Excited-State Double Proton Transfer of 7-Azaindole Dimers in a Low-Temperature Organic Glass

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ABSTRACT

The excited-state double proton transfer of model DNA base pairs, 7-azaindole (7AI) dimers, is explored in a low-temperature organic glass of *n*-dodecane using picosecond time-resolved fluorescence spectroscopy. Reaction mechanisms are found to depend on the conformations of 7AI dimers at the moment of excitation; whereas planar conformers tautomerize rapidly (<10 ps), twisted conformers undergo double proton transfer to form tautomeric dimers on the time scale of 250 ps at 8 K. The proton transfer is found to consist of two orthogonal steps: precursor-configurational optimization and intrinsic proton transfer *via* tunneling. The rate is almost isotope independent at cryogenic temperatures because configurational optimization is the rate-determining step of the overall proton transfer. This optimization is assisted by lattice vibrations below 150 K or by librational motions above 150 K.

INTRODUCTION

Proton transfers have been attracting considerable attention because of their central roles in a wide variety of chemical and biological phenomena (1-5). One of such characteristic phenomena is tautomerization involving two or more hydrogen bonds (H bonds) (3–5). Since the determination of the double helix structure of DNA by Watson and Crick in 1953 (6), the proton-translocating tautomerization of DNA base pairs has been suggested to cause point mutations (7). Thus, photoinduced proton-transfer reactions are often considered to be helpful for understanding the causes of mutagenesis in DNA replications. In this regard, the dimers of 7-azaindole (7AI) molecules are prototypal because they are structurally similar to H-bonded DNA base pairs. Since the original observation of the excited-state double proton transfer (ESDPT) of a 7AI dimer by Taylor et al. in 1969 (8), the photochemistry and photophysics of the dimer and a 7AI monomer, catalyzed by the H-bonded counterpart of a protic solvent molecule, have been extensively investigated by a number of researchers (9-38). Among the studies of the dimer, one of the most widely discussed questions is whether the transfer process of two hydrogen atoms occurs in the concerted manner or through the stepwise manner (Fig. 1).

Although much research effort has focused on the elucidation of the ESDPT mechanism of 7AI dimers, most of the studies have been conducted around room temperature. Thus, it is desired to carry out a time-resolved study on the ESDPT of 7AI dimers at cryogenic temperatures to understand the effect of rigid environment on reaction mechanisms. Studying temperature effects on the fluorescence of 7AI in 3-methylpentane, Ingham et al. have reported that tunneling is involved at least at low temperatures because tautomer fluorescence is still prominent even at 4 K (9,10). From picosecond timeresolved measurements at 77 K, Hetherington and coworkers have observed biexponentially rising tautomer fluorescence to conclude that there are two different pathways of ESDPT (11). One process (<5 ps) is direct relaxation to tautomers from normal 7AI dimers which are excited above the energy barrier. The other process (ca 1 ns) involves the crossing of the energy barrier which is required for excited 7AI dimers at the vibrational zero-point level. Bulska et al. have measured the fluorescence of 7AI in 3-methylpentane at 77 K, proposing that 7AI oligomers, which cannot undergo ESDPT, as well as 7AI dimers are present in the ground state (12). They have also obtained two decay components of 0.6 and 4.2 ns at 77 K, assigning the fast component to the crossing of the energy barrier for tautomerization and the slow component to the relaxation of excited 7AI oligomers. Tokumura et al. have found large deuterium isotope effects not only in the ESDPT of normal 7AI dimers but also in the ground-state reverse double proton transfer of 7AI tautomeric dimers at 130-200 K, suggesting that tunneling is operative in both processes



Figure 1. Two possible pathways of the excited-state double proton transfer of a 7-azaindole dimer. In the concerted mechanism the two protons of the normal dimer are translocated simultaneously with a single transition state, while in the stepwise mechanism a proton moves first to form a zwitterionic intermediate species and the other proton transfers subsequently to form a tautomeric species.

