J|A|C|S
COMMUNICATIONS

Following the Solvent Directly during Ultrafast Excited State Proton Transfer

Sarah J. Schmidtke, David F. Underwood, and David A. Blank*
Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received March 9, 2004; E-mail: blank@chem.umn.edu

Proton transfer, PT, is an important process in numerous areas of chemistry. The static effect of a polar solvent environment on the position of equilibrium has long been appreciated. More recently, a great deal of attention has been given to understanding the dynamic role played by the solvent.[1−3] Experimentally, studies have been limited to measuring the rate of the appearance (disappearance) of the products (reactants). Conclusions concerning the solvent's role in the reaction are often inferred from a comparison between the rate of PT and known time scales associated with the solvent. Following the dynamics from the perspective of the reactants and products has certainly provided significant advancement of our understanding in this important area of chemistry.[1,2,4−16]

To better understand how the solvent participates in chemical events it is advantageous to probe the response of the solvent directly. In addition to providing a direct look at the solvent's role in a reaction, following a reaction via the solvent response can offer a new perspective on the dynamics of the reaction itself. For example, although the spectroscopy of a given reactant and product are often well characterized, mapping observed resonant transitions to intermediate, transient reaction structures can be poorly understood due to overlap between transitions on both the reactant and product side of the transition state.[7] In such cases, the solvent can report on the reaction progress in a way that does not require detailed knowledge of the spectroscopy of transient intermediates. We recently developed a new technique to follow the dynamics from the perspective of the solvent, directly probing the response of the local solvent environment during a dynamic event in solution.[17] Here we report the application of this approach to a reactive system in solution for the first time, directly probing the solvent's role in excited state intramolecular proton transfer, ESIPT.

In this example we examine the role of the solvent, acetonitrile, in controlling ESIPT in 1-chloroacetylaminoanthraquinone, CAAQ. The structures of the normal, $\mathbf{1_N}$, and tautomeric, $\mathbf{1_T}$, forms of CAAQ are shown in Figure 1. In the ground electronic state, S_0, $\mathbf{1_N}$ is the stable form. Following excitation to the first excited electronic state, S_1, ESIPT takes place between $\mathbf{1_N}$ and $\mathbf{1_T}$. In an extensive set of investigations, Barbara and co-workers demonstrated that the ESIPT rate in a series of 1-(acylamino)anthraquinones could be tuned from nearly instantaneous to absent by substitution of acyl groups with larger or smaller electron affinity, respectively.[7] CAAQ was found to be an intermediate case in dipolar solvents, with the majority of the static fluorescence originating from $\mathbf{1_N}$ (S_1), and a measured appearance time for $\mathbf{1_T}$ (S_1) of <300 fs. With higher time resolution, Neuwahl et al. determined an appearance time of 110 fs for $\mathbf{1_T}$ (S_1).[13]

Details of the experiment can be found in reference 17 and the Supporting Information. A laser pulse at 400 nm excites CAAQ to the reactive S_1 state at time $t = 0$. Three 800 nm laser pulses probe the change in the electronically nonresonant Raman response of the solvent molecules as a function of time, t. A delay intrinsic to the Raman probe, 140 fs between the first two and third probe pulses, is set near the maximum of the intermolecular nuclear response of the solvent, a region of the response that is often associated with librational motion of the solvent molecules.[18] The instrument response along t is Gaussian in time with fwhm = 140 fs, and we estimate our time resolution to be 80 fs.

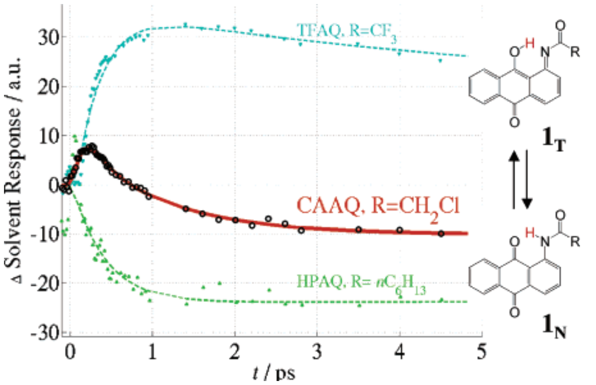

Figure 1. Local solvent response following excitation of three AQs in acetonitrile. The solid line is the fit to the CAAQ data described by eq 1, representing the response of the solvent to the ESIPT dynamics in the S_1 state. TFAQ and HPAQ are limiting cases of rapid and complete ESIPT and no ESIPT, respectively. At the right are the normal and tautomer structures.

