Excited-State Proton Transfer from 4-Hydroxy-1-naphthalenesulfonate to Urea

M. Than Htun,[†,‡] A. Suwaiyan,[†,‡] A. Baig,[‡] and Uwe K. A. Klein*[,†,‡]

Chemistry Department and Laser Research Laboratory, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Received: March 31, 1998; In Final Form: June 16, 1998

The excited-state proton transfer from 4-hydroxy-1-naphthalenesulfonate to urea has been studied in methanol at 25 °C. The decay of the acidic form is single-exponential for all urea concentrations. The proton acceptor concentration has been found to increase nonlinearly with the concentration of urea. The nonlinear behavior is explained by a model proposing urea monomers and, in particular, urea dimers to be the proton acceptors in methanol.

1. Introduction

Intermolecular proton transfer from photoexcited molecules to the solvent has been investigated with the advent of picosecond spectroscopic techniques in the past few years. Such studies[1−6] are essential to gain more insight into the important role of the proton acceptor, usually the solvent, in condensed-phase proton transfer reactions. No proton can be transferred without a proper acceptor, and its dynamics depends on the number of solvent molecules that can accept the detached proton. Water is generally regarded as an ideal proton acceptor and its dynamics in the proton transfer kinetics has been studied substantially in alcohol−water mixtures. A water cluster containing 4 ± 1 water molecules has been proposed to be the proton acceptor in the decay of photoexcited 2-naphthol ($pK^* \cong 2.8$) in methanol−water mixtures.[1] Huppert et al.[5] have also suggested an involvement of a single water molecule in the early stage of the proton-transfer reaction. Our earlier studies on the fluorescence decay of excited 4-hydroxy-1-naphthalenesulfonate ($pK^* \cong -0.10$) in methanol−water and ethanol−water mixtures have shown the participation of a water dimer or a cluster of two water molecules in the hydration of the proton.[4] Another independent study on the quenching of the fluorescence emission of 5-cyano-2-naphthol ($pK^* \cong -1.2$) and 5,8-dicyano-2-naphthol ($pK^* \cong -4.5$) has also shown a water dimer to be the effective proton acceptor.[6]

Apart from water, ammonia has been used as an acceptor in the proton-transfer reactions. The studies of Berstein and co-workers[7] have shown that the proton transfer occurs for at least one configuration of the 1-naphthol$(NH_3)_3$ cluster, indicating the importance of the geometry. Zewail and co-workers[8−10] have also investigated the proton-transfer dynamics of 1-naphthol clustered with ammonia, piperidine, and water and reported that the number of solvent molecules is three for ammonia, two for piperidine, and no proton transfer is observed for water up to 21 molecules.

Urea has been used as an additive in proton-transfer reactions. Politi and Chaimovich[11] have reported that the proton dissociation from the first excited state of 8-hydroxypyrene-1,3,6-trisulfonate and β-naphthol-6-sulfonate in aqueous solution is independent of urea concentrations up to 3.0 M. They have also suggested that a urea−water cluster having properties similar to pure water could possibly be a proton acceptor in aqueous urea solutions. Lee[12] reported that aqueous solutions of urea are "inert" toward proton transfer. However, Lee[12] used 2-naphthol, a weak excited-state acid having a slow rate of proton transfer. Therefore, high acceptor concentrations are required before they show a measurable effect; i.e., the solvent water may mask the contribution of urea to the proton transfer. On the other hand, Suwaiyan et al.[2] have reported an increase in the proton-transfer rate of 8-hydroxypyrene-1,3,6-trisulfonate in methanol−water mixtures in the presence of urea, suggesting that urea is a structure breaker of water.

Urea, being a neutral molecule with two nitrogen atoms and one oxygen atom, could also be a good candidate for use as a proton acceptor itself. In the literature, two different models have been used to describe the thermodynamic properties of urea solutions. In the first one, urea is regarded as a good water structure breaker, while in the second one, it is believed to undergo significant association in solution.[13] Hamilton and Stokes[14] have reported the increase of the apparent molar volume of urea in methanol with an increase in urea concentration. Urea dimers and other higher-order urea aggregates are expected to be present in methanol in addition to urea monomers. Thus, the underlying role of urea in proton-transfer dynamics is still ambiguous and needs more work for further elaboration. It is, therefore, of interest to measure the proton-transfer rate to urea and study its dynamics in the excited-state proton-transfer reaction.