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(13). Catalán *et al.* have studied the ESDPT of 7AI dimers extensively at low temperatures (14,15,30,38), suggesting that the reaction is strongly medium dependent (15).

Although diverse studies have been conducted at low temperatures, the detailed aspects of the ESDPT of 7AI dimers at low temperatures have not been verified clearly yet. In this paper, we have studied the ESDPT mechanisms of 7AI dimers in a low-temperature organic glass of *n*-dodecane. The mechanisms are found to depend on the conformations of 7AI dimers at the moment of excitation; whereas planar conformers tautomerize rapidly, twisted conformers undergo ESDPT on the time scale of 250 ps at 8 K. In addition, precursor-configurational optimization is found to determine the overall rate of ESDPT at cryogenic temperatures, showing a kinetic isotope effect (KIE) to be as small as unity.

MATERIALS AND METHODS

Materials. 7-azaindole (98%), purchased from Lancaster, was recrystallized in cyclohexane and subsequently dried in a vacuum. *n*-Dodecane (\geq 99%), purchased from Merck, was distilled once and dried over sodium for 24 h before use. The protic ¹H atom of 7AI was exchanged with a ²H atom by refluxing a mixture of 7AI and CH₃O²H (isotopic purity \geq 99.9%), received from Sigma-Aldrich, for 1 h and subsequently removing the solvent completely in a vacuum. This cycle was repeated three times. The concentrations of 7AI in our samples were kept at 1.0 mM.

Measurements. Absorption spectra were measured with a UV/Vis spectrophotometer (Scinco, S-2040), and emission spectra were obtained using a home-built fluorometer consisting of a Xe lamp of 75 W (Acton Research, XS432) with a monochromator of 0.15 m (Acton Research, Spectrapro-150) and a photomultiplier tube (Hamamatsu, R928) attached to a monochromator of 0.30 m (Acton Research, Spectrapro-300). A mode-locked Nd:YAG laser of 25 ps (Quantel, YG501) and a streak camera of 10 ps (Hamamatsu, C2830) attached to a CCD (Princeton Instruments, RTE118H) were employed for the excitation and the detection of time-resolved emission spectra, respectively. Samples were excited with 288 nm pulses, generated through a Raman shifter filled with methane at 10 atm and pumped by the fourth-harmonic pulses (266 nm) of the laser. Emission wavelengths were selected by combining band-pass filters and cut-off filters or by using a monochromator of 0.15 m (Acton Research, Spectrapro-150). Time-resolved emission spectra were constructed by measuring a fluorescence kinetic profile every 5 nm. Fluorescence kinetic constants were extracted by fitting kinetic profiles to computer-simulated exponential curves convoluted with instrumental response functions. Both static and time-resolved emission spectra were not corrected for the wavelength-dependent sensitivity variation of the detectors. Sample temperatures were controlled using a closed-cycle He cryostat (Janis, CCS-100).

RESULTS AND DISCUSSION

Figure 2 shows that a *n*-dodecane solution of 1.0 mM 7AI at room temperature has the absorption maximum at 284 nm and distinct dual emission maxima at 323 nm (F₁ band) and 473 nm (F₂ band). It is well known (24,26) that the F₁ band is due to normal fluorescence mostly from 7AI monomers whereas the F₂ band arises from fluorescence of tautomeric 7AI dimers (T*). Thus, Fig. 2 suggests that 7AI molecules form dimers sufficiently at a low concentration of 1.0 mM to produce T* upon absorption of photons. The association constants of 7AI molecules to yield dimers in nonpolar solvents of 3-methylpentane and cyclohexane were reported to be 1.8×10^3 m⁻¹ and 2.2×10^3 m⁻¹, respectively (10,17). Because the ΔH values of association in 3-methylpentane and cyclohexane have been reported to be as largely negative as -9.6 and -9.5 kcal mol⁻¹, respectively (10,17), the association constant is expected to increase rapidly as temperature decreases. Catalán and Kasha have also argued that 10^{-4} M 7AI in 2-methylbutane consists of pure dimers below 227 K, based on the close investigation of their near-ultraviolet absorption spectra (14). Thus, we consider that most of 7AI molecules at the employed concentration in *n*-dodecane exist as dimers at low temperatures such as 8 K (see below).

