THE JOURNAL OF
PHYSICAL
CHEMISTRY A
LETTERS

2009, *113,* 10589–10592
Published on Web 09/11/2009

Triplet-State Acid−Base Reactions of 1-Methyl-7-oxyquinolinium in Water

Sun-Young Park, Oh-Hoon Kwon,[†] Young-Shin Lee, and Du-Jeon Jang*

School of Chemistry, Seoul National University, NS60, Seoul 151-742, Korea

Received: August 10, 2009; Revised Manuscript Received: September 1, 2009

Upon absorption of a photon, the 1-methyl-7-oxyquinolinium zwitterion in neutral water undergoes a proton-transfer cycle involving protonation at the lowest excited triplet state and redeprotonation at the ground state. On one hand, the proton transfer of a water molecule to the triplet-state zwitterion takes place on the time scale of 28 μs with an activation energy of 12.6 kJ mol^{-1}. On the other hand, the ground-state redeprotonation occurs with a rate constant of (13 μs)$^{-1}$, although its reverse reaction of protonation competes with a rate constant of (37 μs)$^{-1}$.

Introduction

Proton or hydrogen transfer has been attracting great attention because it plays a key role in a wide variety of biological and chemical phenomena.[1−8] In particular, hydrogen transfer from hydrogen donors to hydrogen acceptors at triplet excited states is one of the most important and fundamental reactions in organic photochemistry.[6−8] It may usually occur by direct transfer of a hydrogen atom from a donor molecule to an acceptor molecule or by transfer of an electron from the donor to the acceptor followed rapidly by transfer of a proton from the donor cation to the acceptor radical anion.[9,10] Because electron transfer is often the rate-determining step in the latter case,[9,10] proton transfer has been hardly studied at triplet excited states. Thus, we have explored the proton transfer of aqueous 1-methyl-7-oxyquinolinium at the lowest excited triplet state as well as at the ground state by measuring transient absorption kinetics with variation of pH.

The 1-methyl-7-oxyquinolinium cation ($^{+}$MQH), which is imine-blocked 7-hydroxyquinoline (7HQ), can be a good candidate for the simplified study of 7HQ analogues because there are only two prototropic species of the enol-deprotonated zwitterion ($^{+}$MQ^{-}) and the enol-protonated cation $^{+}$MQH (Figure 1). A variety of molecular systems have been extensively studied for photon-initiated Förster cycles involving the first excited and ground singlet electronic states.[11] In a rare case, proton transfer occurs in the lowest triplet state, although it is known to occur as a minor process as compared with that in the first excited singlet state.[12−14] To our knowledge, no report has been made on the Förster cycle via triplet-state proton transfer. Here, we report an anomalous case in which excited-state proton transfer occurs only at the lowest triplet state, completing the Förster cycle by subsequent reverse proton transfer at the ground state.

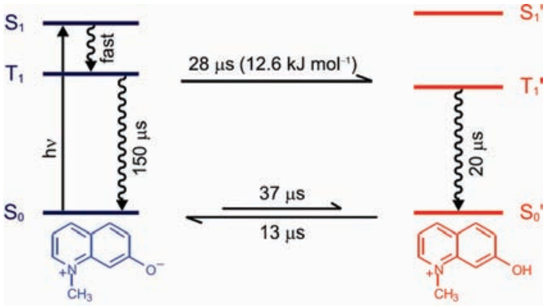

Figure 1. Schematically presented dynamics on the triplet-state protonation reaction of $^{+}$MQ^{-} from water (at pH 11) and the ground-state acid−base reactions of $^{+}$MQ^{-} and $^{+}$MQH with water (at pH 7).

