New Insights on the Photochromism of 2-(2′,4′-Dinitrobenzyl)pyridine

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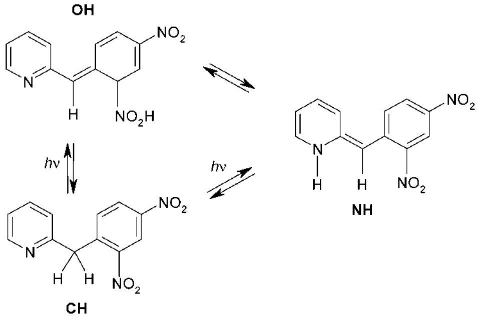
The photochromic behavior of 2-(2′,4′-dinitrobenzyl)pyridine (α-DNBP) has been followed in poly(methyl methacrylate) (PMMA) films and benzene solutions to clarify the behavior of a precursor state, previously identified in studies on crystalline α-DNBP at low temperatures. In PMMA films, photolysis at temperatures ≤50 K led to the concurrent formation of a NH tautomer and a colorless intermediate, which was stable for several hours. On irradiation at low temperatures and warming the sample, the colorless intermediate was seen to react to produce the NH tautomer in a higher yield than that found in the direct photolysis. Further information on this intermediate has come from flash photolysis studies in benzene solution, in which a new transient absorption has been observed at 335 nm and assigned to this species. This decays within a few microseconds at room temperature to form an OH tautomer, which then interconverts to the NH tautomer. The precursor state is not quenched by oxygen or naphthalene. From consideration of the kinetic and spectral data, it is suggested that this new species corresponds to a nonrelaxed tautomeric form of the OH state of α-DNBP.

1. Introduction

The molecule 2-(2′,4′-dinitrobenzyl)pyridine (α-DNBP) is well-known for its photochromic properties, both in liquid solutions and in the solid phase. Since the first report of the photochromism of α-DNBP by Chichibabin (Tschischibabin) and co-workers,[1] a large number of studies have been presented to attempt to characterize the basic photochemical and photophysical processes involved. These have been summarized in ref 2. The earliest studies showed that the photochromism involves an intramolecular proton transfer (PT), leading to different tautomers for which various structures have been suggested. However, it is only recently that definite assignments have been made.[2] These structures and interconversion processes are shown in Scheme 1. For convenience, the three tautomers that have presently been characterized are referred to as the CH, OH, and NH forms. The stable, colorless form is the CH tautomer, which, upon irradiation with UV light, is transformed into the yellow OH form or into the long-lived blue NH form (lifetimes of seconds in solution, hours in crystal at room temperature), or both. The ratio of the two forms depends on both temperature and environment. Back PT reactions can either occur thermally or be photoinduced.

However, although the identification of these photochromic forms has been achieved, little is known about the reaction mechanisms leading to their formation. A theoretical study[3] using ab initio methods, coupled with semiempirical calculations using the PM3 Hamiltonian, has suggested different possible routes for the phototautomerism and has shown that proton transfer in the excited singlet state may proceed through a process with zero activation energy. These studies have been complemented by density functional theory and molecular dynamics calculations, which suggest that transfer of the proton occurs on a time scale of roughly 100 fs.[4] On the basis of femtosecond pump−probe transient absorption spectroscopy, a reaction time for intramolecular proton transfer of α-DNBP in acetone solution of 320−500 fs has been estimated.[5] This is followed on a picosecond time scale by relaxation to the phototautomer. However, the dominant route for proton transfer is likely to depend on the rates of interconversion between the various excited states. The actual reaction pathway does not just involve the initial photoinduced step but follows a complex, but interconnected, scheme.