In this report we discuss the proton-transfer rate of the excited 4-hydroxy-1-naphthalenesulfonate (ROH*) to urea in methanol at 25 °C and emphasize the role of urea as a proton acceptor. We find that not only urea monomers but also urea dimers accept the proton. The proton accepting efficiency of the urea dimer is about 13 times higher than that of the urea monomer. These findings support the view of involvement of high-order clusters in intermolecular proton-transfer reactions.

2. Experimental Section

2.1. Materials. The sodium salt of 4-hydroxy-1-naphthalenesulfonic acid ($pK^* \approx -0.1$) was procured from the Institute of Physical Chemistry, Stuttgart, Germany. Urea and methanol

* To whom correspondence should be addressed.
† Chemistry Department.
‡ Laser Research Laboratory.

10.1021/jp981709j CCC: $15.00
Published on Web 10/03/1998

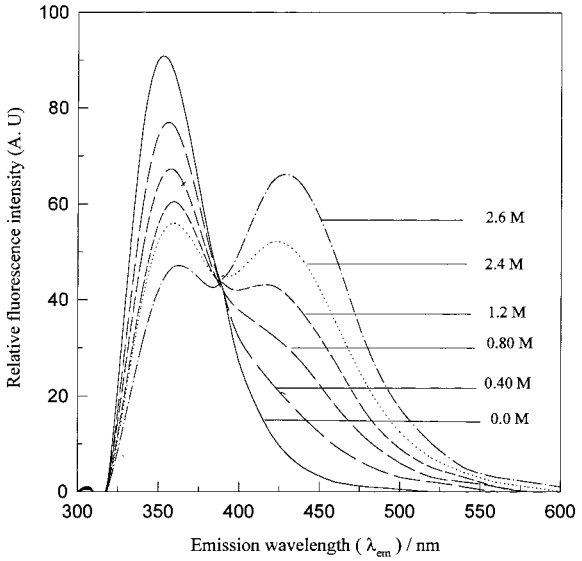


Figure 1. Emission spectra of ROH* in methanol at different concentrations of urea. $\lambda_{ex} = 300$ nm.

(spectral grade) were purchased from Fluka and used as received. Samples having a different concentration of urea, i.e., 0.20−2.8 M were prepared in methanol. The concentration of the probe was kept at about 10^{-5} M in all samples.

2.2. Apparatus and Procedure. A synchronously pumped cavity-dumped dye laser, operated with a mode-locked Nd−YAG laser was used as a light source for the excitation. The mode-locked laser has a 82 MHz pulse train with picosecond pulse durations and was used to pump the rhodamine 6G dye. The output of the dye laser was cavity-dumped at 4 MHz. The excitation wavelength of 300 nm was achieved by using a frequency doubler. A single-photon counting apparatus was used to measure the fluorescence decay of samples at 350 nm and the data were analyzed by deconvolution using the observed time profile of scattered excitation pulses as a reference source. The system response function from the scattered light has a pulse width of about 350 ps. The temperature was controlled to 25 ± 0.1 °C by using a Lauda refrigerating circulator, model RC 6, Brinkmann Instruments, Inc.

3. Results

3.1. Absorption Spectra. As reported in the literature,[15] the absorption maximum of 4-hydroxy-1-naphthalenesulfonate (ROH) is at 299 nm in methanol. The shape and the position of the ROH absorption band do not change with added urea in all samples up to 2.8 M. This suggests that ground-state complexation between ROH and urea does not take place and no proton transfer occurs in the ground state.

3.2. Emission Spectra. Initial fluorescence measurements of ROH are carried out in methanol. The fluorescence emission band of ROH* is observed at 355 nm and a new fluorescence band appears at 440 nm upon addition of urea. This new band is attributed to the conjugate base (RO^- *) of the ROH*.[15] The fluorescence spectra of ROH* and RO^- * are shown in Figure 1. The fluorescence intensity of ROH* decreases while the intensity of RO^- * increases as the concentration of urea increases in methanol. This observation indicates that urea accepts the proton from ROH*. The appearance of an isosbestic point at about 389 nm suggests the proton transfer to be an adiabatic process.