Experimental Section

7HQ, purchased from Eastman Kodak, was refluxed with methyl iodide in dry toluene for 48 h to prepare 1-methyl-7-hydroxyquinolinium iodide (MQHI).[15] The solid product of MQHI was precipitated by adding ether and recrystallized twice in an ethanol−ether mixture. Aqueous solutions were prepared simply by dissolving the obtained yellowish crystalline MQHI in triply distilled water without using a buffered solution. The pH was adjusted by adding a dilute HCl or NaOH solution to an aqueous MQHI solution. The typical concentration of MQHI was 1×10^{-4} M. Absorption spectra were obtained using a UV/vis spectrometer (Scinco, S-3100). Microsecond transient absorption kinetic profiles were obtained by monitoring transmittance changes of a Xe lamp (Spectral Energy, LH 150) beam of 75 W passing a sample, which was excited by a pulsed beam (1 mJ, 6 ns, 10 Hz) from a dye laser (Quantel, TDL90) pumped by a Nd:YAG laser (Quantel, YG980). The wavelength of the Xe lamp beam was selected by using a monochromator of 0.15 m (ARC, SP-150) and a double monochromator of 0.20 m (Kratos, GM 200). The probe beam was detected with a photomultiplier tube (Hamamatsu, R928) and digitized with an oscilloscope of 1 GHz (Lecroy, Wavepro 950). Samples were flowed during kinetic measurements using a peristaltic pump (ISCO, 1612) to avoid sample decomposition. The kinetic profiles were collected every 5 nm to generate time-resolved

---

* To whom correspondence should be addressed. Tel: +82(2)875-6624. Fax: +82(2)875-6624. E-mail: djjang@snu.ac.kr.

[†] Present address: Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125.

10.1021/jp907687a CCC: $40.75

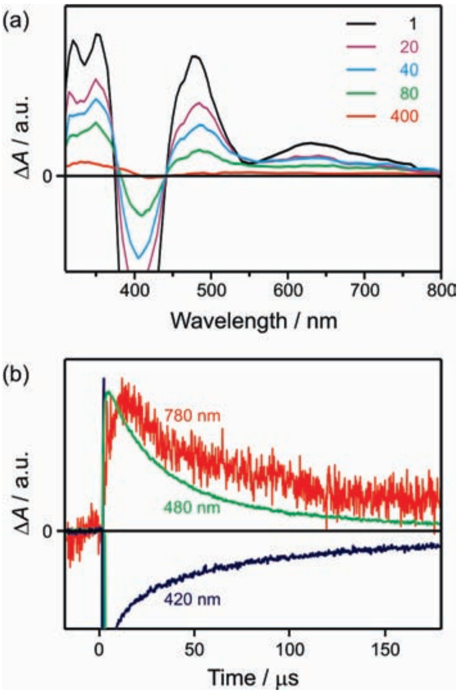

Figure 2. Time-resolved transient absorption spectra (a) and kinetic profiles (b) of MQHI in water at pH 11 with excitation at 400 nm. Time delays after excitation, in the units of microseconds, and probe wavelengths are indicated inside.

transient absorption spectra. The sample temperature was controlled using a refrigerated bath circulator (Jeio Tech, RC-10 V). All of the measurements were carried out under Ar atmosphere at room temperature, if not specified otherwise.

Results and Discussion

Figure S1 in the Supporting Information shows that the lowest absorption bands of aqueous MQHI are spectrally well distinguishable. $^+MQ^-$ and ^+MQH have the lowest absorption peaks at 405 and 350 nm, respectively. Only $^+MQ^-$ exists at pH 11 at the ground state because ^+MQH has a pK_a value of 5.6 (Figure S2 in the Supporting Information). When we excite $^+MQ^-$ by a photon into its first excited singlet state, we cannot observe protonation at S_1, but we can observe fluorescence only around 505 nm due to the extremely low pK_a* value (−13) of ^+MQH.[11] However, the transient absorption spectra and kinetic profiles show somewhat complex behaviors in a microsecond time domain, giving a clue that proton transfer is operative at the lowest triplet state as well as at the ground state.