SCHEME 1



Recent transient absorption experiments on longer time scales performed on crystalline α-DNBP over a wide temperature range have shown that two competitive proton-transfer routes exist upon irradiation of the CH stable tautomer: a fast, direct, and temperature-independent one, assigned to an excited-state process, and a much slower, thermally activated one, involving a multistep proton transfer in the ground state via a colorless precursor state. This was detected kinetically but not observed spectroscopically.[6] Possible assignments for this precursor state, having a lifetime of about 10 μs at room temperature for a

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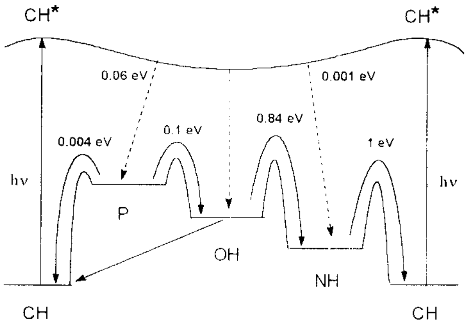

Figure 1. Schematic potential energy curves of photoinduced proton transfer in crystalline α-DNBP and energy barriers of the thermally activated processes from ref 6.

polycrystalline film, include a long-lived excited triplet state, a biradical, or an additional ground-state tautomer.

The level diagram shown in Figure 1 has been sketched from these previous studies realized in polycrystalline films of α-DNBP.[6] This shows the occurrence of a precursor state P between the CH excited state and the OH species in the ground state, which is tentatively assigned to an additional ground-state tautomer. Direct connections between the excited state and the two OH and NH species have been detected, but their rates were too fast to be measured with the experimental setup used in ref 6. For slower processes occurring in the ground state, the rate constants were identified from flash photolysis measurements and from the time evolutions of each tautomer under continuous irradiation. These data permitted the determination of activation energy barriers existing for the multistep PT mechanism indicated in Figure 1.

The objective of this paper is to elucidate the properties of this precursor state in an attempt to characterize it. Because the spectral characterization of this P state is not possible in crystalline samples for the reasons given below, the experiments presented here were conducted in a polymer matrix and in liquid solutions. The transient absorption spectra obtained for α-DNBP in such samples show that the reaction mechanism does not depend significantly on the environment, and two similar PT routes have been detected in these media.

2. Experimental Section

2.1. Transient Absorption Measurements in PMMA Films. Samples of poly(methyl methacrylate) (PMMA) films of a few tens of micrometers thickness doped with 4% α-DNBP (Lancaster Synthesis, after recrystallization from ethanol) were prepared by a standard method using toluene or chloroform as solvent and then evaporating the solvent in the dark. The UV irradiations were performed with a filtered 500 W Hg lamp ($\lambda < 326$ nm), while the probe beam consisted of a 50 W halogen lamp. Two mechanical shutters (60 ms opening time) were used to define the irradiation and acquisition durations. Because of possible degradation of the photochromic molecule, new samples taken from different regions of the same polymer film were used for each series of transient absorption measurements. Temperature control in the range 10−300 K was maintained using an Oxford Instrument cryostat CF 1204. The detection system involved a Jobin-Yvon Spex 270M spectrometer associated with a cooled photodiode array.

2.2. Flash Photolysis Experiments in Solution. Flash photolysis studies in solution were performed using a Q-switched, frequency-tripled JK Lasers System 2000 Nd:YAG laser for excitation and a xenon arc lamp, high-radiance monochromator, and photomultiplier setup for detection. The photomultiplier output was sent via a transient digitizer to the data processing system as described in ref 7.

3. Results and Discussion

3.1. Photochromism of α-DNBP-Doped PMMA Films. *3.1.1. Preliminary Observations.* It has been known for over 30 years that no detectable coloration appears after UV irradiation of polymer samples doped with α-DNBP at liquid nitrogen temperature but that heating a previously irradiated sample in the dark results in a transient blue coloration.[8] This behavior reflects the existence of a colorless precursor in the photochromism of α-DNBP, in agreement with the results of ref 6 described in the Introduction. Thus, a more systematic study of this “trapping” phenomenon has been carried out at low temperature to study the colorless reaction intermediate assigned to be the P form (Figure 1), by monitoring the effect of irradiation duration and temperature variations on solid samples.