3.3. Fluorescence Decay of ROH* in Methanol. Some fluorescence decays of ROH* in methanol measured at 49 ps/channel are shown in Figure 2. Irrespective of the concentration of urea in methanol, the fluorescence decays of ROH* are nicely fit to a single exponential for all samples:

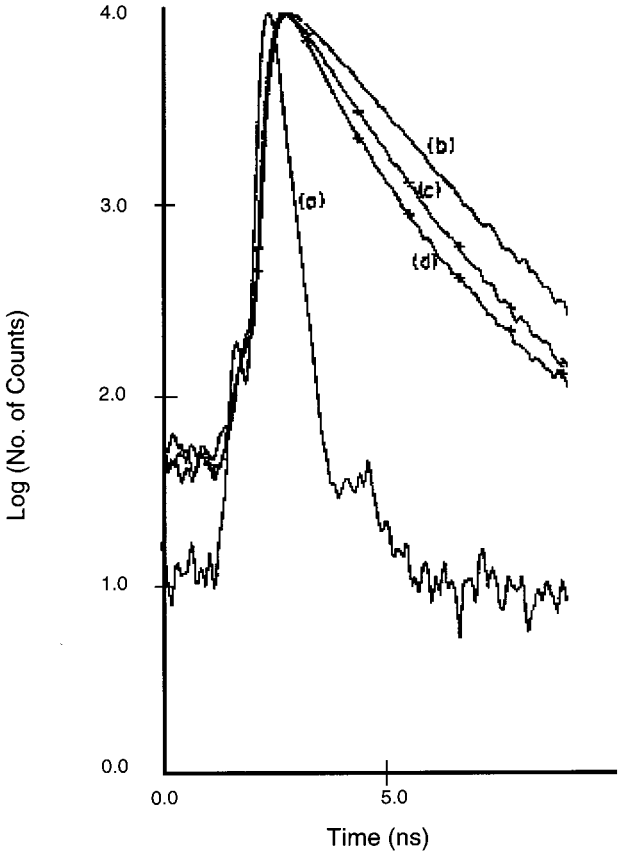


Figure 2. Fluorescence decays of 4-hydroxy-1-naphthalenesulfonate in methanol at 25 °C. (a) Pump pulse; (b) 0 M urea; (c) 1.0 M urea; (d) 2.0 M urea.

$$I(t) = A\, e^{-t/\tau} \tag{1}$$

This observation suggests that a recombination between the detached proton and RO^- * could not be detected within the resolution of our photomultiplier. The lifetimes of ROH* in methanol at different concentrations of urea are obtained through the deconvolution of the instrument response function and reported in Table 1. The lifetime of the ROH* in the absence of urea, τ_0, is 1.60 ns and it decreases to 815 ps with 2.8 M urea in methanol.

By varying the temperature, an estimate of the activation energy for the reaction through the Arrhenius equation is found to be in the range of 6−8 kJ/mol, which is well below the activation energy limit (i.e., 20−21 kJ/mol) for diffusion-controlled reactions.[16] Therefore, the proton transfer of ROH* to urea is considered to be a diffusion-controlled reaction and the bimolecular rate constant, k_{dc}*, may thus be calculated by using Smoluchowski's equation:[16]

$$k_{dc}^* = \frac{2RT}{3\eta}\frac{(r_A + r_B)^2}{r_A r_B} \tag{2}$$

where R is the gas constant, η is the measured viscosity of the medium, r_A is the radius of the probe (≈ 3.83 Å), r_B is the radius of the urea (≈ 2.45 Å), and T is the temperature of the medium. The calculated values of k_{dc}* are also reported in Table 1. The measured viscosity of the solution is found to

TABLE 1: Kinetic Parameters of ROH* in Methanol at 25 °C

[urea] (M)	lifetime τ (ns)	measured rate constant k_{mesd} $(=1/\tau)$ $(10^9\ s^{-1})$	dissociation rate constant $k_1^* = 1/\tau - 1/\tau_0$ $(10^8\ s^{-1})$	viscosity of the solution η (cP)	diffusion-controlled bimolecular rate constant k_{dc}^* $(10^9\ M^{-1}\ s^{-1})$	[proton acceptor] $(10^{-2}$ M)
0.0	1.60	0.625	0	0.558	11.8	0
0.20	1.49	0.671	0.460	0.585	11.9	0.387
0.40	1.39	0.719	0.940	0.620	11.2	0.839
0.60	1.31	0.763	1.38	0.639	10.9	1.27
0.80	1.27	0.787	1.62	0.678	10.2	1.59
1.0	1.19	0.840	2.15	0.692	10.0	2.15
1.2	1.10	0.909	2.84	0.699	9.93	2.86
1.4	1.06	0.943	3.18	0.746	9.30	3.42
1.6	1.02	0.980	3.55	0.763	9.09	3.91
1.8	0.992	1.01	3.85	0.800	8.67	4.44
2.0	0.935	1.07	4.45	0.841	8.25	5.39
2.2	0.891	1.12	4.95	0.853	8.14	6.08
2.4	0.833	1.20	5.75	0.863	8.04	7.15
2.6	0.817	1.22	5.95	0.907	7.65	7.78
2.8	0.815	1.23	6.05	0.947	7.33	8.25

