

β -Cyclodextrin and the anionic α -DNBP in DMSO solution

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Abstract

2-(2',4'-Dinitrobenzyl)-pyridine is a photochromic molecule presenting a proton transfer reaction from the methylene group to the nitrogen of the pyridine, both in solution and in the crystalline state. Its photochromism in solution depend on the solvent characteristics as: his polarity, his protic character (tendency of liberating a proton), or on his hydroxylic properties (aptitude of creating hydrogen bonds solute-solvent). In this report, the disappearing of the stable anion of α -DNBP in dimethyl sulfoxide solution is investigated at the addition of β -cyclodextrin. This comportment is compared with the similar effect observed in the presence of water.

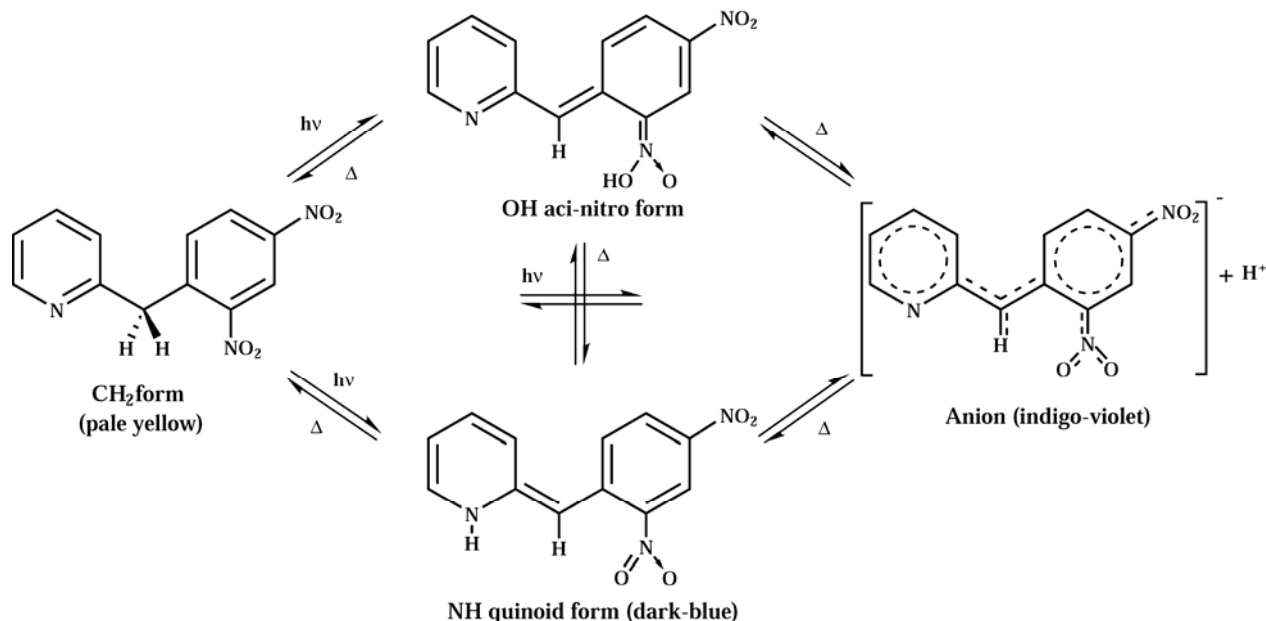
Key words: α -DNBP anion, DMSO, β -cyclodextrin.

1. INTRODUCTION

2-(2',4'-Dinitrobenzyl)-pyridine (α DNBP) is known to show photochromism since 1925 [1]. This phenomenon results from a photoinduced intramolecular proton transfer (PIPT) reaction from the methylene group to the nitrogen of the pyridine, after irradiation in the near-UV spectral region, and takes place both in the crystalline state and in solution. Scheme 1a shows the proposed reaction mechanism in solution and the tautomers of α -DNBP: the thermodynamically stable 'CH₂' form, the 'NH' quinoid and the 'OH' aci-nitro forms, and the anion. The metastable NH tautomer is relatively long-lived (4.7 s in ethanol [2] at 298 K and about 4.6 h in the crystal [3,4]) and absorbs in the visible ($\lambda_{\text{max}}=550$ nm). Systems of this kind have attracted renewed attention in recent years [2-6], because they represent the basis of optical switches in optical data processing and data-storage applications.

In solid state, the tautomerization process can take a direct path, CH₂→NH, or an indirect path through OH intermediate states, NH→OH→CH₂ [6]. Previous semi-empirical and DFT calculations have shown that in both cases, the *o*-nitro group, play an essential role either as an active intermediate, OH, or as a chaperon that escorts the moving proton along a hydrogen bond,

thus lowering the barrier along the direct path [7-8]. In solution, another way for the proton transfer becomes possible, as we can see in Scheme 1, via the anion. For solvated γ -DNBP, where the nitrogen of the pyridine ring is in the *para* position, this will remain the only way by which the NH quinoid form is produced [9].