In thin pure polycrystalline samples of α-DNBP, such as that used in ref 6, UV irradiation at low temperature (10 K) resulted in a blue coloration of very low efficiency involving only the excited-state PT route. However, no further coloration was detected upon heating the sample in the dark. This lack of trapping of the P precursor in microcrystals can be related to an efficient deactivation of this form at low temperature to produce the stable CH tautomer, in preference to the formation of the colored OH form (see Figure 1). This interpretation is consistent with the kinetic data obtained for polycrystalline samples in ref 6 because the k_{PO}/k_{PC} ratio is expected to be very small at 10 K ($\sim 10^{-40}$; where k_{PO} is the rate of the P → OH process and k_{PC} is the rate of the P → CH one). Thus, no trapping of the P form is expected in crystals at this temperature or even at temperatures up to 150 K, where this ratio reaches unity. An additional necessary condition for observation of the delayed blue coloration upon heating an irradiated sample is the occurrence of an efficient OH → NH process. Because the kinetic data available shows that this is unlikely for α-DNBP crystals, we have turned to the study of polymer samples, in which such a process has been already observed.[8]

3.1.2. Effect of Photolysis and Heating of Films. In α-DNBP-doped PMMA samples, the trapping of a colorless intermediate following photolysis was found to be efficient, even at 10 K. Thus, the kinetic parameters of the P decay in PMMA, that is, the activation energies and preexponential factors, must be quite different from those measured in the crystal. This is consistent with the fact that the ground-state PT process involves large conformational changes, which are expected to be sensitive to the environment. In agreement with this remark, large differences in the activation energies of the NH → CH process have been previously reported in going from crystal, where the activation energy is found to be ~90 kJ/mol,[9−13] to polymer matrixes, where this value falls to ~25 kJ/mol.[13,14] The importance of molecular packing factors in photoinduced proton transfers of 2,4-dinitrobenzylpyridine derivatives has been discussed in detail elsewhere.[12,15−17]

Figure 2 presents the absorption spectra observed following successive irradiations of equal duration of α-DNBP-doped PMMA films performed at 50 K. Similar experiments done at 10 K showed that the formation efficiencies of the NH tautomer (maximum absorption wavelength $\lambda_{max} = 570$ nm) were the same at these two temperatures. This can be compared with results in the crystal,[6] where the formation efficiency of NH was found to be temperature-independent between 10 and 220 K. This nonthermally activated NH formation is assigned to a

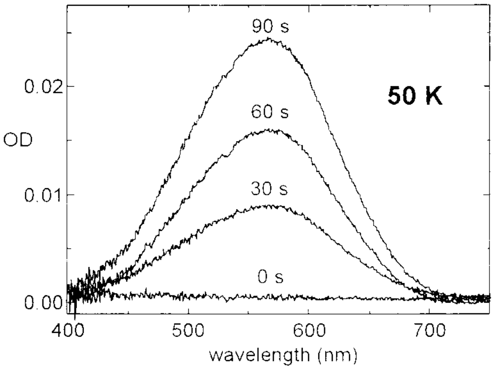

Figure 2. Formation efficiencies at 50 K after cumulative irradiations of 30, 60, and 90 s of α-DNBP in a PMMA film.

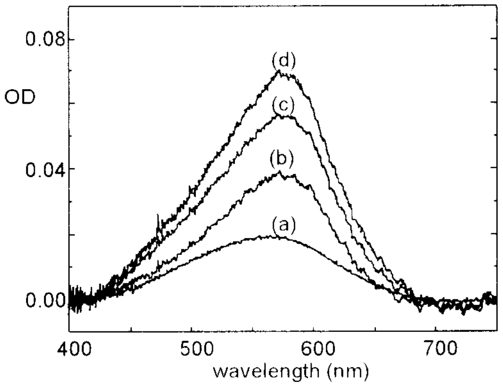

Figure 3. Absorption spectra of α-DNBP in a PMMA film: (a) after an irradiation of 60 s at 50 K and then with the sample kept in the dark at increasing temperatures of (b) 150 K, (c) 200 K, and (d) 250 K. To correct for a drift with time of the baseline, the ODs have been set to zero at 400 and 750 nm, wavelengths at which there is no NH absorption.

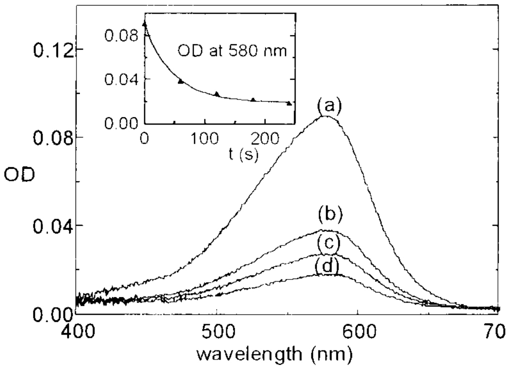

Figure 4. Absorption spectra of α-DNBP in a PMMA film at room temperature (a) just after an irradiation of 60 s and after (b) 1 min, (c) 2 min, and (d) 4 min in the dark. The insert shows the corresponding time evolution of the OD at 580 nm.

