Intramolecular Proton Transfers of 2-hydroxy-4,5-naphthotropone

Du-Jeon Jang

Spectroscopy and Color Laboratory, Korea Standards Research Institute, Taejeon 305-606.
Received April 9, 1991

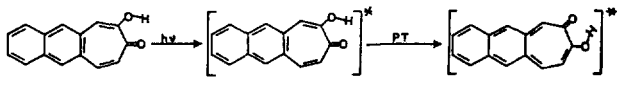
The intramolecular proton transfers of 2-hydroxy-4,5-naphthotropone in room temperature solutions are studied using static and time-resolved absorption and emission spectroscopy. Dual normal and tautomer fluorescence is observed in ethanol solution, while only the tautomer fluorescence is observed in cyclohexane solution. The fluorescence lifetimes and quantum yields in ethanol and cyclohexane solutions indicate that in hydrocarbon solvents, rapid intersystem crossing competes with proton transfer in the first excited singlet state. Transient absorption spectra and kinetics indicate that proton transfer also undergoes in the first triplet state with a transfer time of ~3 ns. No transient absorption from the tautomer ground state indicates a rapid back proton transfer in the ground state.

Introduction

Acid dissociation constant (p*Ka*) can be different by many orders of magnitude between excited and ground states of molecules. In the case where functional groups with opposite p*Ka* tendencies in excited states occupy nearby sites within one molecule, the proton may move from one group to the other, generating either a transient tautomer or photochromic isomer of the original molecules. Because a stable encounter complex is always present with an intramolecular hydrogen bond, the proton transfer can be quickly initiated by absorption of a photon providing an excellent source for understanding the dynamics within the encounter complex.[1] A variety of molecular systems have been extensively studied for excited state intramolecular proton transfer recently.[2-7] However, the role of triplet states in intramolecular proton transfer is still unknown.

It has been reported[8,9] that for 2-hydroxy-4,5-naphthotropone (HNT, **1**) the lowest excited singlet and triplet states are (π, π^*) states. The first singlet (n, π^*) state lies slightly above S_1 and the first triplet (n, π^*) state lies slightly lower than S_1.[8-11] Recent results have indicated that the lowest triplet (π, π^*) state in 2-phenoxy-4,5-naphthotropone has an energy of 35-40 kcal/mol and that the lowest triplet state in 7-phenoxy-3,4-naphthotropone, the tautomer form of 2-phenoxy-4,5-naphthotropone has an energy of ~12 kcal/mole.[10] The electronic states of HNT also seem to be the same as those of tropolone except that the first triplet (n, π^*) state of the normal molecule might lie slightly above S_1 in hydrogen bonding solvents such as ethanol.[9]

In this paper, we report the results of time-resolved and steady-state fluorescence studies which indicate that for the excited molecules of HNT, intramolecular transfer occurs in the T_1 state as well as in the S_1 state, forming 7-hydroxy-3,4-naphthotropone (**2**), the tautomer form of HNT, as indicated in the following Scheme 1.



1 **2***

Scheme 1

Experimental Section

HNT and 2-phenoxy-4,5-naphthotropone were gifts from Professor O.L. Chapman and they were purified by recrystallization and vacuum sublimation. Coumarin 500 and Rhodamine 640 were obtained from Exciton and used as received. All solvents for the fluorescence measurements were spectral grade and were shown to have negligible impurity fluorescence at wavelength longer than 420 nm. Solvents were refluxed over activated 4 Å molecular sieves for 2 h to remove traces of water and then distilled. Typical solution concentration were $1\sim5\times10^{-3}$ M. Concentration variation or degassing of the samples had no effect on either spectra or kinetics. Samples of HNT were observed to slowly decompose during irradiation resulting in another fluorescence band in the blue region close to the green band. In all cases fresh samples were used for the time-resolved fluorescence and absorption spectra to minimize this problem. Samples were contained in 2 mm quartz cuvettes.

Static absorption spectra were measured on a Cary 219 UV/Vis spectrophotometer. Steady-state fluorescence spectra were recorded on a 1902 Fluorolog spectrofluorometer. The static fluorescence spectra reported here are uncorrected for the detector sensitivity as a function of the wavelength.