Figure 1 shows the change in the Raman response of the local solvent environment following resonant excitation of CAAQ. The data were fit with the sum of three components. To emphasize the response of the solvent to the reactive dynamics in the S_1 state two of the fitting components, a 16 ps exponential decay due to rotation of CAAQ and the background measured from a sample of neat acetonitrile under identical conditions, have been subtracted from the data presented in Figure 1. The raw data and complete fit are presented in the Supporting Information. The data in Figure 1 have been fit as a series of three steps,

$$(-7.3)\mathbf{A} \xrightarrow{100\ \text{fs}} (17)\mathbf{B} \xrightarrow{180\ \text{fs}} (4.5)\mathbf{C} \xrightarrow{1.1\ \text{ps}} (-10)\mathbf{D} \qquad (1)$$

Equation 1 was convoluted over the instrument response function, and the time scales above the arrows and weighting factors in parentheses were varied to obtain the best fit to the data in Figure 1.

The measured response reflects the change in the polarizability of the intermolecular motions in the local solvent environment following excitation of CAAQ. For reference the measured responses for two other 1-(acylamino)anthraquinones, TFAQ and HPAQ, are also presented, see Figure 1. TFAQ undergoes ballistic and complete PT in the excited state, and HPAQ does not undergo PT in the excited state.[7] These two limiting cases demonstrate that there is a positive change in the solvent response when undergoing PT to $\mathbf{1_T}$(S_1) and a negative change in the response when exciting to $\mathbf{1_N}$(S_1) in the absence of subsequent PT. This observation can be explained in terms of the change in the solvent−solute interaction following solute excitation, with the dipole moment increasing relative to $\mathbf{1_N}$(S_0) upon transition to $\mathbf{1_T}$(S_1) and decreasing relative to $\mathbf{1_N}$(S_0) upon transition to $\mathbf{1_T}$(S_1).[20] The details of this effect will be addressed elsewhere.[23] For the purpose of discussion here we

10.1021/ja048639g CCC: $27.50 © 2004 American Chemical Society

will limit the assignment of the solvent response to time-dependent changes in the ratio of $\mathbf{1_T}/\mathbf{1_N}$. An increase in the response indicates progress toward the product ($\mathbf{1_T}$), and a decrease in the response indicates progress toward the reactant ($\mathbf{1_N}$), depicted vertically on the right side of Figure 1.

Upon excitation, $\mathbf{1_N}$ is placed in the S_1 state, which is the starting point labeled **A** in eq 1. Impulsive excitation from $\mathbf{1_N}(S_0)$ to $\mathbf{1_N}(S_1)$ at $t = 0$ is reflected in the negative weight for **A**. There is an initial 100 fs rise in the solvent response, consistent with the 110 fs appearance time measured for $\mathbf{1_T}(S_1)$.[13] This is followed by a decrease in the signal with time scales of 180 fs and 1.1 ps. The decrease in the $\mathbf{1_T}/\mathbf{1_N}$ ratio indicates a shift back toward $\mathbf{1_N}$ on the S_1 surface. The fact that the solvent response falls to a negative value in the first 1−2 ps and remains negative is consistent with the static fluorescence spectrum, which is dominated by emission from $\mathbf{1_N}$.[7]