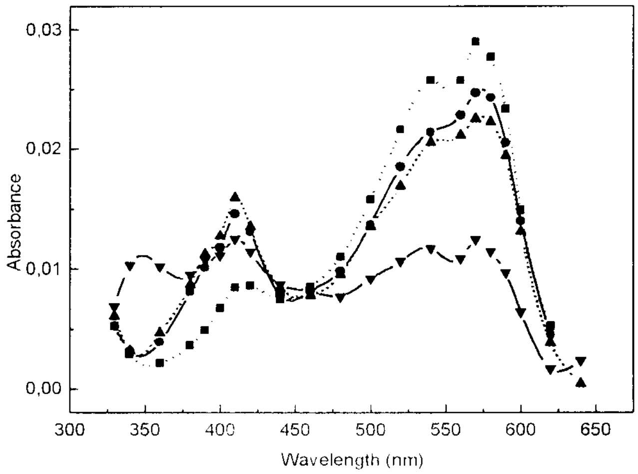

Figure 5. Transient absorption spectra of an Ar-saturated solution of α-DNBP (1.03 × 10^{-3} M) in benzene obtained 2.9 μs (▼), 14 μs (▲), 25 μs (●), and 83 μs (■) after excitation by a 15 ns laser pulse at 355 nm.

fast PT reaction in the excited state. No formation of absorption between 400 and 430 nm, attributable to the OH tautomer, was detected under these experimental conditions, in contrast to what was found with the crystal. This can be due either to a much lower formation efficiency of this species in the polymer matrix than in the crystal, where this form is detected even upon irradiation at 10 K, or to a shorter lifetime of the OH form, that is, less than the 60 ms necessary to record the transient absorption spectrum.

Because similar behaviors were observed over the whole spectral window with a sample irradiated at 10 K and then heated to 50 K while maintained in the dark and with samples irradiated at 50 K (Figure 2), subsequent experiments were performed starting from this higher temperature. These were carried out as follows: the sample was irradiated for 60 s at 50 K and then kept in the dark. No significant changes (less than or equal to a few percent) were observed in the OD, even after 10 min at this temperature, indicating a lifetime greater than a few hours. The temperature was then increased in a controlled fashion keeping the sample in the dark. A noticeable increase was observed in the OD of the NH form. This OD increase upon heating in the dark (Figure 3) was observed for temperatures up to about 250 K. At higher temperatures, the OD started to decrease due to a reduction in the NH lifetime. At room temperature, this lifetime was found here to be 47 s from the data of Figure 4.

Comparison of the evolution of the ODs in Figures 2 and 3 shows that, as in the crystal phase, the photochromic reaction efficiency is higher in the route involving the precursor state and the multistep PT in the ground state than through the competing mechanism, involving only PT in the excited state (OD max = 0.02 after 60 ms irradiation at 50 K reaches 0.07 after heating).

It must be noted from Figure 4 that the NH optical density (λ_{max} = 570 nm) at long times does not become zero but instead decreases to a constant, nonzero value. This can be related to the fact that incorporation of α-DNBP in a polymer matrix can lead not only to isolated molecules but also to nanocrystalline aggregates, as reported for highly doped (33%) poly(vinyl chloride) (PVC) films.[14] Assuming similar behavior in PMMA and PVC, comparison of the maximum OD value at λ_{max} = 570 nm just after irradiation (0.09) with the constant OD value reached after several lifetimes (0.02) allows the estimation of the concentration of nanocrystallites in the film as being ~20%.