Scheme. 1. – Photochromic mechanism for α -DNBP in solution.

The cyclodextrins are the well known cyclic oligosaccharides composed of 6, 7 or 8, α -1,4-linked, glucopyranose units (α -, β - and γ -cyclodextrines), having a toroidal shape, which can form inclusion compounds encapsulating a wide variety of molecules.

In this article we report the disappearing of the anionic form of α DNBP existing in dimethyl sulfoxide (DMSO) solution at the addition of β -cyclodextrin (β CD). This comportment is compared with a similar effect observed in the presence of water.

2. EXPERIMENTAL

α DNBP (Lancaster Synthesis) was purified by repeated crystallization from ethanol. DMSO (Fluka) was spectrophotometric grade containing a maximum of 0.3 % water. β CD (ACROS ORGANICS) was used as received. The water was simply distilled. At the beginning we have prepared a 3.86 mM stock solution, dissolving 1mg α -DNBP per ml DMSO. The equilibrated solution had a stable indigo-violet colour, due to the presence of the anionic α -DNBP. At this solution we added increasing amounts of water or of β -cyclodextrin.

The total concentration of the anion was determined by absorbance measurements with a SPECORD UV VIS spectrophotometer (Carl-Zeiss, Jena).

3. RESULTS AND DISCUSSION

The equilibrium between the photochemically produced α DNBP tautomers in solution [10-11] is known to be solvent dependent, shifting toward the aci-nitro and/or quinoid forms in non-polar solvents and toward anion form in polar solvents. The anionic form of α DNBP, the subject of this article, has been also produced chemically in basic media [12].

Even if we couldn't find any reference dealing with α DNBP in DMSO solution, due to the similarity of its absorption spectrum, having two bands with maxima centered at 498 nm and 665 nm, with that of the anion found in literature [10-12], and because it was stable during two hours in the dark, we have concluded that, in this solvent, α DNBP is mainly deprotonated. We think that this behaviour is a consequence of the fact that, DMSO is a highly polar molecule (dipole moment 3.9 debye), being known to have a great affinity for cations, and especially for protons (H^+). For comparison, we mention that the life-time of the α DNBP anion photochemically produced in acetonitrile, aprotic solvent which have a dipole moment of 3.5 debye, is 15 s [5].

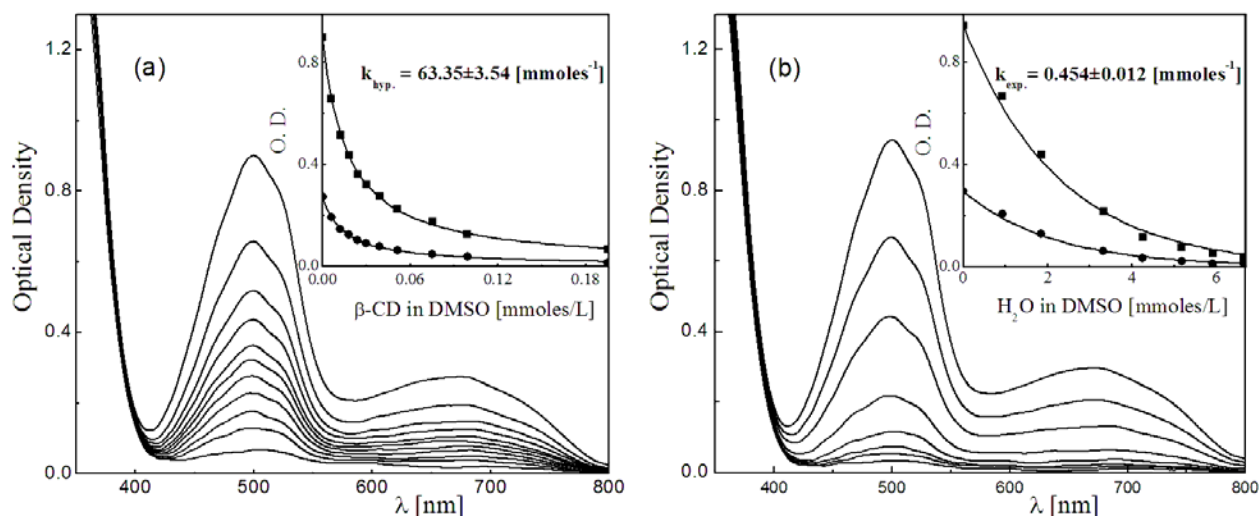


Fig. 2. The disappearance of the α DNBP anion in DMSO solution at the addition of β CD (a) or water (b). The inset contains the variation of the optical density at the maximums of the absorption bands situated at 498 and 667 nm. The reaction rate constants obtained from the fit of these values using a hyperbolic dependence (a) or an exponential one (b), are also presented.

