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Exceptionally Fast Intermolecular Hydrogen Abstraction by 4,4′-Bipyridine from Alcohols: Picosecond Time-Resolved Raman Analysis

C. Didierjean and G. Buntinx

Laboratoire de Spectrochimie Infrarouge et Raman (LASIR) du CNRS, Centre d'Etudes et de Recherches Lasers et Applications, Université de Lille I, 59655 Villeneuve d'Ascq, France

O. Poizat*

Laboratoire de Spectrochimie Infrarouge et Raman (LASIR), CNRS, 2 rue Henri-Dunant, 94320 Thiais, France

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We present a picosecond resonance Raman pump−probe study of the photochemical reactivity of 4,4′-bipyridine in methanol and ethanol. The data show the decay of the $S_1(n\pi^*)$ state via two parallel routes, intersystem crossing toward the T_1 state and hydrogen abstraction from the solvent, with estimated rate constants of $k_{ISC} = (3.0 \pm 0.7) \times 10^{10}$ s^{-1} and $^1k_q = (6.0 \pm 1.4) \times 10^{10}$ s^{-1}, respectively. This ^1k_q rate value is 5 orders of magnitude higher than that found for the same abstraction process by the $T_1(\pi\pi^*)$ state. The mechanism of this surprisingly fast process is discussed on the basis of a comparison of these data and those obtained previously from picosecond transient absorption. Although the reaction is nondiffusional and takes place within H-bonded 4,4′-bipyridine/alcohol complexes, it results from the abstraction of an alkyl hydrogen of the alcohol donor and does not involve the H-bond. It is an example of reaction with a very low structural barrier where the rate is governed in part by the dynamics of reorientation of the alcohol molecules in the solvent cage following the photoexcitation.

1. Introduction

The photoreduction of 4,4′-bipyridine (44BPY) by hydrogen-donating solvents has been studied by laser flash photolysis[1,2] and time-resolved resonance Raman scattering[2,3] in the microsecond−nanosecond time domain. The reaction yields the N-hydro radical $NC_5H_4{-}C_5H_4NH^\bullet$ (44BPYH$^\bullet$). The detailed analysis[2] of the kinetics of appearance of the radical in the presence of alcohols as hydrogen donor molecules reveals a double, fast and slow, component.

The slow component corresponds to the decay kinetics of the lowest triplet state, T_1 44BPY. It characterizes a process of hydrogen atom abstraction from the alcohol by the T_1 state, with a rate constant increasing with the hydrogen donor character of the alcohol ($^3k_q = (1{-}5) \times 10^5$ M^{-1} s^{-1}). Spectroscopic data from time-resolved Raman,[2,4] electron paramagnetic resonance, and phosphorescence[5−7] measurements agree to ascribe the T_1 state to a $\pi\pi^*$ state.

In a recent investigation of the short-time photophysics of 44BPY by picosecond transient absorption measurements,[8,9] the excited S_1 state has been characterized and attributed to a $n\pi^*$ state in regard to its rapid conversion to the $\pi\pi^*$ T_1 state (a few tens of picoseconds) via intersystem crossing (ISC). The shortest lifetimes were found in alcohols (10−20 ps) and alkanes (≈11 ps) where the fast formation of the N-hydro radical, already evidenced in the nanosecond measurements, was confirmed. This fast process was assumed to take place from the S_1 state in parallel to ISC. However, the kinetics of the appearance of the radical could not be observed as the strong S_1 absorption bands overlap the radical bands at all wavelengths in the investigated 300−700 nm range. In alcohols, the rate constants for quenching of the S_1 state by the radical formation process, estimated from the shortening of the S_1 lifetime relative to the value in water, were found to increase with the protic character of the alcohol rather than with its hydrogen donor ability. In addition, in alcohol/aprotic solvent binary solutions, the 44BPYH$^\bullet$ yield was found proportional to the population of hydrogen-bonded 44BPY molecules preexisting in the ground state rather than to the alcohol concentration. It was concluded that the fast formation of 44BPYH$^\bullet$ results from a nondiffusional, intracomplex reaction of H atom abstraction by the S_1 state via homolytic breaking of the OH bond of the H-bonded alcohol. However, this tentative mechanism remains unsatisfactory as it cannot explain the fast formation of 44BPYH$^\bullet$ in alkanes. In addition, the involvement of a solute/solvent hydrogen-bonding complex in the mechanism is not convincing in regard to the predicted $n\pi^*$ nature of the precursor S_1 state since a releasing of the H-bond is expected in this state.

We have undertaken picosecond time-resolved resonance Raman experiments in order to characterize the nature and structure of the 44BPY S_1 state and to obtain more information on the fast mechanism of formation of the N-hydro radical. The vibrational and structural analysis of S_1 44BPY will be the object of another account.[10] The present report focuses on the picosecond dynamics of the photoinduced radical appearance process in methanol and ethanol. The S_1 state origin of the radical will be definitely confirmed, owing to a much better discrimination between these two transient species by Raman spectroscopy than by UV−visible absorption. On the other hand, we shall show from data acquired for specifically deuterated alcoholic solvents that the reaction in the S_1 state

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arises, as in the T_1 state, from homolytic breaking of a CH bond of the alkyl group of the alcohol rather than from the hydroxyl group. This result is thus contradicting the above-described mechanism we proposed previously. It shows that similar processes of hydrogen abstraction arise in the S_1 and T_1 states with comparable yields although the S_1 and T_1 lifetimes differ by 5 orders of magnitude. This opportunity of comparing directly the $S_1(n\pi^*)$ and $T_1(\pi\pi^*)$ reactivities within the same molecule is particularly interesting as little information is available on the relative reactivities of these two types of excited states and as hydrogen abstraction by S_1 states is much less documented as abstraction by T_1 states.[11] Intermolecular hydrogen abstraction by singlet excited states and comparison with the triplet state reactivity have been reported essentially for carbonyls,[12−20] and particularly detailed comparative analyses have been recently performed by the groups of Nau and Scaiano for some ketones and azoalkanes.[18−22] The reactivity of 44BPY will be discussed in light of these earlier studies.