Time-resolved fluorescence measurements were made with a picosecond Nd:YAG laser-streak camera apparatus. Sample excitation was performed by 355 nm, ~25 ps, 0.5 mJ pulses, focussed to a ~1 mm spot size. The resulting emission was imaged through a 0.25 m SPEX monochromator and onto a Hamamatsu C979 streak camera. The streak camera was coupled to P.A.R. 1254E SIT vidicon which was interfaced into a DEC LSI 11/02 computer. This apparatus provided a ~30 ps temporal resolution.

For time-resolved transient absorption studies,[12] the remaining 1064 nm fundamental after splitting off 532 nm and 355 nm was focused through an H_2O/D_2O (=3/1) cell to produce a visible continuum probe pulse. This white light pulse is split into reference and interrogation components then recombined and focused through the 0.25 m SPEX spectrometer. The above mentioned same OMA-computer system was used for signal detection and accumulation.

The transient absorption kinetics were measured using a picosecond streak camera absorption spectrometer.[13] The fluorescence from a laser dye, excited by a third harmonic pulse, is used for the probe light. Transient absorption in

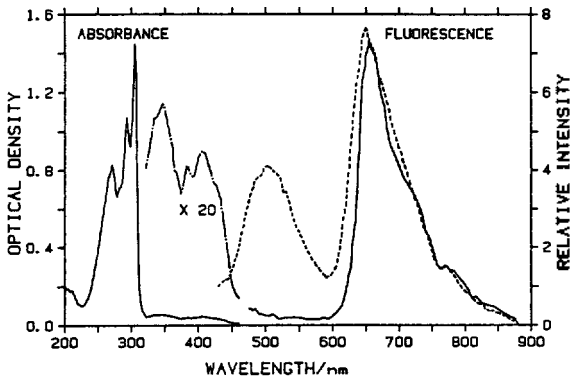


Figure 1. Absorption spectrum of HNT in cyclohexane and fluorescence spectra of HNT in ethanol (dotted line) and cyclohexane (solid line).

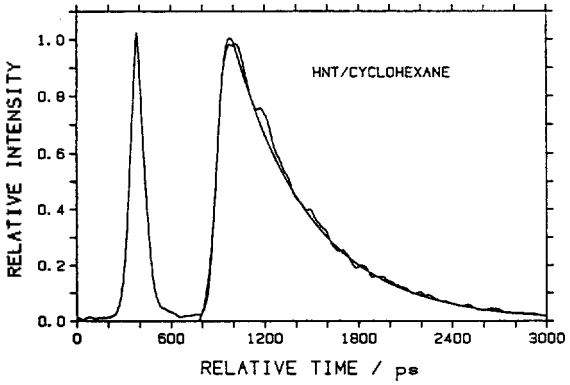


Figure 2. Fluorescence decay kinetics of HNT in cyclohexane. The solid curve was generated from a 500 ps exponential decay convoluted with instrument response functions. The sharp peak is a timing marker and was used as the instrument response function after normalization.

the sample alters the apparent kinetics of the dye emission seen by the streak camera. Comparison of the dye emission kinetics without and with the sample excitation yields transient absorption kinetics.

Results and Discussion

The absorption and emission spectra of HNT and shown in Figure 1. The slight (~3 nm) red shift of the 450 nm absorption edge in ethanol compared to that in cyclohexane and the vibrational structure indicates that the lowest excited singlet state is (π, π^*) in nature. The higher lying (n, π^*) transition is buried under the more intense (π, π^*) transition and therefore not observed.

Ethanol solutions of HNT show dual fluorescence in the 450-590 nm (green band) and 600-850 nm (red band) regions, while cyclohexane solutions show only the red band. The green band is fluorescence from the S_1 state of the normal molecule. The red band has too large Stokes shift to be assigned to fluorescence from the normal molecule. The lack of concentration or oxygen dependence indicates that it is not due to excimer emission or phosphorescence, respectively. This band is assigned to fluorescence from the tautomer form of HNT following proton transfer. The emission