The multiplex structure of the transient absorption spectra in Figure 2a has five peaks around 320, 350, 405, 480, and 630 nm with an additional tail around 780 nm. While the bleach recovery around 405 nm is unambiguously attributed to $^+MQ^-(S_0)$, the transient absorption having the maximum around 480 nm can be assigned to $^+MQ^-(T_1)$, which is instantly populated by the intersystem crossing from S_1 and whose spectrum is similar to the triplet-state absorption of the zwitterionic form of 7HQ.[12] The bands around 320 and 630 nm can also be assigned to the transient absorption of $^+MQ^-(T_1)$ because they behave kinetically similar to the band around 480 nm. To elucidate the origin of the tail around 780 nm, we have analyzed the kinetic profiles measured at three distinctive wavelengths of 420, 480, and 780 nm (Figure 2b).[16] The decay time of 27 μs at 480 nm for $^+MQ^-(T_1)$ matches well with the risetime of 28 μs at 780 nm. This suggests that transient absorption around 780 nm comes from the $^+MQH(T_1)$ species, which forms via the triplet-state protonation of $^+MQ^-$ and then relaxes into S_0 on the time scale of 20 μs. At pH 11, the observed total rate constant of protonation comes entirely from the rate constant of H_2O-assisted protonation (k_{H_2O}*) having a value of (28 μs)$^{-1}$. On the other hand, the diffusional rate constant of hydroxide ion in the deprotonation process of 7HQ at the ground state is reported to be 2.5×10^{11} M^{-1} s^{-1}.[17] Therefore, we can estimate that the ground-state deprotonation of ^+MQH to form $^+MQ^-$ is completed within several nanoseconds at pH 11. Consequently, we observe that the bleach recovery rate constant of $^+MQ^-(S_0)$ monitored at 420 nm is determined by the convoluted rate constants of the protonation (28 μs) and the relaxation (150 μs) of $^+MQ^-(T_1)$. The spectral band structure at 350 nm is speculated to come from the convolution of $^+MQ^-(S_0)$ bleach and $^+MQH(T_1)$ high energy absorption. The addition of O_2 into samples makes all of the transient bands disappear, implying that the proton-transfer cycle can be completely blocked by the drastic quenching of the $^+MQ^-(T_1)$ species by $O_2(T_0)$.

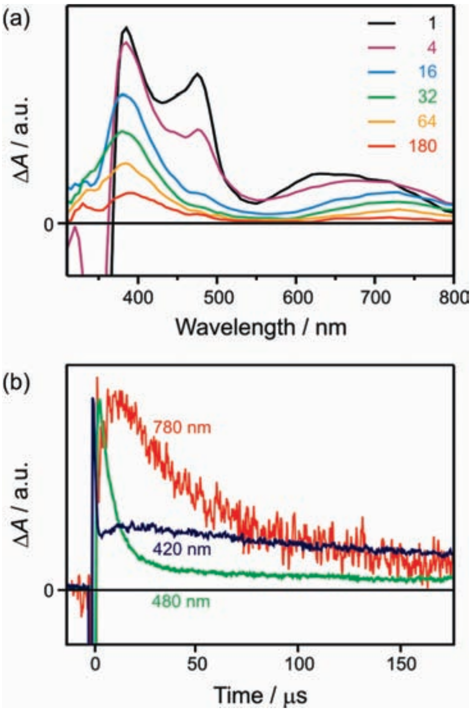

Figure 3. Time-resolved transient absorption spectra (a) and kinetic profiles (b) of MQHI in water at pH 3 (pH 4.4 for the kinetic profile at 420 nm) with excitation at 355 nm. Time delays after excitation, in the units of microseconds, and probe wavelengths are given inside.

Figure 3a clearly shows the transient absorption band of $^+MQH(T_1)$ around 780 nm. The protonation process is sensitively accelerated by [H_3O^+]. Hence, the bands of $^+MQ^-(T_1)$ at 630 nm and $^+MQH(T_1)$ at 780 nm are now clearly resolved. $^+MQH(S_0)$ is the major prototropic equilibrium species (pK_a = 5.6) at pH 3. However, the cationic species can be deprotonated at the first excited singlet state due to its extremely low pK_a* value of −13 to generate $^+MQ^-(S_1)$,[18] which then relaxes into $^+MQ^-(T_1)$ by intersystem crossing. Overall, we can observe triplet-state protonation initiated at the triplet state of $^+MQ^-$ regardless of the photoexcitation of $^+MQH(S_0)$ or $^+MQ^-(S_0)$. It has been reported that acid−base equilibria are established fast within the triplet-state lifetimes of aromatic ketones, which become longer with a pH increase according to the Rayner−Wyatt and the Ware equations.[19,20] We could also observe that the

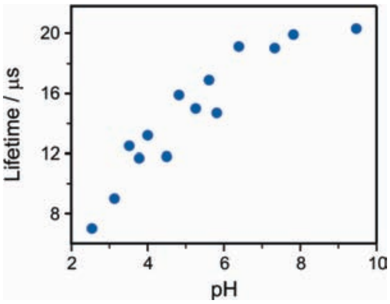

Figure 4. Triplet-state lifetime changes of $^{+}MQ^{-}$ with pH, monitored at 480 nm, indicating that H_3O^+ accelerates the depletion of the triplet state of $^{+}MQ^{-}$.