Although, the steady-state fluorescence spectrum of 7AI in a room-temperature solution shows the F_1 band at 323 nm (Fig. 2), the time-resolved emission spectrum of 7AI in an organic glass at 8 K does the F_1 band at 365 nm at the time delay of 0 ns (Fig. 3). As described above, equilibrium between monomers and dimers shifts to dimers with decreasing temperature (10); the F_1 band observed at room temperature is attributed mostly to 7AI monomers whereas the band observed at 8 K is ascribed mainly to 7AI dimers. Kwon and



Figure 2. Absorption (solid) and fluorescence spectra with excitation at 285 nm (dashed) of 1.0 mM 7-azaindole in *n*-dodecane at room temperature.



Figure 3. Time-resolved emission spectra of 1.0 mm 7-azaindole in *n*-dodecane at 8 K. The sample was excited at 288 nm, and time delays after excitation are indicated inside.

Zewail have reported that at room temperature, the emission spectrum of 7AI in *n*-heptane with excitation at 290 nm shows the F_1 band at 320 nm while the emission spectrum with excitation at 315 nm, where only 7AI dimers absorb photons, shows the F_1 band at 350 nm (34). Figure 3 shows that the maximum of the F1 band is redshifted from 365 nm at the time delay of 0 ns to 375 nm at the time delay of 8 ns. Moreover, the relative intensity of the F₂ band to the F₁ band increases with the elapse of time. These suggest that the precursors of T* giving the F₂ band are normal 7AI dimers. However, the F₁ band does not disappear completely even at a long time delay of 8 ns. This implies that the dimer is not the sole species that gives rise to the F_1 band. Thus, we consider that in a lowtemperature organic glass, there exist not only 7AI dimers, which can undergo ESDPT, but also 7AI oligomers, which cannot undergo ESDPT (12). This is also supported by the result that the kinetic profile of normal fluorescence gives the long relaxation time besides the short proton-transfer time of dimers (see below).

Figure 4a and Table 1 show that the fluorescence kinetic profiles of 7AI in n-dodecane, monitored at 360 nm, has biexponential decay times of 250 ps (35%) and 3400 ps (65%) at 8 K. The kinetic profile of the same sample has two rise components at the emission wavelength of 500 nm (Fig. 4b). The dominant component (75%) rises instantly while the other one (25%) does on the time scale of 250 ps. Considering the presence of two rise components at 500 nm, we suggest that there are two different formation mechanisms of the T* species. The rise time of 250 ps observed at 500 nm complies with the decay time of 250 ps observed at 360 nm, indicating that 25% of T* molecules are produced on the time scale of 250 ps. To elucidate the ESDPT mechanisms of 7AI dimers in n-dodecane at 8 K, we intimate that there are two different conformers, which can undergo ESDPT to give T*, of 7AI normal dimers (N) in the ground state. Various structures of 7AI aggregates are known to exist at low temperatures (12.36– 38). However, as far as the tautomerization of 7AI dimers is concerned, the only structures that can go through ESDPT need to be considered. For example, 7AI molecules in crystalline phases form the tetrameric structure in which ESDPT is prohibited (37). Moreover, it has been also known that 7AI oligomers can not undergo ESDPT (12). Thus, we exclude those forms of 7AI aggregates such as tetramers and oligomers when we discuss the ESDPT mechanisms of 7AI dimers. We consider that the majority (75%) of 7AI dimers in the ground state have a planar, cyclically H-bonded structure (Np) and undergo ESDPT immediately upon absorption of a photon to produce T*. The rest (25%) of N molecules are suggested to pose a somewhat twisted, cyclically H-bonded structure (Nt), and they go through ESDPT on the time scale of 250 ps at 8 K to transform into T* molecules. These indicate that the reaction pathway of a N* molecule to produce a T* molecule depends on the conformation of a ground-state N molecule at the moment of excitation. In condensed phases, while the overall ESDPT time of 7AI dimers was reported to be $1 \sim 2$ ps at room temperature (34), the ESDPT time of Nt has been found to be 250 ps at 8 K. ESDPT in a room-temperature solution usually occurs via tunneling assisted vibrationally with solvent fluctuations. Nuclear motions such as heavy-atom rearrangement to form an optimized precursor configuration for efficient proton