The effect of the solvent on reactive dynamics is typically considered in the equilibrium limit, where the solvent responds rapidly compared to progress along the reaction coordinate, and one envisions a single minimum free energy path from reactants to products.[3] In this limit it is the barrier along the motion of the proton from the donor to acceptor site that determines the rate of proton transfer, and for intermolecular PT this can be strongly influenced by small structural changes in reactants.[13] If this limit applied to ESIPT in CAAQ, then we would expect to observe a single rise in the solvent response as equilibrium is established starting from the initially prepared $\mathbf{1_N}(S_1)$. However, the most striking feature of the CAAQ response in Figure 1 is that following initial progress toward the product the reaction turns around and proceeds back toward the reactant. The fact that the reaction initially proceeds from $\mathbf{1_N}$ to $\mathbf{1_T}$ and then returns to $\mathbf{1_N}$ in the first 1−2 ps clearly indicates that on the time scale of this reaction there is not a single, solvated reaction coordinate. Rather the dynamics are dictated by a time-dependent free energy path between $\mathbf{1_N}$ and $\mathbf{1_T}$ that evolves as the solvent reorganizes. We note that in the reported time-resolved stimulated emission from $\mathbf{1_T}(S_1)$ there is no evidence of the return to $\mathbf{1_N}(S_1)$.[13] The authors present only the first 600 fs after excitation, and we speculate that within this time frame the overlapping emission from different points along the PT, as discussed by Barbara and coworkers,[7] masks the start of the return event in these measurements. This potential complication is avoided when probing the solvent.

In a detailed theoretical study, Kiefer and Hynes recently considered the limit where PT is rapid on the time scale of solvent reorganization, and the reaction rate is determined by dynamic solvent reorganization.[19] In this limit the relative free energy of the reactants and products becomes time dependent as the solvent configuration evolves. This limit is represented schematically for ESIPT in CAAQ in Figure 2. We calculate that in the S_1 state $\mathbf{1_N}$ and $\mathbf{1_T}$ are nearly isoenergetic based on vertical excitation from the ground state.[20] At $t = 0$, CAAQ is excited to the S_1 state, but the solvent is still in the initial equilibrium configuration established around the ground state, $\mathbf{1_N}(S_0)$. In the long time limit, static fluorescence indicates greater stabilization of $\mathbf{1_N}(S_1)$ than $\mathbf{1_T}(S_1)$.[6,7] This is consistent with the larger change in the magnitude and direction of the dipole moment going from $\mathbf{1_N}(S_0)$ to $\mathbf{1_N}(S_1)$ verses $\mathbf{1_T}(S_1)$.[20] In the first 100 fs there is an increase in the $\mathbf{1_T}/\mathbf{1_N}$ ratio from zero as equilibrium along the PT coordinate is established. As the solvent reorganizes, the relative free energy of $\mathbf{1_N}$ versus $\mathbf{1_T}$ falls, and equilibrium shifts back toward $\mathbf{1_N}$ with a bimodal response consistent with measured solvation dynamics in acetonitrile.[21,22] In this system the local solvent motions play the lead role in dictating the dynamics of excited state proton transfer. A more complete accounting of this work will include the ability of the technique to spread the solvent response into a second time dimension, allowing a detailed analysis of the specific solvent coordinate(s) that participate as the PT proceeds from reactants to products and back.[23]

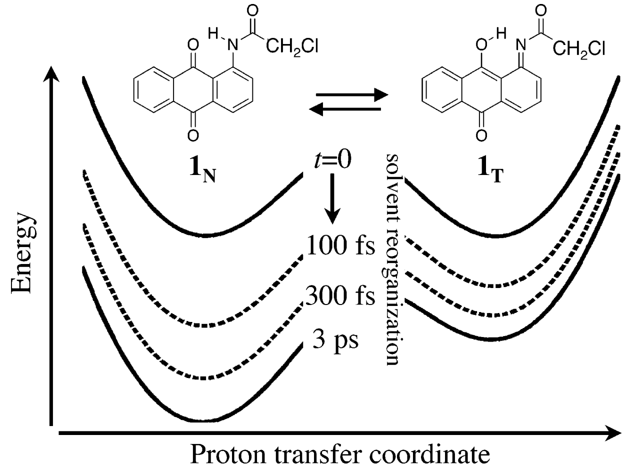

Figure 2. Normal and tautomer structures for CAAQ . Schematic representation of the proton transfer coordinate in the excited S_1 state. Lowering of the energy due to solvent reorganization is depicted relative to the equilibrium solvent configuration around the electronic state of $\mathbf{1_N}$, $t = 0$.