2. Experimental Section

4,4′-Bipyridine (Aldrich) was sublimed at 80 °C in vacuo prior to each measurement. Methanol and ethanol (Prolabo, spectrophotometric grade) were used as received. Water was distilled and deionized. Measurements were carried out on 10^{-3} M solutions. These solutions were not deaerated.

Picosecond pump−probe Raman experiments were carried out by using a Ti−sapphire laser system based upon a Coherent (MIRA 900D) oscillator and a BM Industries (ALPHA 1000) regenerative amplifier. The oscillator can be utilized in femtosecond[8] or picosecond[23] configurations. For Raman purposes, the system was set in the picosecond regime, providing $\cong$2.5 ps (0.8 mJ) pulses at 800 nm (1 kHz) and, after frequency tripling (2.0 mm BBO crystals), 100 μJ pulses at 266 nm. Probe pulses at 370 and 380 nm (10−20 μJ) were obtained from frequency doubling the Ti−sapphire fundamental tuned at 740 and 760 nm, respectively. The corresponding third harmonic pulses (247 and 253 nm, respectively) were used as pump excitation (20 μJ, 25 mJ/cm^2 per pulse). The pump/probe cross correlation fwhm was 5 ps. The probe pulse was delayed in time relative to the pump pulse using an optical delay line (Microcontrol model MT160-250PP driven by an ITL09 controller, precision ±1 μm) and then focused with a 30 cm lens collinearly to the pump beam on the sample contained in a flow cell. The zero time position of the experiment was determined using the difference frequency generation technique between the pump and probe pulses in a BBO crystal. All spectra were measured at the magic angle. Scattered light was collected at 90° to the incident excitation, passing through a Notch filter, and dispersed in a home-built multichannel spectrometer coupled with a CCD optical multichannel analyzer (Princeton Instrument LN-CCD-1100-PB-UV/AR detector + ST-138 controller). The wavenumber shift was calibrated using the Raman spectra of indene. Data collection times ranged from 5 to 30 min. To eliminate the undesirable light due to the solvent Raman bands and to a fluorescence background induced by the pump pulse, we subtracted, for each measurement, a spectrum acquired with the probe pulse only and a spectrum recorded with the pump pulse only from the pump and probe spectrum. The intensities of various transient spectra recorded at different pump and probe time delays were normalized relative to the solvent bands before their subtraction.

3. Results

The first excited singlet state of 44BPY is characterized by two $S_1 \rightarrow S_n$ transitions peaking at 378 and 590 nm in water, methanol, and ethanol.[8] The N-hydro radical is also identified by two absorptions maximizing at 370 and 540 nm in alcohols,[1,2,24] whereas only one $T_1 \rightarrow T_n$ transition at 340 nm is observed for the lowest triplet state.[1,24] To be able to follow simultaneously, by time-resolved Raman spectroscopy, the kinetic evolution of the S_1 state and radical transient species after laser pulse photolysis, it is necessary to choose the probe wavelength in such a way that the Raman spectra of these two species are enhanced by resonance. We have used two probe excitations at 370 and 380 nm which are in strong resonance conditions for the S_1 44BPY and N-hydro radical species but in lower resonance for the T_1 state. Similar results were obtained in both cases. On the other hand, no perceptible differences in the spectra and in their time evolution were observed on going from aerated to Ar-purged solutions.

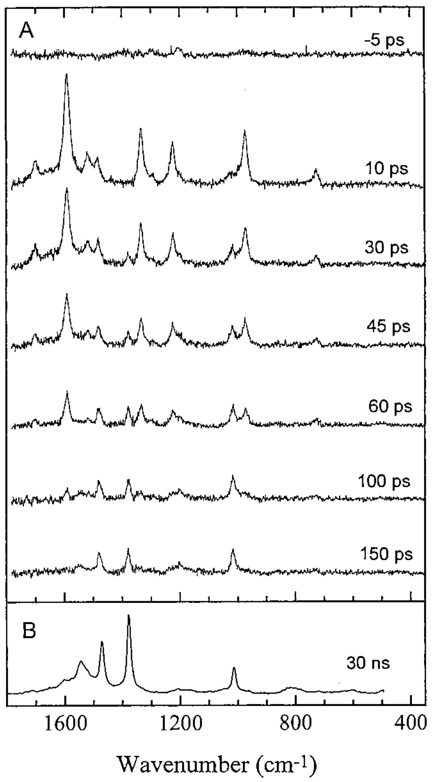


Figure 1. Time-resolved resonance Raman spectra of a solution of 44BPY (10^{-3} M) in water after pulsed laser photolysis: (A) picosecond Raman spectra probed at 370 nm at different times following pump excitation at 247 nm; (B) reference spectrum for the 44BPY triplet T_1 state obtained at a delay of 30 ns by using nanosecond pump (248 nm) and probe (340 nm) excitations (from ref 2).