Figure 4. Fluorescence kinetic profiles of 1.0 mm 7-azaindole in *n*-dodecane at 8 K. The sample was excited at 288 nm and monitored at 360 nm (a), and 500 nm (b, c). Solid lines are best-fitted kinetic curves.

Table 1. Fluorescence kinetic constants extracted from the kinetic profiles of Fig. 4.*

Figure	$\lambda_{\rm em} (\rm nm)$	Rise time (ps)	Decay time (ps)
4a	360	Instant	250(35%) + 3400(65%)
4b,c	500	Instant (75%) + 250 (25%)	3900

 $*\lambda_{em}$ is the collection wavelength of emission, and numbers in parentheses are initial amplitude percentages.

tunneling become much more important at cryogenic temperatures, where solvent motions are highly restricted, than at room temperature. This is in line with the observation that the ESDPT of Nt was slowed down enormously in a lowtemperature organic glass. This is supported by the fact that the KIE of the ESDPT of Nt in a low-temperature organic glass is almost unity (see below). The fluorescence kinetic profile of 7AI in *n*-dodecane at 500 nm shows a singleexponential decay time of 3900 ps at 8 K (Fig. 4c). We have assigned the decay time of 3900 ps monitored at 500 nm to the relaxation time of T* and the slow decay time of 3400 ps monitored at 360 nm to the relaxation time of 7AI oligomers that cannot undergo ESDPT.

The presented several fluorescence kinetic profiles of 7AI in n-dodecane, monitored at 360 nm, show that the slow decay component hardly changes in time as temperature increases (Fig. 5). This suggests that the relaxation rate of 7AI oligomers, dominated by nonradiative processes, remains almost invariant in the organic glass of n-dodecane at temperatures below 200 K. However, the fast decay component becomes notably short in time as temperature rises. This suggests that the ESDPT time of Nt to form T* becomes short significantly with temperature increment.

Figure 6 shows the detailed temperature-dependent behaviors of the ESDPT time (k_{PT}^{-1}) of the Nt species to yield the T^{*} species. First, it is noteworthy that $k_{\rm PT}$ is as high as 4×10^9 s⁻¹ even at the temperature extrapolated to 0 K, implying that the ESDPT of Nt is still active at cryogenic temperatures via tunneling (9-13). As temperature rises, the rate constant of $k_{\rm PT}$ increases almost linearly up to 150 K and exponentially above 150 K. The temperature dependence of $k_{\rm PT}$ arises from the temperature-dependent formation of a precursor configuration which is optimal for facile tunneling and suggests that the assisting process of the ESDPT of Nt changes as temperature increases. Precursor-configurational optimization for optimal bond angles and short H-bond lengths is required for Nt to undergo intrinsic ESDPT via tunneling (4,5,32). We suggest that the configurational optimization is assisted mostly by lattice vibrations at low temperatures below 150 K. The activation energy of



Figure 5. Temperature-dependent fluorescence kinetic profiles of 1.0 mM 7-azaindole in *n*-dodecane. The sample was excited at 288 nm and monitored at 360 nm, and temperatures are indicated inside.



Figure 6. Temperature dependence of $k_{\rm PT}$ for 1.0 mM 7-azaindole in *n*-dodecane. Inset: Arrhenius plot of $k_{\rm PT}$ above 150 K. The activation energy from the best-fitted solid line is 0.70 kcal mol⁻¹.