TABLE 2: Decay Analysis of RO^- * at λ_{em} at 500 nm

[urea] (M)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)
1.0	−4.62	1.19	4.18	1.74	1.87	7.92
1.2	−3.54	1.10	2.93	1.71	2.03	7.57
1.4	−2.99	1.06	2.38	1.58	2.10	7.38
1.6	−2.73	1.02	2.06	1.43	2.23	7.15
1.8	−2.71	0.992	2.07	1.33	2.25	7.37
2.0	−3.83	0.935	2.71	1.31	2.35	8.61
2.2	−2.45	0.891	1.38	1.56	2.23	8.34
2.4	−2.76	0.833	1.55	1.30	2.33	8.29
2.6	−2.64	0.817	1.41	1.26	2.34	8.38
2.8	−3.09	0.815	1.79	1.11	2.42	8.34

increase by 60% from pure methanol ($\eta = 0.588$ cP) to 2.8 M urea in methanol ($\eta = 0.947$ cP) (see also Table 1). The radius of the urea, r_B, is estimated from its apparent molar volume, i.e., 37 cm^3/mol in methanol at 25 °C.[14]

3.4. Fluorescence Decay of RO^- * in Methanol. While the fluorescence decay of the excited acid is single-exponential, the fluorescence decay of the excited base taken at $\lambda_{em} = 500$ nm is triexponential. The first exponential describing the rise, i.e., having a negative exponential factor, is the same as the decay of the acid. The actual decay of the base is biexponential. We first allowed all three exponentials to be fitted freely, which resulted in up to 30% difference in the lifetime of the first exponential compared to the acid decay. This is expected for free fitting. However, to get better data on the base, we decided later to fix the first lifetime to be the same as the corresponding decay of the acid. Table 2 summarizes the results. It is obvious that there is no single constant lifetime of the base as would be expected for a normal acid−base reaction scheme with forward reaction only. As we will discuss later, it is possible that the excited base−urea interaction varies with the concentration of urea. However, more experiments have to be done in order to fully understand the behavior of the excited base in the presence of urea.

4. Discussion

4.1. Stern−Volmer Evaluation. As shown in Figure 1, the fluorescence intensity of ROH* is quenched upon addition of urea. To obtain information on the fluorescence quenching mechanism, the relative quantum yields of ROH* in methanol in the presence (ϕ) and absence (ϕ_{max}) of urea are calculated from the height and maximum height of the recorded fluorescence spectra. As shown in Figure 3, the Stern−Volmer plot

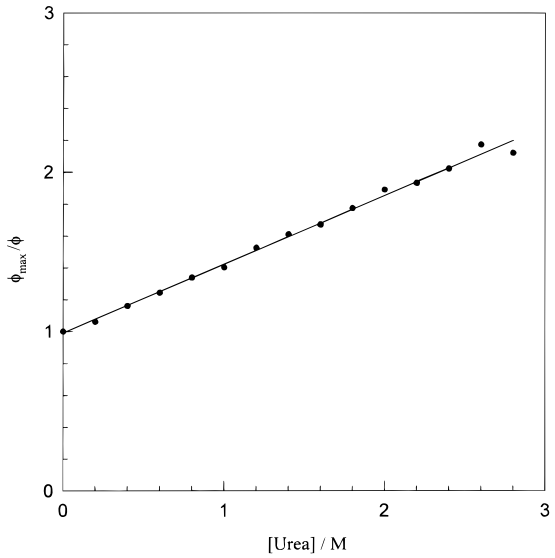


Figure 3. Stern−Volmer plot of ϕ_{max}/ϕ versus [urea].

of ϕ_{max}/ϕ versus [urea] (eq 3) shows a linearity with a correlation coefficient of 0.994 and gives a slope of 0.432.