Figure 1 (part A) shows a series of time-resolved Raman spectra of 44BPY in water ($\sim10^{-3}$ M) probed at 370 nm for different times between 10 and 150 ps following pump excitation at 247 nm. A spectrum recorded at a negative delay, i.e., for an excitation configuration where the sample is probed before being excited by the pump pulse, is also shown for comparison (−5 ps trace). The 150 ps spectrum corresponds clearly to the 44BPY T_1 state spectrum obtained[2] at 340 nm in previous nanosecond experiments (part B in Figure 1) although it presents different relative intensity enhancements. Its low intensity is consistent with the poor resonance accordance of the 370 nm probe relative to the $T_1 \rightarrow T_n$ absorption. The T_1 spectrum appears with a characteristic time of ~30 ps. A different spectrum is observed at shorter times in addition to the T_1 bands and is ascribed unambiguously to the excited 44BPY S_1 state as its decay parallels the appearance of the T_1 spectrum. The

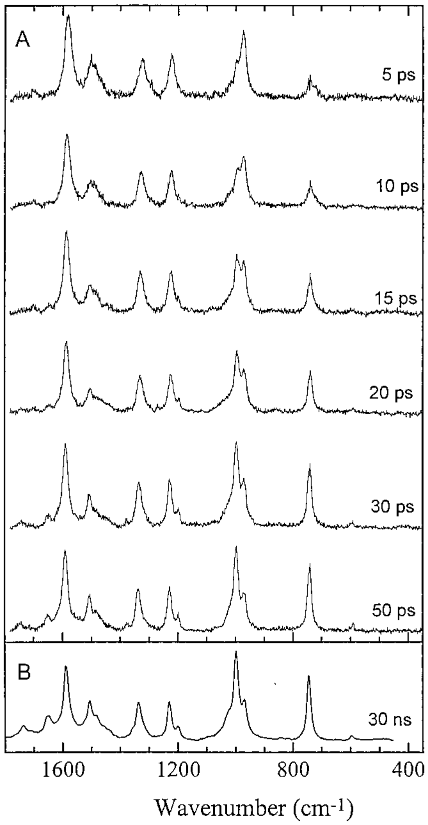


Figure 2. Time-resolved resonance Raman spectra of a solution of 44BPY (10^{-3} M) in ethanol after pulse laser photolysis. (A) Picosecond Raman spectra probed at 370 nm at different times following pump excitation at 247 nm. All spectra are normalized with respect to the solvent bands which have then been subtracted. (B) Reference spectrum for the N-hydro radical 44BPYH$^\bullet$ obtained at a delay of 30 ns by using nanosecond pump (248 nm) and probe (370 nm) excitations (from ref 2).

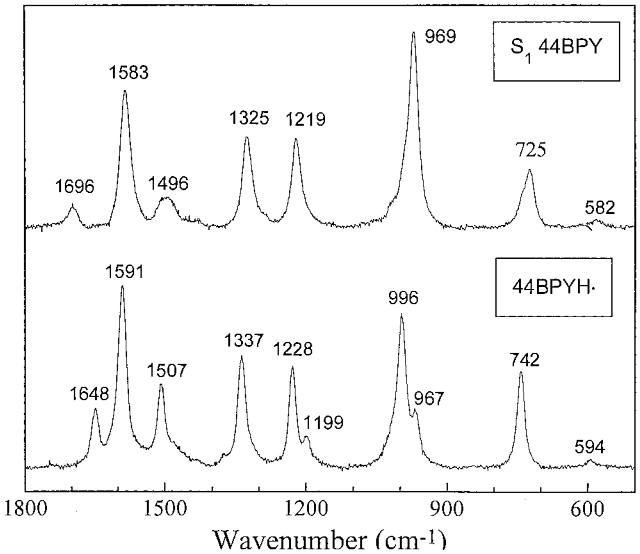


Figure 3. Time-resolved resonance Raman spectra of S_1 44BPY (5 ps delay time) and 44BPYH$^\bullet$ (100 ps delay time) in methanol: pump, 253 nm; probe, 380 nm. Solvent bands are subtracted.

~30 ps decay time of the S_1 Raman spectrum is consistent with the 27 ps lifetime of S_1 measured from transient absorption.[8] The spectral evolution in Figure 1 is thus reflecting the structural changes that accompany the $S_1 \rightarrow T_1$ intersystem crossing relaxation process.