0.70 kcal mol⁻¹ (240 cm⁻¹) obtained from the Arrhenius plot of Fig. 6 corresponds approximately to the librational energy of the Nt* molecule in the organic glass of *n*-dodecane. Note that the librational energy of most organic molecules in an organic glass has the magnitude of $30-300 \text{ cm}^{-1}$ (39). Thus, we intimate that the librational motions of Nt* become active and compete with lattice vibrations to assist the formation of the pretunneling configuration of ESDPT as temperature increases. Above 150 K, the configurational reorganization of Nt to undergo ESDPT is assisted mostly by the hindered rotational motions of Nt.

The KIE of k_{PT} is defined as the ratio of $k_{PT}({}^{1}H)$ to $k_{PT}({}^{2}H)$, where $k_{PT}({}^{1}H)$ and $k_{PT}({}^{2}H)$ are the k_{PT} values of nondeuterated Nt and deuterated Nt, respectively. KIE has small values close to unity to indicate that the ESDPT of Nt is almost isotope independent at low temperatures below 60 K, and its value starts to increase with the temperature increment (Fig. 7). As temperature decreases, the contribution of configurational optimization to the ESDPT of Nt increases, so that the



Figure 7. Temperature dependence of the kinetic isotope effect of $k_{\rm PT}$ (KIE) for 1.0 mm 7-azaindole in *n*-dodecane.

contribution of tunneling to ESDPT decreases to reduce the KIE of ESDPT; the rate of proton tunneling can be veiled if configurational optimization determines the overall rate. Anomalous behaviors in the KIE of the solvent-assisted ESDPT of 7AI in water or alcohols have been explained by the two-step model, which consists of solvent reorganization and intrinsic proton transfer (16,32). Thus, we suggest that the overall ESDPT of Nt can be divided into two orthogonal steps: pretunneling motion to make an optimized precursor configuration and intrinsic proton transfer via tunneling. In one limit, the precursor-configurational optimization, which is independent of isotope effects, can be the rate-determining step, so that KIE becomes unity. In the opposite limit, the precursorconfigurational optimization is rapid relative to the overall ESDPT of Nt and the intrinsic proton transfer dominates the overall process. Thus, we suggest that the precursor-configurational optimization of Nt* assisted by lattice vibrations, as discussed with Fig. 6, determines the ESDPT rate of Nt completely at low temperatures. As temperature increases, the configurational reorganization of Nt* assisted by librational motions becomes active to increase the role of the intrinsic proton transfer such as tunneling in the rate-determining step of the overall ESDPT. Thus, KIE increases exponentially with temperature increase, although it is not large yet in the organic glass of *n*-dodecane. KIE was reported to be as large as 7.4 in *n*-heptane at room temperature (34). This suggests that the intrinsic proton transfer via tunneling dominates the ratedetermining step at high temperatures. The important role of tunneling in the ESDPT of 7AI dimers has been discussed widely in previous reports (9-15,18,24).

CONCLUSION

The reaction mechanisms of the ESDPT of 7AI dimers in a low-temperature organic glass of *n*-dodecane depend on the ground-state conformations of the dimers at the moment of excitation. Whereas planar normal dimers (Np) undergo ESDPT within our temporal resolution (<10 ps) to form tautomeric dimers (T*), twisted normal dimers (Nt) go through ESDPT on the time scale of 250 ps at 8 K. The precursor-configurational optimization of Nt*, which is prerequisite to facile intrinsic proton transfer via tunneling, determines the overall proton-transfer rate to reduce the KIE as small as unity, and it is assisted by lattice vibrations below 150 K or by librational motions above 150 K. At cryogenic temperatures where solvent motions are almost frozen, nuclear motions such as heavy-atom rearrangement, essential prior to intrinsic proton transfer, are highly retarded. Consequently, whereas tunneling contributes mainly to the rate of ESDPT at room temperature, configurational optimization does at cryogenic temperatures.

Acknowledgements—This work was financially supported by research grants through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (2010-0015806 and 2011-0001216). H.L. is also thankful to the BK21 scholarship.

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