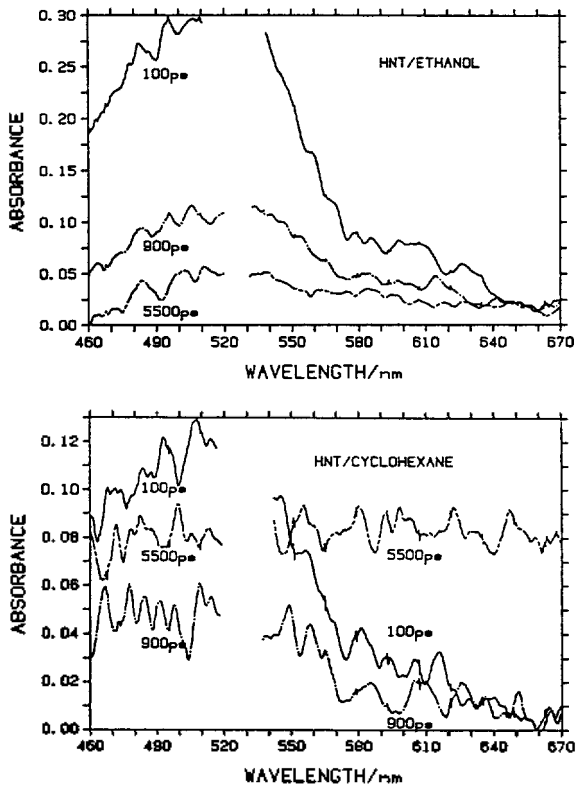


Figure 3. Transient absorption spectra of HNT in ethanol (a) and in cyclohexane (b) measured at three different delay times after sample excitation. The samples were excited at 355 nm and probed by 30 ps pulses of continuum-generated white light. The missing signals around 532 nm are due to the scattering of the second harmonic laser frequency.

spectra of 2-phenoxy-4,5-naphthotropone in ethanol solutions show a nearly identical green band and no red band. This fact also supports the assignment of the red band to the tautomer.

The emission form normal molecules in ethanol has no measurable risetime and a lifetime of 650 ps. Figure 2 shows the tautomer fluorescence decay kinetics of HNT in cyclohexane. The tautomeric emissions also have < 30 ps risetimes and 500 ps and 550 ps lifetimes in cyclohexane and ethanol, respectively. To explain these results, we suggest that in hydrogen bonding solvents there is a ground-state equilibrium between the molecules which are intramolecularly hydrogen-bonded and those which are hydrogen-bonded to the solvent molecule(s). It follows from the kinetic data that only those molecules which are intramolecularly hydrogen-bonded at the time of excitation undergo proton transfer and that proton transfer proceeds very rapidly (< 30 ps). The present work does not permit any distinction between the proton transfer of intramolecularly hydrogen-bonded species and a solvent mediated cooperative two proton transfer as has been reported in 2-hydroxy-4,5-benzotropone[14] and 3-hydroxylflavone.[15] In the latter paper the term "intramolecularly hydrogen-bonded" may include "cyclically intermolecularly hydrogen-bonded" if cooperative two proton transfer also occurs. The fact that the tautomer emission of the ethanol solution very closely follows a 550 ps exponential decay indicates that the 650 ps quenching of the normal emission is not

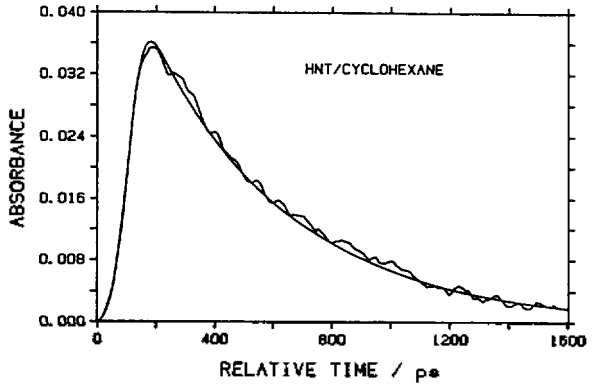


Figure 4. Transient absorption kinetics of HNT in cyclohexane, excited at 355 nm and probed at 510 nm. The solid curve was generated from a 500 ps exponential decay convoluted with the instrument response function.