Figure 2 (part A) shows Raman spectra obtained with a solution of 44BPY in ethanol, in the same excitation conditions as above, for various pump/probe delays from 5 to 50 ps. All spectra have been normalized with respect to the solvent peaks which have then been subtracted. Comparable data were obtained by using methanol instead of ethanol as solvent, in agreement with our previous results by transient absorption.[8] The 5 ps spectrum in Figure 2 is similar to that observed at 10 ps in water (Figure 1) and corresponds thus to the 44BPY S_1 state. The 50 ps spectrum is essentially characteristic of the N-hydro radical 44BPYH$^\bullet$ by analogy with the spectrum previously identified[2,3] for this radical from nanosecond measurements (part B in Figure 2). An additional weak line at 1380 cm^{-1} can be attributed to the T_1 species. The other triplet lines are masked by the radical peaks which are much more enhanced by resonance at 370 nm. Highly accumulated spectra of the S_1 state (5 ps delay) and of the radical (100 ps delay) probed at 380 nm are displayed in Figure 3. Although these two species have close band wavenumbers, the 44BPYH$^\bullet$ radical has two distinctive strong lines at 742 and 996 cm^{-1}. These lines are discerned as weak shoulders at 738 and 994 cm^{-1} in the 5 ps spectrum (Figure 3) and are clearly growing to 50 ps (Figure 2), with a characteristic time of 10−15 ps, which matches satisfactorily with the 11.5 ps lifetime of the 44BPY S_1 state measured from transient absorption in ethanol and methanol solutions.[8] This observation demonstrates definitely our previous assumption that the 44BPYH$^\bullet$ radical is produced from the S_1 state. As a result of this relationship and of the vicinity of the S_1 44BPY and 44BPYH$^\bullet$ Raman peaks, the decay of S_1 leads essentially to frequency shifts from the S_1 values to the radical values rather than to a decrease in intensity of the S_1 bands.

To determine the origin of the alcoholic hydrogen (hydroxyl or alkyl hydrogen) which is transferred to the 44BPY S_1 state, we have compared the Raman spectra of the radical species, as probed at a delay time of 100 ps, produced in CH_3OH and C_2H_5-OH and in the specifically deuterated alcohols C_2H_5OD and CD_3OD. Either the N-hydro radical 44BPYH$^\bullet$ or the N-deutero radical 44BPYD$^\bullet$ may be formed depending on which atom is transferred. We have shown[3] that these two radicals can be distinguished by their resonance Raman spectra. Typically, two ring distortion modes in the 950−1020 cm^{-1} region (ring breathing modes) and one ring vibration around 1650 cm^{-1} are sensitive to N−H/N−D exchange and undergo frequency downshifts of 5−10 cm^{-1}. Note that a similar specific mass effect has been observed for the N,N′-dihydro cation radical ($44BPYH_2/D_2^{\bullet +}$) and satisfactorily described by ab initio calculations.[25] Considering these weak frequency differences, discriminating the N−H and N−D radical species requires a precise measurement of the peak position, and serious caution must be taken in the subtraction of the overlapping solvent spectrum. Only radical bands lying in a spectral window common to all solvents can be taken into account. In this respect the two ring breathing components of 44BPYH$^\bullet$ (997 and 1019 cm^{-1}) are too close to the strong CH_3 rocking line of ethanol (980 cm^{-1}) or methanol (1035 cm^{-1}) to allow an accurate measurement. For this reason, we realized the experiment with the perdeuterated isotopomer, 44BPY-d_8, for which one of these components (949 cm^{-1}) is sufficiently distant from the solvent lines and also from the intense CD_3 bending line of CD_3OD (873 cm^{-1}). Figure 4 compares, for example, for the spectral regions 875−1025 and 1500−1675 cm^{-1} the 100 ps spectra of solutions of 44BPY-d_8 in methanol, ethanol−OD, and fully deuterated methanol. These spectra display exclusively radical bands as the solvent bands have been subtracted.

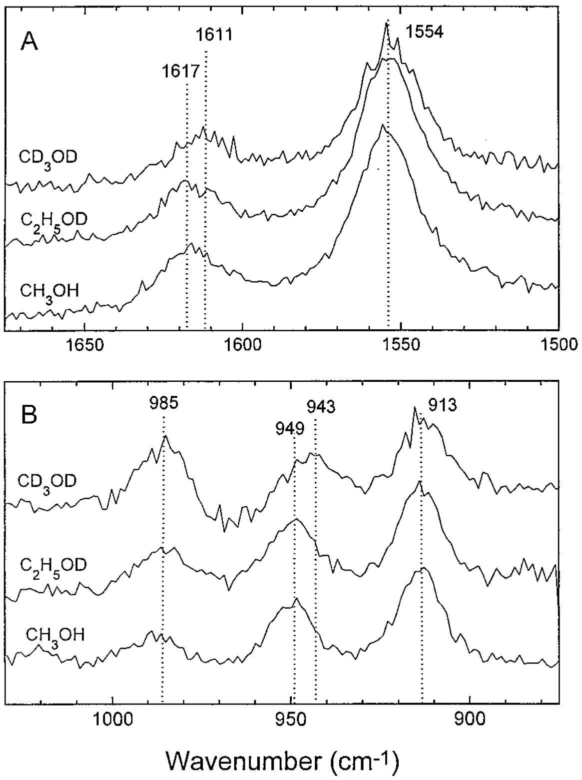


Figure 4. Time-resolved resonance Raman spectra, in the 875−1030 cm^{-1} (A) and 1500−1675 cm^{-1} (B) spectral regions, of solutions of 44BPY-d_8 (10^{-3} M) in ethanol (lower trace), ethanol−OD (medium trace), and fully deuterated methanol (upper trace). Pump, 247 nm; probe, 380 nm; delay time, 100 ps. Solvent bands are subtracted in all cases.