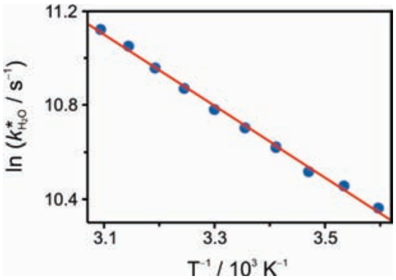

Figure 5. Arrhenius plot of the k_{H_2O}* of $^{+}MQ^{-}$. The activation energy and the preexponential factor from the fitted line are 12.6 kJ mol^{-1} and 7.4 × 10^6 s^{-1}, respectively.

lowering of pH accelerates the triplet-state protonation of $^{+}MQ^{-}$ (Figure 4). $^{+}MQ^{-}(T_1)$ decays on the time scale of 8 μs at pH 3 with the concurrent rise of $^{+}MQH(T_1)$, which relaxes into its ground state in 20 μs (Figure 3b). This indicates that the protonation of $^{+}MQ^{-}(T_1)$ is assisted by H_3O^+ as well as by H_2O.

At pH 4.4, we could happen to observe the short-lived $^{+}MQ^{-}(S_0)$ at 420 nm having the lifetime of 1.5 μs (Figure 3b), which undergoes protonation to produce $^{+}MQH(S_0)$. It is very difficult to observe ground-state proton transfer because $^{+}MQH(S_0)$ and $^{+}MQ^{-}(S_0)$ are in equilibria and their transient absorption bands are spectrally superimposed. The observed total protonation (k_p) and deprotonation rate constants (k_d) of $^{+}MQ^{-}(S_0)$ can be represented as[17]

$$k_p = k_{H_2O} + k_{H_3O^+}[H_3O^+] \tag{1}$$

$$k_d = k_{H_2O}' + k_{OH^-}[OH^-] \tag{2}$$

where $k_{H_3O^+}$ and k_{H_2O} are the rate constants of H_3O^+- and H_2O-assisted protonation, respectively, and k_{OH^-} and k_{H_2O}' are those of OH^-- and H_2O-assisted deprotonation, respectively. Considering the pK_a value (5.6) of $^{+}MQH(S_0)$, the observed lifetime (1.5 μs) of $^{+}MQ^{-}(S_0)$ at pH 4.4, and eqs 1 and 2, we can derive the diffusion rate constant of the hydronium ion to be 2.5 × 10^{10} M^{-1} s^{-1}, which is similar to the reported value of 1.5 × 10^{10} M^{-1} s^{-1}.[17] The rate constants of k_{H_2O} and k_{H_2O}' can also be calculated as (37 μs)$^{-1}$ and (13 μs)$^{-1}$, respectively.

The temperature dependencies of transient absorption kinetics were explored at 420, 480, and 780 nm, but significant dependencies were observed only in the decay at 480 nm and in the rise at 780 nm. This supports our interpretation on proton transfer, which is a thermally activated process. The Arrhenius plot of Figure 5 for the decay of $^{+}MQ^{-}(T_1)$, monitored at 480 nm in the temperature range of 5−50 °C, gives the activation energy of 12.6 kJ mol^{-1} for the water-assisted triplet-state protonation of $^{+}MQ^{-}$, which is in the reasonable order of diffusion-controlled activation energy. Now, we can express H_2O-involved acid−base equilibria as eqs 3−5.

$$^{+}MQ^{-} + H_2O \xrightarrow{k_{H_2O}^*} {}^{+}MQH + OH^{-} \text{ at } T_1 \tag{3}$$

$$^{+}MQ^{-} + H_2O \xrightarrow{k_{H_2O}} {}^{+}MQH + OH^{-} \text{ at } S_0 \tag{4}$$

$$^{+}MQH + H_2O \xrightarrow{k_{H_2O}'} {}^{+}MQ^{-} + H_3O^{+} \text{ at } S_0 \tag{5}$$

The intersystem crossing of $^{+}MQ^{-}(S_1)$ into $^{+}MQ^{-}(T_1)$ is expected to be considerably enhanced due to a small $\Delta E_{S_1-T_1}$ gap. Subsequently, triplet-state proton transfer can be clearly observable due to the enhanced population of $^{+}MQ^{-}(T_1)$, together with the increased basicity of the O^{-} group.