Acknowledgment. This work was supported by NSF under Award Number CHE-0211894. This work was supported in part by the MRSEC Program of the NSF under Award Number DMR-0212302. We thank the donors of the Petroleum Research Fund for support of this work. D.B. thanks the Camille and Henry Dreyfus Foundation, the David and Lucille Packard Foundation, and 3M Company for their generous support. S.J.S. thanks the NSF for Fellowship support and the Minnesota Supercomputing Institute for computing time and resources.

Supporting Information Available: Details of the experiment, fitting, and calculated values referred to in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Barbara, P.; Walker, G.; Smith, T. *Science* **1992**, *256*, 975−981.
(2) Elsaesser, T.; Bakker, H., Eds. *Ultrafast Hydrogen Bonding Dynamics and Proton Transfer Prosesses in the Condensed Phase*; Kluwer Academic Publishers: Boston, 2002.
(3) Voth, G.; Hochstrasser, R. *J. Phys. Chem.* **1996**, *100*, 13034−13049.
(4) Barbara, P.; Trommsdorff, H. P. E. *Chem. Phys.* **1989**, *136*, 153−360.
(5) Douhal, A.; Lahmani, F.; Zewail, A. *Chem. Phys.* **1996**, *207*, 477−498.
(6) Smith, T.; Zaklika, K.; Thakur, K.; Barbara, P. *J. Am. Chem. Soc.* **1991**, *113*, 4035−4036.
(7) Smith, T.; Zaklika, K.; Thakur, K.; Walker, G.; Tominaga, K.; Barbara, P. *J. Phys. Chem.* **1991**, *95*, 10465−10475.
(8) Taylor, C.; El-Bayoumi, M.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *63*, 253−60.
(9) Moog, R.; Maroncelli, M. *J. Phys. Chem.* **1991**, *95*, 10359−69.
(10) Chou, P.-T.; Liu, Y.-I.; Liu, H.-W.; Yu, W.-S. *J. Am. Chem. Soc.* **2001**, *123*, 12119−12120.
(11) Das, K.; English, D.; Petrich, J. *J. Am. Chem. Soc.* **1997**, *119*, 2763−2764.
(12) Herbich, J.; Hung, C.-Y.; Thummel, R.; Waluk, J. *J. Am. Chem. Soc.* **1996**, *118*, 3508−3518.
(13) Neuwahl, F.; Bussotti, L.; Righini, R.; Buntinx, G. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1277−1283.
(14) Lochbrunner, S.; Wurzer, A.; Riedle, E. *J. Phys. Chem. A* **2003**, *107*, 10580−10590.
(15) Hoefer, T.; Kruck, P.; Elsaesser, T.; Kaiser, W. *J. Phys. Chem.* **1995**, *99*, 4380−4385.
(16) Waluk, J. *Acc. Chem. Res.* **2003**, *36*, 832−838.
(17) Underwood, D.; Blank, D. *J. Phys. Chem. A* **2003**, *107*, 956−61; ibid 9736.
(18) Maroncelli, M.; Kumar, V.; Papazyan, A. *J. Phys. Chem.* **1993**, *97*, 13−17.
(19) Kiefer, P.; Hynes, J. *J. Phys. Chem. A* **2002**, *106*, 1834−1849.
(20) See Supporting Information
(21) McMorrow, D.; Lotshaw, W. *J. Phys. Chem.* **1991**, *95*, 10395−406.
(22) Rosenthal, S.; Xie, X.; Du, M.; Fleming, G. *J. Chem. Phys.* **1991**, *95*, 4715−18.
(23) Manuscript in preparation.

JA048639G