3.2. Flash Photolysis Experiments. Following flash photolysis of an Ar-saturated solution of α-DNBP (6.1 × 10^{-4}M) in benzene using 15 ns pulses from a frequency-tripled Nd:YAG laser (355 nm), three absorption bands were observed at 335, 400, and 540−570 nm (Figure 5). The bands at 400 and 540−570 nm are attributed to the OH and NH phototautomers of α-DNBP. The rate of grow-in of the OH phototautomer at 400 nm is, within experimental error, identical to that of decay of the 335 nm transient, suggesting that the 335 nm transient is a precursor to this species. We therefore feel that the species absorbing at 335 nm corresponds to the P form, identified kinetically here in PMMA films, and previously in crystalline α-DNBP.[6] The kinetics were studied with an Ar-

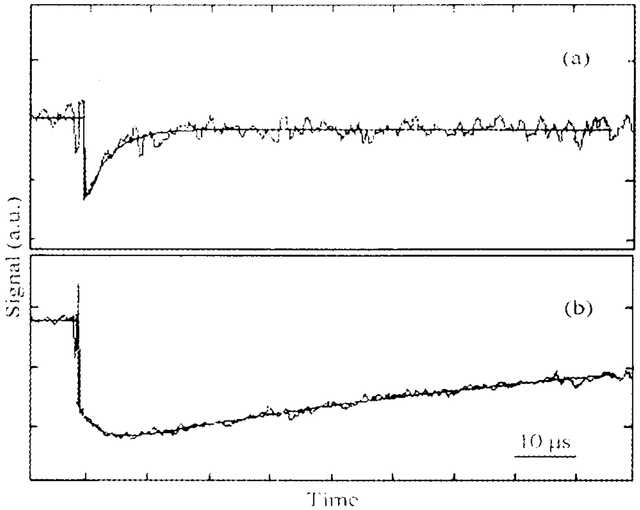

Figure 6. Transient absorption recorded at (a) 335 nm and (b) 410 nm of an Ar-saturated solution of α-DNBP (1.03×10^{-3} M) in benzene following excitation by a 15 ns laser pulse at 355 nm.

TABLE 1: Rate Constants, *k* (s^{-1}), Obtained from Laser Flash Photolysis of Solutions of DNBP (1.03×10^{-3} M) in Benzene

	Ar-saturated	aerated
decay at 335 nm	2.42×10^5	2.25×10^5
grow-in at 410 nm	3.20×10^5	3.77×10^5
decay at 410 nm	1.00×10^4	0.91×10^4

saturated solution of DNBP (1.03×10^{-3} M) in benzene. The decay at 335 nm and the grow-in and decay at 410 nm all followed good first-order kinetics (Figure 6). The lifetime for the P form in benzene solution at room temperature of ~4 μs is close to the reported rise time (~10 μs) for formation of the OH form in transient absorption studies on crystalline α-DNBP.[6] In benzene solutions, the OH form decayed with a lifetime of ~100 μs. Further information on the nature of P was obtained by studying the kinetic behavior of aerated solutions of α-DNBP in benzene at the same concentration. Within experimental error, oxygen ($[O_2] = 1.9 \times 10^{-3}$ M)[18] had no effect on the kinetic behavior. Rate constants are presented in Table 1.

The fact that the decay of the 335 nm transient is not affected by oxygen suggests that it is unlikely to be either a triplet state of α-DNBP or a biradical. Further evidence that P is not a triplet state comes from attempted quenching studies using naphthalene. From pulse radiolysis experiments[19] and theoretical calculations,[3] the triplet energy of α-DNBP is estimated to be around 2.8 eV. The triplet energy of naphthalene (2.65 eV)[18,20] is expected to be lower than this, and if the 335 nm transient is the α-DNBP triplet state, quenching is expected to be observed. Aerated solutions of DNBP (1.51×10^{-3} M) in benzene in the presence of naphthalene (0.062 M) were studied by laser flash photolysis. Following flash photolysis of this solution, both the spectra and the kinetic behavior at 335, 410, and 570 nm were very close to that in the absence of naphthalene. Considering errors introduced by the strong absorption of naphthalene at the analytical wavelength, the decay at 335 nm was similar in the presence ($3.45\ (\pm 7.8\%) \times 10^5\ s^{-1}$) and the absence ($2.22\ (\pm 14.1\%) \times 10^5\ s^{-1}$) of the additive. If the small observed difference is real and because of a second-order process involving the 335 nm transient and naphthalene, the calculated rate constant ($k_2 \leq 2 \times 10^6\ M^{-1}\ s^{-1}$) would appear to be very low for a process involving triplet–triplet energy transfer. These results support the idea obtained from the oxygen quenching experiments that the species P is not a triplet state of DNBP.