To feel more confident about the frequency measurement and to check the eventual influence of the subtraction treatment, we have achieved different treatments with voluntary overestimated or underestimated solvent contributions and found that the radical frequency values are not affected by the solvent subtraction. We observe that all the radical frequencies are rigorously identical in CH_3OH and C_2H_5OD. The same values are found in C_2H_5OH. In contrast, weak but undeniable frequency shifts arise on going to the CD_3OD solution for two vibrations at 949 cm^{-1} (→943 cm^{-1}) and 1617 cm^{-1} (→1611 cm^{-1}) whereas the other modes are not perceptibly affected. These results indicate clearly that the 44BPYH$^\bullet$ species is formed in C_2H_5OD as in CH_3OH and C_2H_5OH while the 44BPYD$^\bullet$ species is produced in CD_3OD. Similar spectra performed with solutions of 44BPY-h_8 in C_2H_5OH and C_2H_5-OD reveal the insensitivity of the 1650 cm^{-1} radical line, which confirms the conclusion that the same 44BPYH$^\bullet$ species is formed in these solvents. Therefore, the dependence of the radical nature on the donating alcohol isotopomer strongly indicates that the transferred hydrogen (deuterium) atom originates from the alkyl part of the alcohol.

4. Discussion

4.1. Mechanism of the Fast Radical Formation Process.

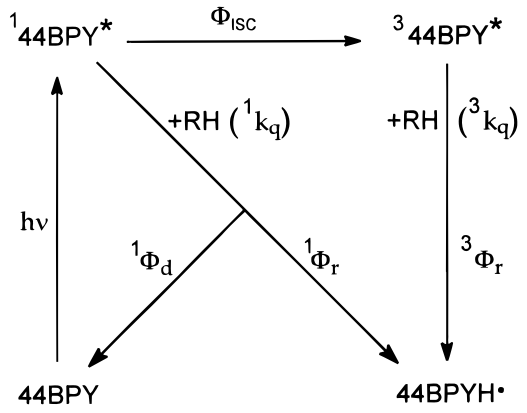
The above results obtained from time-resolved resonance Raman measurements clarify the mechanism of fast formation of the N-hydro radical in alcohols upon photolysis. They confirm that the reaction takes place from the excited S_1 state of 44BPY and show that it results from the abstraction of an alkyl hydrogen atom of the alcoholic solvent. Therefore, the fast and slow components of the radical appearance kinetics correspond to the same hydrogen transfer processes arising at the S_1 and T_1 states, respectively. However, whereas the reaction issuing from the T_1 state obeys the Stern−Volmer theory[26] for diffusion-controlled processes,[2] a purely diffusional reaction from the S_1 state is improbable in reason of the short lifetime of this state (11 ps in methanol and ethanol). From diffusion theory[27] this lifetime corresponds to an average diffusional distance of about 1 Å ($k_{\mathrm{diff}} = 0.5 \times 10^{10}$ M^{-1} s^{-1} in ethanol). Accordingly, the bimolecular hydrogen transfer reaction in the S_1 state can be efficient only if the two partners are in contact at the time of the photolytic pulse. This condition is fulfilled if 44BPY is solvated by an alcohol cage in the ground state, in which case the formation of hydrogen bonding is inevitable. H-bonding of the two pyridyl rings has been evidenced by Raman measurements.[8] The above condition accounts for our previous observation[8] that the yield of radical produced from the S_1 state in alcohol/aprotic solvent binary solutions is proportional to the amount of H-bonded 44BPY molecules in the ground state. This relationship was thus wrongly interpreted in our previous report as indicating that the hydrogen transfer arises through the H-bond.

In view of these results, the following scheme can be proposed for the S_1 state reactivity. In protic solvents, the two pyridyl rings of the ground-state 44BPY molecule are H-bonded to solvent molecules. After excitation within the strongly allowed $S_0 \rightarrow S_n(\pi\pi^*)$ transition peaking at 240 nm, the molecule relaxes rapidly to the lowest excited singlet state $S_1(n\pi^*)$ via internal conversion (IC). According to a detailed analysis of the resonance Raman vibrational spectrum of S_1 44BPY in terms of structure,[10] the electronic excitation appears localized mainly in one pyridyl ring, the second ring being weakly perturbed with respect to the ground-state structure. As expected from the $n\pi^*$ character of S_1 which is by nature unfavorable to H-bonding, a release of the hydrogen-bond involving the excited pyridyl ring arises in the S_1 state whereas the H-bond localized on the unaffected ring is probably preserved.[10] The $S_n \rightarrow S_1$ IC relaxation process must be thus followed by a solvent cage reorganization accompanying the H-bond release. This process is certainly completed in a subpicosecond time range as there is no indication of its dynamics from the picosecond transient Raman and UV−visible absorption measurements. In contrast, in a similar study of the photophysics of 4-phenylpyridine (4PPY) for which the S_1 state is also of $n\pi^*$ character,[23] we observed, in protic solvents exclusively, a manifest short-time evolution (1−10 ps time delay range) of the transient absorption spectra which precedes the appearance of the S_1 spectrum and may be due to the solute/solvent relaxation dynamics accompanying the IC process.