$$\frac{\phi_{max}}{\phi} = 1 + \frac{k_q^*}{n}[\text{urea}] \tag{3}$$

where $n = 1/\tau_0$ describes the overall deactivation process of ROH* and $n = 6.25 \times 10^8\ s^{-1}$. k_q^* can be calculated from the slope to be $2.7 \times 10^8\ M^{-1}\ s^{-1}$. The change in the measured rate constant, k_{mesd} $(=1/\tau)$, due to increasing urea concentration also follows the Stern−Volmer equation:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_q^*[\text{urea}] \tag{4}$$

where τ and τ_0 are the measured lifetimes of ROH* in the presence and absence of urea in methanol and k_q^* is the bimolecular quenching constant. The correlation coefficient is about 0.997 and the slope and intercept are about 2.26×10^8 $M^{-1}\ s^{-1}$ and $6.23 \times 10^8\ s^{-1}$, respectively (see Figure 4). Therefore, the quenching constant k_q^* of ROH* by urea is estimated to be $2.26 \times 10^8\ M^{-1}\ s^{-1}$, which is about 20% less than k_q^* determined from steady-state measurements. Assuming that k_q^* determined from steady-state data and k_q^* determined from decay data are the same within experimental error, these

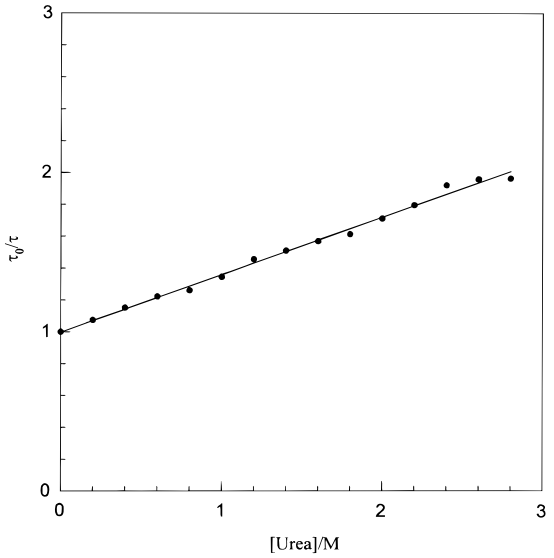


Figure 4. Plot of τ_0/τ versus [urea].

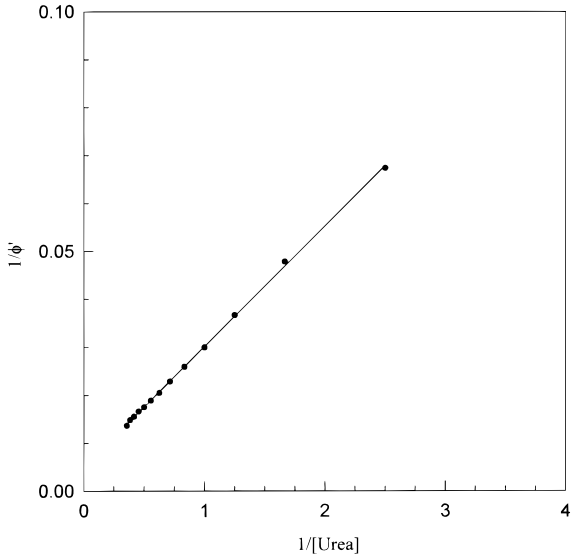


Figure 5. Change in the quantum yield of RO^- * versus the concentration of urea in methanol.

results indicate that the quenching process is due to dynamic quenching only. Also, these results rule out ground-state complex formation, which is, of course, in agreement with the observation that there is no change in the absorption spectra of ROH in the presence of urea. The change of the quantum yield of RO^- * due to the urea concentration also follows the linear Stern−Volmer equation:

$$\frac{1}{\phi'} = \frac{1}{\phi'_{\max}} + \frac{n}{k_q^*}\frac{1}{\phi'_{\max}}\frac{1}{[\text{urea}]} \tag{5}$$