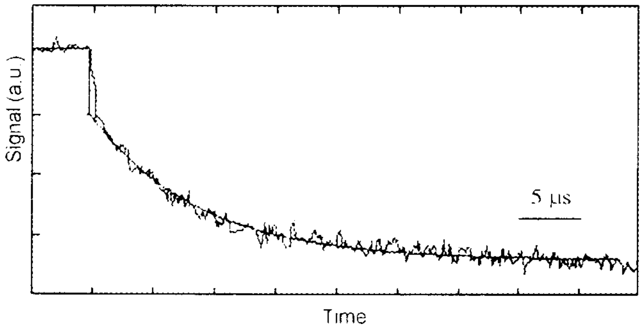

Figure 7. Transient absorption recorded at 570 nm following laser flash photolysis of an Ar-saturated solution of 6.1×10^{-4} M α-DNBP in benzene.

The formation of the absorption at 540–570 nm, assigned to the NH tautomer, follows complex kinetic behavior. For the Ar-saturated solution (6.1×10^{-4} M), part of the absorption is fully formed within the measurement time of the system (ca. 1 μs (Figure 7)), as expected for the ultrafast photoinduced proton transfer from the CH to NH tautomer.[2,5] The rest grew-in on a longer time scale. Detailed kinetic studies were not carried out on the Ar-saturated solution, but with the aerated solution of 1.03×10^{-3} M DNBP, the grow-in did not appear to fit either first- or second-order kinetics. However, the rate of this grow-in is similar to that of the decay of the absorption at 410 nm, supporting the view from previous studies[2] that some of the NH form is produced from the OH tautomer of DNBP.

4. Conclusions

Previous studies on photolysis of crystalline α-DNBP at temperatures between 10 and 300 K have shown that there is a delay in the formation of the OH tautomer and have suggested the presence of a precursor state, P, absorbing outside of the observed spectral window.[6] The present studies show that in PMMA this precursor also exists and feeds the NH species. Various possible candidates can be suggested for this species. In time-resolved resonance Raman studies on α-DNBP in acetonitrile solution, a short-lived transient assigned to the anion radical was reported.[21] However, the formation of such a charged species as a relatively stable entity in crystals or doped PMMA films at low temperatures is highly unlikely. Another possibility is a biradical, as suggested from picosecond transient absorption spectroscopic studies of *o*-nitrobenzyl compounds.[22] In contrast to the normally accepted proton-transfer mechanism for α-DNBP photochromism,[2] with the *o*-nitrobenzyl systems studied, it was suggested that hydrogen abstraction may be involved and that this may proceed through a biradical intermediate. Could P be such a biradical? Another potential candidate is the triplet state of α-DNBP. However, both species seem unlikely candidates with α-DNBP because the species P is stable for hours at low temperature and there are no precedents for such long-lived triplet states or biradicals with simple organic compounds. Further information comes from flash photolysis experiments in benzene solution, in which a transient species was detected absorbing at 335 nm, which was assigned to the P on the basis of observation of the expected behavior of interconversion to the OH form. This was not quenched by either oxygen or naphthalene, so is unlikely to be either biradical or triplet state. The only likely candidate that remains after eliminating these other species that can have a lifetime of several hours at low temperature is some other ground-state tautomer.

Some assumptions can be made on the nature of this additional tautomer. Actually, it cannot be a conformer of the

NH form, which, in this case, would not feed the OH form in contrast to what is observed in crystal and solution. We can also exclude formation of a different CH conformer because this would mean that for this route no proton transfer could take place in the excited state. The most reasonable explanation that we have found is that the P form involves some ground-state OH species that is not completely relaxed and that has a conformation intermediate between the original CH one and the final OH form. This must be associated with a weaker conjugation of the molecule, as can be seen by the position of its absorption band at 335 nm, which is located between the absorption band of CH form (below 300 nm) and the one of OH at 410 nm. It will be a challenge now for high-level theoretical calculations to suggest a structure.

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