Important observations and our proposed mechanism for the photochemical and photophysical phenomena of excited $^{+}MQ^{-}$ in neutral water are summarized in Figure 1. The instantly excited $^{+}MQ^{-}(S_1)$ species relaxes into the lowest triplet state by intersystem crossing or into the ground state. The $^{+}MQ^{-}(T_1)$ species, then, undergoes H_2O-assisted proton transfer on the time scale of 28 μs with an activation energy of 12.6 kJ mol^{-1} to form the $^{+}MQH(T_1)$ species, which relaxes into the ground state within 20 μs. The Förster cycle is established by subsequent reverse proton transfer to restore the depleted $^{+}MQ^{-}(S_0)$ species. For the first time, to our knowledge, we are reporting a photoinitiated Förster cycle involving a base reaction at the lowest triplet state and an acid reaction at the ground state. The detailed reaction mechanism and the evaluation of the pK_a* value at the triplet state are now under investigation.

Acknowledgment. This work was financially supported by research grants through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (KRF-2008-313-C00399 and 2009-0082846). We are also thankful to the SRC program of NRF (R11-2007-012-01002-0), while S.-Y.P. acknowledges the Seoul fellowship and the BK21 scholarship as well.

Supporting Information Available: Absorption spectra and pK_a determination. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Park, S.-Y.; Lee, Y.-S.; Kwon, O.-H.; Jang, D.-J. *Chem. Commun.* **2009**, 926.
(2) Kwon, O.-H.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 8703.
(3) Kwon, O.-H.; Lee, Y.-S.; Yoo, B. K.; Jang, D.-J. *Angew. Chem., Int. Ed.* **2006**, *45*, 415.
(4) Garczarek, F.; Gerwert, K. *Nature* **2006**, *439*, 109.
(5) Kwon, O.-H.; Kim, T. G.; Lee, Y.-S.; Jang, D.-J. *J. Phys. Chem. B* **2006**, *110*, 11997.
(6) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.
(7) Turro, N. J.; Dalton, J. C.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D.; Niemczyk, M.; Schore, N. *Acc. Chem. Res.* **1972**, *5*, 92.
(8) Monroe, B. M.; Weed, G. C. *Chem. Rev.* **1993**, *93*, 435.
(9) Yuasa, J.; Fukuzumi, S. *J. Am. Chem. Soc.* **2006**, *128*, 14281.
(10) Singh, A. K.; Palit, D. K.; Mukherjee, T. *J. Phys. Chem. A* **2002**, *106*, 6084.

(11) Tolbert, L. M.; Solntsev, K. M. *Acc. Chem. Res.* **2002**, *35*, 19, and references therein.

(12) Lee, S.-I.; Jang, D.-J. *J. Phys. Chem.* **1995**, *99*, 7537.

(13) Gormin, D.; Heldt, J.; Kasha, M. *J. Phys. Chem.* **1990**, *94*, 1185.

(14) Martinez, M. L.; Studer, S. L.; Chou, P.-T. *J. Am. Chem. Soc.* **1990**, *112*, 2427.

(15) Bardez, E.; Chatelain, A.; Larrey, B.; Valeur, B. *J. Phys. Chem.* **1994**, *98*, 2357.

(16) $F(t)_{480} = 0.97e^{-t/27} + 0.03e^{-t/500}$, $F(t)_{780} = 0.91(1-e^{-t/28})e^{-t/20} + 0.09e^{-t/500}$, and $F(t)_{420} = -(0.60e^{-t/28} + 0.33e^{-t/150} + 0.07e^{-t/500})$, in the time units of microseconds. The minor component of 500 μs due to impurities is neglected in the interpretation.

(17) Kim, T. G.; Lee, S.-I.; Jang, D.-J.; Kim, Y. *J. Phys. Chem.* **1995**, *99*, 12698.

(18) Bardez, E.; Fedorov, A.; Berberan-Santos, M. N.; Martinho, J. M. G. *J. Phys. Chem. A* **1999**, *103*, 4131.

(19) Shizuka, H.; Kimura, E. *Can. J. Chem.* **1984**, *62*, 2041.

(20) Hoshi, M.; Shizuka, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2711.

JP907687A