This first-stage relaxation is followed by hydrogen abstraction from a surrounding alcohol molecule. Interestingly, the photoreactivity of 4PPY in alcohols is analogous to that of 44BPY and shows the formation of the N-hydro radical from the $S_1(n\pi^*)$ state with comparable kinetics.[23] This analogy indicates that, in regard to the S_1 reactivity, 44BPY behaves as a pyridine molecule substituted by an inert group, which is in agreement with the localization of the S_1 excitation in one ring. The migrating hydrogen atom is thus abstracted by the nitrogen atom of the electronically excited pyridyl ring. Since this atom originates from the alkyl part of the donor alcohol, after the 44BPY−alcohol H-bond located on the disturbed ring is released upon formation of the S_1 state, a reorganization of the solvent cage from the initial collinear N- - -H−O geometry to a collinear N- - -H−C geometry suitable to hydrogen transfer is necessary for the reaction to be efficient. In fact, the rate of abstraction reactions has a large dependence on the alignment of the reactants, collinear reaction geometries giving rise to much lower activation barriers than bent geometries.[28] Therefore, though the reaction is not truly diffusion-controlled since the donor and acceptor must be in contact with each other before the reaction (the Stern–Volmer formulation cannot be used), it cannot be purely of first order since a diffusional contribution due to this reorientational motion of the solvent is expected to play a role in the reaction dynamics. In this respect it is rather analogous to the rotation-controlled unimolecular processes of intramolecular H-abstraction, and the measured rate constant ${}^{1}k_{q}$ is probably affected by the reorientational dynamics of the solvent molecules around the nitrogen atom of the excited ring. Our observation[8] that, for a series of aliphatic alcohols, the order of the rate constants did not correlate with the hydrogen donor character of the alcohols, i.e., with the strength of their C–H bonds (for example, ${}^{1}k_{q}$ (5.0×10^{10} s^{-1} in methanol and ethanol and $\sim 1.8 \times 10^{10}$ s^{-1} in 2-propanol for C–H bond dissociation energies of 94, 91, and 88 kcal mol^{-1},[29] respectively), suggests that the homolytic break of the C–H bond of the donor alcohol is not the rate-determining step in the reaction and that the dynamics of reorientation of the solvent cage is an essential parameter in the reaction control.

4.2. Kinetics and Efficiency Considerations. In pure water the main decay channel of S_1 44BPY is intersystem crossing (ISC) to the T_1 state. However, a certain contribution from nonradiative return to the S_0 state via internal conversion (IC) has been found to be probable[8] in such a way that the ISC quantum yield, Φ_{ISC}, is certainly lower than unity. The absolute value of Φ_{ISC} is not known for 44BPY, but it can be reasonably assumed comparable to the values of 0.83 and 0.84 determined for the neighboring molecules 2,2′-bipyridine[30] and biphenyl,[31] respectively. On this basis and according to the fact that the variations of the relative k_{ISC} values in the different solvents do not exceed 40%,[8] a rate constant of $k_{ISC} = (3.0 \pm 0.7) \times 10^{10}$ s^{-1} can be assumed from the relation $\Phi_{ISC} = \tau_{S_1} k_{ISC}$ ($\tau_{S_1} = 27$ ps in water[8]). In alcohols, Φ_{ISC} is notably reduced in reason of the shortening of the S_1 lifetime. Imputing this shorter lifetime to be due exclusively to the additional decay route of S_1 via hydrogen transfer led[8] to rate constants ${}^{1}k_{r}$ for the radical formation in the 1×10^{10} to 5×10^{10} s^{-1} range with a solvent dependence approximately in agreement with the measured radical yields. It was assumed that the rate constant for quenching of the S_1 state (${}^{1}k_{q}$) is equal to the rate constant for formation of the radical product (${}^{1}k_{r}$); i.e., the reaction is entirely efficient. However, Nau and Scaiano have shown for some carbonyl and azo compounds[18–22] that, whereas the efficiency for radical formation from triplet states (${}^{3}\Phi_{r}$) is close to unity, the efficiency of the singlet reactions (${}^{1}\Phi_{r}$) is notably lower. This low efficiency is accounted for in terms of state correlation diagrams, which present an avoided crossing or a conical intersection between the S_0 and S_1 energy surfaces.[18,20,32] Consequently, part of the excited complex between the reactant S_1 state and the hydrogen donor can return to the ground state, leading to a deactivation route competing with the radical formation (${}^{1}\Phi_{r} = 1 - {}^{1}\Phi_{d}$). A representation of the reactivity of 44BPY toward hydrogen donors concordant with this analysis is given in Scheme 1.

SCHEME 1



The effective rate constant for radical formation from S_1 is thus ${}^{1}k_{r} = {}^{1}k_{q}{}^{1}\Phi_{r}$. An estimation of the S_1 state reaction efficiency ${}^{1}\Phi_{r}$ is possible from the observed relative radical quantum yields ${}^{1}\Phi_{44BPYH^{\bullet}}$ and ${}^{1}\Phi_{44BPYH^{\bullet}}$ produced from the S_1 and T_1 states, i.e., the relative heights of the fast and slow components of the kinetics of radical appearance measured in the microsecond time scale. From Scheme 1, these yields can be expressed as

$$ {}^{3}\Phi_{44BPYH^{\bullet}} = \Phi_{ISC}{}^{3}\Phi_{r} \tag{1} $$

$$ {}^{1}\Phi_{44BPYH^{\bullet}} = (1 - \Phi_{ISC})^{1}\Phi_{r} \tag{2} $$

From the previously reported Stern–Volmer analysis,[2] the T_1 state of 44BPY appears preponderantly quenched by hydrogen abstraction in the presence of a large excess of alcohol. Hence, in pure alcoholic solvents, ${}^{3}\Phi_{r}$ can be considered as equal to unity, and with $\Phi_{ISC} = k_{ISC}/(k_{ISC} + {}^{1}k_{q})$, the expected ratio in radical formation from the triplet and singlet states is

$$ {}^{1}\Phi_{44BPYH^{\bullet}}/{}^{3}\Phi_{44BPYH^{\bullet}} = ({}^{1}k_{q}/k_{ISC})^{1}\Phi_{r} \tag{3} $$

