3 \begin{cases} A \simeq 10^{9\cdot7} \\ E \simeq 10\,\mathrm{kcal\,mol^{-1}} \end{cases} \qquad k_1 \begin{cases} A \simeq 10^{11\cdot5} \\ E \simeq 12\,\mathrm{kcal\,mol^{-1}} \end{cases}$$

In a solvent not very different from pure methanol (in fact a mixture of ethanol–methanol, 7:3) and at low temperature (−120°C) Fischer measured nearly the same value.[4]

Using benzene as solvent we observed an oscillogram of type b with:

$$k_1 = 0{\cdot}07\,\mathrm{s^{-1}} \qquad k_2 + k_3 = 0{\cdot}45\,\mathrm{s^{-1}} \qquad t_\mathrm{m} = 5\,\mathrm{s}$$

Clearly, the rate ($k_2 + k_3$) of interconversion of the tautomers is solvent-dependent. Moreover, in this case, the rates depend linearly on the ground state concentration and do not follow an Arrhenius law. It should be mentioned that for λ_a located in the azo band, a bleaching is observed with methanol and benzene as solvent. Moreover, careful treatment of the transient signal reveals two components. The corresponding rates are in agreement with those derived for λ_a located in the hydrazone band, a result which substantiates the validity of the proposed kinetic scheme.

$K_\mathrm{e} \gg 1$

We were unable to detect any transient. As the case $K_\mathrm{e} \gg 1$ corresponds to strong protic solvents such as dichloromethane or chloroform, this lack of transient could be attributed to $\mathrm{H^+}$ catalysis. However, in benzene, selective excitation in the hydrazone absorption band does not induce a transient signal. These results confirm the non-photochromic behaviour of the hydrazone tautomer in contrast to the azo tautomer.

$K_\mathrm{e} \ll 1$

This is the case using ether as solvent. A transient signal (depletion) was observed only when analysing in the azo band. It follows that $k_2 + k_3 \gg k_1$. The relaxation is governed by the $\mathrm{A}_{cis} \rightarrow \mathrm{H}$ step and follows a pseudo first-order kinetic with $k_1^0 \simeq 6 \times 10^{-3}\,\mathrm{s^{-1}}$ and an activation energy of only $0{\cdot}6\,\mathrm{kcal\,mol^{-1}}$. These parameters do not correspond to a classical *cis* → *trans* isomerization and therefore confirm that the route $\mathrm{A}_{cis} \rightarrow \mathrm{H}$ is energetically 'cheaper' than the direct one as proposed by Fischer.[4]

CONCLUSION

These results indicate that the overall photochemical behaviour of **I** depends mainly on the (non-) hydroxylic properties of the solvent as does the equilibrium constant K_e:

(i) In hydroxylic solvents, interconversion of the tautomers occurs through participation of protons available from the solvent.

(ii) In non-hydroxylic solvents this interconversion implies a bimolecular mechanism (A—A or A—H or H—H); hence k_1 and $k_2 + k_3$ are pseudo first-order rate constants. In relation to this, it is important to note that impurities can considerably enhance the rate constants. Addition of traces of acid or water to a non-hydroxylic solvent dramatically changes the shape of the oscillogram.

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