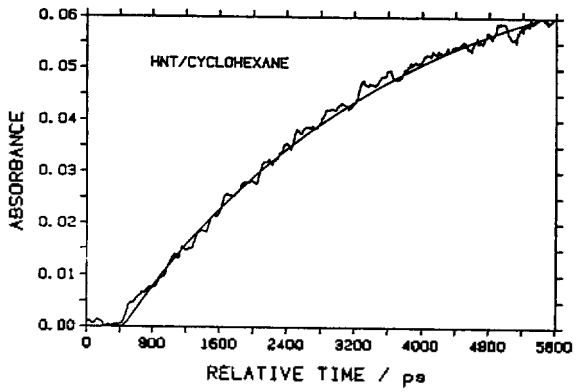


Figure 5. Transient absorption kinetics of HNT in cyclohexane, excited at 355 nm and probed at 650 nm. The solid curve was generated from a 3.3 ns exponential rise convoluted with the instrument response function.

due to excited state intramolecular proton transfer and must be due to other radiationless processes such as intersystem crossing and/or internal conversion. The absence of normal emission in cyclohexane solutions indicates that the normal molecules of the excited singlet state are very short-lived. The rapid appearance of tautomer emission indicates that at least some of this quenching is due to proton transfer.

The fluorescence quantum yields of HNT were measured following Parker and Rees[16] using Coumarin 500 and Rhodamine 640 as standards for the normal and tautomer bands, respectively. The fluorescence quantum yields of HNT were 2.8×10^{-3} and 2.0×10^{-3} for the ethanol and cyclohexane solutions, respectively. The quantum yields of the normal fluorescence of the ethanol solution was 1.1×10^{-3}. The fraction of molecules that are intramolecularly hydrogen-bonded in cyclohexane is larger than in ethanol due to the lack of intermolecular hydrogen bonding. The larger tautomer fluorescence quantum yield in ethanol than in cyclohexane therefore suggests that in cyclohexane there is another competing relaxation process. We hypothesize that in hydrocarbon solvents such as cyclohexane the T_2 $^3(n, \pi^*)$ state is at about the same energy as the S_1 $^1(n, \pi^*)$ state, facilitating a very rapid intersystem crossing which competes with proton transfer. In hydroxylic solvents such as ethanol, the T_2 $^3(n, \pi^*)$ state is significantly higher than the S_1 $^1(n, \pi^*)$ state and the intersystem crossing occurs at a rate of $<(650\ \text{ps})^{-1}$.

Figure 3 shows picosecond time-resolved transient absorption spectra of HNT in ethanol (a) and in cyclohexane (b). The transient absorption spectra of HNT in cyclohexane show that the absorption at 510 nm rises rapidly and decays with a lifetime of 500 ps, as shown in Figure 4, and that the transient absorption at 650 nm rises slowly with a rise-time of 3.3 ns, as shown in Figure 5. However, ethanol solutions show only the fast rising transient absorption at 510 nm with a decay time of 550 ps, as shown in Figure 3(a). The transient absorption at 510 nm is assigned as absorption from the S_1 state and the slow rising transient absorption at 650 nm is assigned to absorption from the T'_1 state of the tautomer. This indicates that in cyclohexane the rapid intersystem crossing to the T_2 competes with proton transfer to the S'_1 state from the S_1 state. A rapid internal conversion to the T_1 state from the T_2 state follows the intersystem

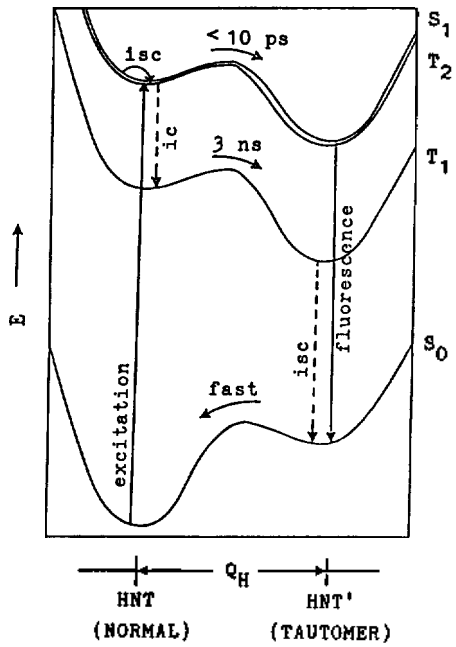


Figure 6. Six level intramolecular proton transfer scheme (S_0, T_1, S_1, S'_0, T'_1, S'_1) and relaxation processes of HNT in cyclohexane. The ic and isc indicate internal conversion and intersystem crossing, respectively.

crossing. Then excited state proton transfer undergoes from the T_1 state to the T'_1 state with a transfer time of 3.3 ns. The transient absorption from the ground state of the tautomer was not observed, indicating a rapid back proton transfer to the normal molecule in the ground state.