In methanol, from the above k_{ISC} value of $(3.0 \pm 0.7) \times 10^{10}$ s^{-1} and a quenching rate constant ${}^{1}k_{q} = (5.0 \pm 1.2) \times 10^{10}$ s^{-1} estimated[8] from the shortening of the S_1 lifetime on changing the solvent from water to methanol in the hypothesis that the variation is only due to quenching of S_1 by H atom transfer, eq 3 becomes

$$ {}^{1}\Phi_{44BPYH^{\bullet}}/{}^{3}\Phi_{44BPYH^{\bullet}} = (1.7 \pm 0.8)^{1}\Phi_{r} \tag{4} $$

Comparing eq 4 to the experimental value deduced from the observed radical appearance kinetics in methanol shows that a satisfying accord is found if the singlet state reaction efficiency is maximum, i.e., ${}^{1}\Phi_{r} \approx 1$. Conversely, solving eq 3 for a yield ratio of 2 leads to a quenching rate constant of $(6.0 \pm 1.4) \times 10^{101}\Phi_{r}$, consistent with the above 5.0×10^{10} s^{-1} value if we assume ${}^{1}\Phi_{r} \approx 1$. In other words, the observed quenching kinetics and the relative amount of radical produced from the 44BPY S_1 and T_1 states are in agreement if we suppose that there is no significant deactivation of the excited singlet state on its way toward the radical formation (${}^{1}\Phi_{d} \approx 0$). We have thus ${}^{1}k_{r} \approx {}^{1}k_{q}$ as it was arbitrarily assumed in our previous report.[8] This situation is quite different from that found for acetone and azoalkanes where the deactivation route is dominant (${}^{1}\Phi_{d}/{}^{1}\Phi_{r} \geq 3$).[18–22]

4.3. Comparison of the Singlet and Triplet Reactivitiy. The above rate constant ${}^{1}k_{q}$ is superior by about 5 orders of magnitude to that found for the T_1 state quenching process. An obvious cause for such a reactivity difference is the higher singlet energy, which gives rise to a higher reaction exothermicity. The energies of the 44BPY S_1 and T_1 states are not known precisely but can be approximated from the reported low-temperature absorption and emission measurements. From phosphorescence data, Yagi et al. identified the ν_{00} ($T_1 \rightarrow S_0$) transition at 24 630 cm^{-1},[7] which corresponds to a triplet energy E_T of 70 kcal mol^{-1}. This value is in accord with the vertical and adiabatic $S_0 \rightarrow T_1$ energy values of 72 and 66 kcal mol^{-1}, respectively, predicted from ab initio calculation.[33] On the other hand, McAlpine ascribed the lowest energy band (30 300 cm^{-1}) in the absorption spectrum of 44BPY diluted in a crystal of biphenyl to a $S_0 \rightarrow S_1(n\pi^*)$ vibronic component but expressed a doubt about its assignment to the 0−0 transition.[34] A singlet energy of $E_S \leq 86$ kcal mol^{-1} is thus deduced, and a singlet−triplet energy gap of $\Delta E_{ST} = 14-16$ kcal mol^{-1} can be estimated, which confirms that the thermodynamics is much more favorable to the S_1 reaction. Interestingly, Nau et al. have studied a bicyclo cycloalkane molecule that undergoes, as 44BPY, hydrogen abstraction by both the S_1 and $T_1(n\pi^*)$ states and presents a comparable energy gap ($\Delta E_{ST} = 16$ kcal mol^{-1}).[18] A certain analogy can thus be expected from thermodynamic considerations between these two species concerning the difference of reactivity of the S_1 and T_1 states. However, in the presence of 2-propanol as hydrogen donor, the singlet−triplet reactivity ratio expressed as the rate constant ratio $^1k_q/^3k_q$ is much lower for this azoalkane (≥ 140) than that obtained for 44BPY (0.75×10^5) from the experimental rate constants $^1k_q = 1.8 \times 10^{10}$ s^{-1}[8] and $^3k_q = 2.4 \times 10^5$ M^{-1} s^{-1}.[2] This difference arises from the exceptionally high singlet reactivity of 44BPY compared to that of the azoalkane ($^1k_q = 8.9 \times 10^7$ M^{-1} s^{-1} [18]). In fact, the rate constant for hydrogen abstraction by S_1 44BPY from alcohols is much higher than the rates usually encountered in hydrogen abstraction.[11−22,35]