Because DMSO dissolves β CD up to 40 g/100 mL at 25°C [13], the starting idea was to investigate a possible formation of an inclusion complex between α DNBP anion and β CD. We added, gradually, increasing amounts of β CD, and after each solubilization and equilibration, one spectrum was acquired. In Figure 2a we present the spectra obtained. As we can see, the solution fades gradually until it becomes transparent. No visible shift of the two absorption bands is observed, only the progressive disappearing of the anion. This effect is clearly due to the fact that, when β CD appear, the DMSO molecules will preferentially form hydrogen bonds with β CD hydroxyl groups and with the water with which β CD is normally crystallized [14], leaving the

engine proton of the photochromic mechanism of α DNBP to this molecule. However, this effect turn to be interesting if we look at the molar ratios between the molecules involved, α DNBP, DMSO, β CD and water, which varied in the range 1:3572:(1.5-25.6):(18.4-307), where we have also considered the water of crystallization of β CD. At the beginning, when the first quantity of β CD was added, even if we had approximately 50 DMSO molecules for every hydroxyl group, counting all 21 of β CD and 2 for water, the concentration of the α DNBP anion decreased. Moreover, as we can see in the small window inserted in Figure 2 (a), where we represent the evolution of the optical density corresponding to the two absorption maximums, function of the quantity of β CD added per liter DMSO, the disappearing of the anion is more accentuated at small concentrations of β CD and diminishes at high concentrations. To understand this behaviour, we remember that, at room temperature where all these spectra were taken, the energy of molecules ($k_B T = 0.6$ kcal/mol) is sufficient to break hydrogen bonds which range between 3 and 7 kcal/mol [15]. Consequently, water and β CD molecules are diffusing in this environment, decreasing to some extent the capacity of the DMSO molecules to keep the proton taken from α DNBP. Additionally, at small concentrations their mobility is greater than when the solution becomes saturated.

The recombination of the anion being essentially a bimolecular process between the anion and the protonated DMSO, influenced by the quantity and the diffusivity of water and β CD molecules, was found to follow a hyperbolic law:

$$c_{anion}(c_{\beta CD}) = c_{anion}(0)/(1 + k_{hyp} \cdot c_{\beta CD}), \quad (1)$$

where $c_{anion}(c_{\beta CD})$ is the concentration of the anion, $c_{\beta CD}$ the concentration of β CD and k_{hyp} the reaction rate constant.

Since β CD contains water as mentioned, subsequently we performed a similar analysis adding only water at the initial stock solution. As we can see in the Figure 2 (b), the α DNBP anion disappeared as well but, in this case, the kinetics of reaction is different. Even if primarily we used also a hyperbolic function to fit the experimental values of optical densities of both bands maximums obtained for different concentrations of water, this function didn't performed well, the dependence being in this case exponential:

$$c_{anion}(c_{H_2O}) = c_{anion}(0) \exp(-k_{exp} \cdot c_{H_2O}). \quad (2)$$

The coefficient of determination describing the goodness of fit was greater than 0.995, the two reaction rate constants obtained being also presented in Figure 2.

The fact that the stoichiometric ratio water/DMSO at which the anion disappeared entirely, was determined to be just about 1:2, tell us that this effect occur when every DMSO molecule will be 'hydrogen bonded' with water, two of them for every water molecule, being a logical and intuitive result.

Because, as mentioned, no visible shift of the absorption maxima is observed, we can't say anything about a probable supramolecular complex between α DNBP and β -CD.

Finally, as applicability, we suppose that this method can be used in a general manner to determine the reaction rate constants corresponding to a broad range of other molecules containing hydroxyl groups or which are soluble in DMSO. The temperature dependence of this parameter can be other interesting domain to examine.

4. CONCLUSIONS

The decrease of the α DNBP anion concentration in dimethyl sulfoxide solution was investigated at the addition of β CD and water, using absorption spectroscopy. The dependence of the optical densities at the wavelengths 498 and 667 nm function of the concentration of β CD or water has been adjusted using a hyperbolic and respectively an exponential law and the reaction rate constants have been determined to be: $k_{\text{hyp.}} = 63.35 \pm 3.5 \text{ mmoles}^{-1}$ et $k_{\text{exp.}} = 0.45 \pm 0.01 \text{ mmoles}^{-1}$.

We suggested that this method can be used to determine the reaction rate constants for broad range of other molecules containing hydroxyl groups or which are soluble in DMSO.

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