The proton transfer in the triplet state is first observed to our knowledge. Usually the first triplet state acidity is much more similar to the ground state acidity than to the first excited singlet state acidity.[1] As the results, intramolecular proton transfer in the triplet state is not common. However, for some molecules such as benzophenones, the pK difference between the triplet state and the ground state is much larger than that between the first excited singlet state and the ground state.[1,17] It was reported[11] that the T_1 state in 2-phenoxy-4,5-naphthotropone has an energy of 35-40 kcal

and that in 7-phenoxy-3,4-naphthotropone, the tautomer form of 2-phenoxy-4,5-naphthotropone, has an energy of just 12 kcal/mol. According to Forster cycle[18] and these energy differences, the p*Ka* of the OH group in HNT decreases by 18 and 12 units in the T_1 and S_1 states, respectively, compared to that in the ground state. This rough estimation indicates that for HNT the intramolecular proton transfer in the triplet state is plausible as well as in singlet states. This is the first observation of intramoleculr proton transfer in a triplet state.

Figure 6 summarizes the relaxation and intramolecular proton transfer and relaxation processes of HNT in hydrocarbon solvents such as cyclohexane. Upon absorption of a photon, intramolecular proton transfer to the S'_1 state and intersystem crossing to the T_2 state compete rapidly (<10 ps) for the excited molecules in the S_1 state. The proton transferred molecules in the S'_1 state relaxes to S'_0 *via* internal conversion or radiaton. A rapid internal conversion to the T_1 state from the T_2 state follows the intersystem crossing. Then excited state proton transfer undergoes from the T_1 state to the T'_1 state with a transfer time of ~3 ns. The molecules in the T'_1 state relax to S'_0 *via* intersystem crossing. The molecules in the S'_0 state undergo back proton transfer very rapidly. In hydroxylic solvents such as ethanol, only those molecules which are intramolecularly hydrogen-bonded at the time of excitation undergo proton transfer very rapidly (<30 ps) in the first excited singlet state. The proton transferred molecules in the S'_1 state relax to S'_0, then undergo a rapid back proton transfer to S_0 as observed in hydrocarbon solvents. These molecules which are intermolecularly hydrogen-bonded at the time of the excitation relax to S_0 *via* internal conversion or radiation. The proton transfer in the T_0 state is observed only in hydrocarbon solvents and the observation of intramolecular proton transfer in a triplet state is for the first time to our knowledge.

Conclusions

Steady-state absorption and emission spectroscopy and picosecond time-resolved absorption and emission spectroscopy have been used to investigate the intramolecular proton transfer and the excited state relaxation dynamics of HNT. Ethanol solutions show dual green and red fluorescence, while cyclohexane solutions show only the red fluorescence. The green fluorescence arises from the intermolecularly hydrogen-bonded normal molecules, and the red from the tautomeric molecules following proton transfer at the first excited singlet state. The risetime of the tautomer fluorescence is fast, indicating that the intramolecularly hydrogen-bonded species in both cyclohexane and ethanol undergo rapid (<30 ps) proton transfer. The kinetics also indicate that proton transfer is not a significant relaxation mechanism of the molecules which are intermolecularly hydrogen-bonded at the time of excitation. The fluorescence lifetimes and quantum yields in ethanol and cyclohexane solutions indicate that in hydrocarbon solvents, rapid intersystem crossing competes with proton transfer in the first excited singlet state. Transient absorption spectra and kinetics indicate that proton transfer also undergoes in the first triplet state with a transfer time of ~3 ns. No observation of transient absorption from the tautomer ground state indicates a rapid back proton transfer to the normal molecule in the ground state.

Acknowledgement. The author wishes to thank Professor David F. Kelley at the Colorado State University, Fort Collins for his kind guidance and help and Professor Orville L. Chapman at the University of California, Los Angeles for supplying the compounds. This work was financially supported by the Ministry of Science and Technology and the Korea Science and Engineering Foundation.

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