This unusual reactivity of S_1 44BPY is also clearly evidenced by comparing with the reactivity of ketones toward alcohols. The triplet energy of 44BPY (70 kcal mol^{-1}) is comparable to that of benzophenone (69 kcal mol^{-1} [35]) whereas its singlet energy (~86 kcal mol^{-1}) is close to that of acetone (85 kcal mol^{-1} [18]). If we compare the reactivity toward 2-propanol which has been studied in all cases, we observe in fact a certain analogy between the triplet reactivity of 44BPY ($^3k_q = 2.4 \times 10^5$ M^{-1} s^{-1}) and benzophenone ($^3k_q = 1.8 \times 10^6$ M^{-1} s^{-1} [19,20]). The slightly lower reaction rate for 44BPY may be due to the $\pi\pi^*$ nature of its T_1 state (triplet benzophenone is $n\pi^*$), $n\pi^*$ states having an electronic configuration more appropriate to hydrogen abstraction than $\pi\pi^*$ states where a rehybridization of the heteroatom and a stronger structural reorganization are necessary.[11,35] In contrast, the singlet reactivity of 44BPY ($^1k_q = 1.8 \times 10^{10}$ s^{-1}) is considerably higher than that reported for acetone ($^1k_q = 9.1 \times 10^6$ M^{-1} s^{-1} [18]). It is even higher than the rate constant for H-abstraction by singlet acetone from tributyltin hydride ($^1k_q = 1.0 \times 10^9$ M^{-1} s^{-1} [18]), which is a much stronger hydrogen donor (C−H bond dissociation energy 70 kcal mol^{-1}) than 2-propanol (88 kcal mol^{-1}). Such comparisons between different molecules must be considered with caution since the bonds to be cleaved/formed are not the same in the different species. However, it is quite obvious that the surprisingly large $^1k_q/^3k_q$ reactivity ratio in 44BPY compared to that in the other chemical systems studied cannot be explained solely by thermodynamic considerations and is due to an exceptionally high singlet reactivity. Note in addition that, since the rate constant ^1k_q does not follow the expected trend in hydrogen donor ability of the alcohols, simple thermodynamic models cannot be applied. Our above interpretation of this anomalous dependence of the reaction rate on the donor species, which assumes that the reaction is controlled, at least in part, by the reorientational dynamics of the solvent, implies that the effective hydrogen abstraction rate constant is still higher than the measured ^1k_q value. In any event, a very low reaction barrier can be predicted for this process.

Structural considerations may contribute to understanding this low reaction barrier and explain the large difference in reactivity of the S_1 and T_1 states. In fact, the analysis of the T_1 state Raman spectrum of 44BPY has revealed[4] a D_{2h} coplanar structure similar to the T_1 structure of biphenyl, characterized by a quinoidal distortion extended to the whole molecule and a notable increase of the inter-ring bond order. This structure is quite different from that established, also from time-resolved Raman data, for the N-hydro radical 44BPYH$^\bullet$,[3] in which the electronic conjugation between the two pyridyl rings appears weak, the electronic perturbation being more localized in the N-hydrogenated ring. In this respect the unsymmetrical structure of S_1 where the excitation is essentially localized in one ring resembles much more the radical structure. This resemblance is manifestly confirmed by the similarity of the S_1 and radical Raman spectra probed at 380 nm (see Figure 3). This structural aspect and its implication in the S_1 reactivity is discussed in detail in another report devoted to the analysis of the S_1 Raman spectra of 44BPY.[10] Therefore, hydrogen abstraction by the S_1 state to form the N-hydro radical requires much less change in geometry and in electronic distribution than abstraction by the T_1 state, which supports the assumption of a very low barrier for the singlet reaction, in agreement with the observed fast reaction rate.

5. Conclusion

The data obtained from picosecond resonance Raman pump−probe measurements show that, in methanol and ethanol solvents, both the $S_1(n\pi^*)$ and $T_1(\pi\pi^*)$ states of 44BPY undergo the abstraction of an alkyl hydrogen atom of the alcohol to produce the N-hydro radical 44BPYH$^\bullet$ with yields of the same orders of magnitude although the S_1 lifetime is shorter by 5 orders of magnitude than the T_1 lifetime. The mechanism found for the reaction involving the S_1 state is in disagreement with that proposed previously,[8] which assumed the abstraction of a hydroxyl hydrogen atom through a H-bonded alcohol/44BPY entities. It is in better accord with the formation of radical in aprotic solvents such as *n*-hexane and with the $n\pi^*$ nature of the S_1 state, which is by nature unfavorable to H-bonding.

The exceptionally high S_1 reactivity compared to that of T_1 is accounted for by its higher energy (ΔE_{ST} ~16 kcal mol^{-1}) and by its $n\pi^*$ nature, but also by its geometry and electronic distribution being much closer to the structure of the N-hydro radical product. Due to its intrinsic short lifetime, the S_1 state undergoes hydrogen abstraction only if the acceptor and donor species are in contact with each other prior to the photoexcitation. The reaction is thus nondiffusional and takes place in competition with ISC for the 44BPY molecules which are H-bonded to alcohol molecules in the ground state. It follows the break of the H-bond arising on relaxation of the initially pumped S_n state of 44BPY to the $S_1(n\pi^*)$ state and requires a reorientation of the alcohol molecules in the solvent cage until a geometrical configuration of the acceptor and donor suitable for hydrogen transfer occurs. The fact that, for a series of aliphatic alcohols, no relationship was observed between the relative reaction rates and the hydrogen donor character of the alcohols[8] confirms that the reaction dynamics is controlled, at least in part, by the rotational dynamics of the solvent cage. The implication of the S_1 structure of 44BPY in the reactivity is discussed in a further report.[10]

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