In this equation, $\phi'_{\max}$ and ϕ' are the fluorescence intensities in arbitrary units of the base RO^- * in the absence and presence of ROH* in methanol, respectively. The value of ϕ' is calculated by

$$\phi' = H_{RO^-*} - 0.042H_{ROH^*} \tag{6}$$

where H_{ROH^*} and H_{RO^-*}, respectively, are the heights of the recorded fluorescence spectra of ROH* and RO^- *. The ratio of the analytical concentration of ROH* to the concentration of RO^- * in the absence of ROH* at 440 nm is about 0.042. As shown in Figure 5, a plot shows a straight line with a regression coefficient of 0.983 and yields a slope of 0.0203 and an intercept of 8.81×10^{-3}. It is found that the value of k_q* in eq 5 is about 2.71×10^8 M^{-1} s^{-1}, which is practically the same k_q* as that obtained from the steady-state measurement for the acid. The rate of the decrease in the fluorescence intensity of ROH* may therefore be the same rate of increase in the intensity of the RO^- * fluorescence (i.e., $\phi/\phi_{\max} + \phi'/\phi'_{\max} \cong 1$), indicating that the proton transfer is an adiabatic process.

However, a second look at these Stern−Volmer plots leaves some questions open. The values of k_q* determined from steady-state measurements may be the same by coincidence. First, the calculation of k_q* from RO^- * fluorescence measurements depends on the choice of the correction factor due to the fluorescence of the acid ROH*. The uncertainty is probably 10%. Second, as indicated in section 3.4, the lifetimes of the RO^- * fluorescence are not single-exponential, and therefore, the quantum yields $\phi'_{\max}$ of the RO^- * will be affected, too. This in turn affects the calculation of k_q* from the slope (see eq 5), introducing another 10% uncertainty. Third, some nonlinearity is visible in Figure 5 at higher concentrations of urea. Finally, k_q* determined from steady-state fluorescence measurements is 20% less than that obtained from lifetime measurements of the acid. This difference may be significant.

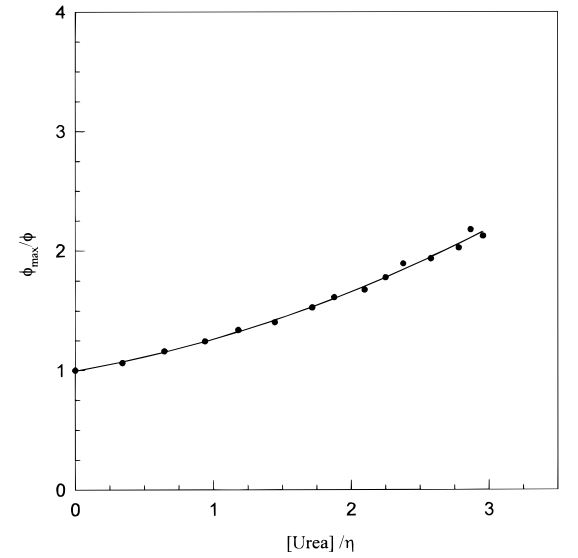


Figure 6. Stern−Volmer plot of $\phi_{\max}/\phi$ versus [urea]/η.

4.2. Effect of Viscosity on Proton Transfer. In the aforementioned Stern−Volmer evaluation, the variation of the viscosity with the concentration of urea was not taken into account. However, as shown in Table 1, the viscosity actually changes by about a factor of 2 within the concentration range used. Inclusion of the viscosity into the Stern−Volmer plot, i.e., $\phi_{\max}/\phi$ versus [urea]/η, is necessary. The viscosity is an important parameter in the diffusion-controlled process and cannot be ignored. Thus, we need to find an explanation for the nonlinear behavior of the Stern−Volmer plot when viscosity changes are included (see Figure 6). Urea monomers may not simply be the only proton acceptor as indicated by the Stern−Volmer plot in section 4.1, and the possible involvement of higher-order urea aggregates in methanol, for example, urea dimers, may have to be considered.

4.3. Ground-State Concentration of the Proton Acceptors. The simplest higher-order aggregate is a dimer. Adopting

dimerization of urea in methanol,[14] the following equilibrium is expected to occur between urea monomers and urea dimers:

$$2\mathrm{U} \overset{K}{\rightleftharpoons} \mathrm{U}_2 \tag{7}$$

where U and U_2 are the urea monomer and dimer, respectively. Hence, the concentration of urea dimers, $[U_2]$, is

$$[\mathrm{U}_2] = K[\mathrm{U}]^2 \tag{8}$$

where [U] is the concentration of urea monomers and K is the equilibrium constant for the formation of urea dimers. The original concentration of urea, $[U]_0$, may be expressed by:

$$[\mathrm{U}]_0 = [\mathrm{U}] + 2[\mathrm{U}_2] \tag{9}$$

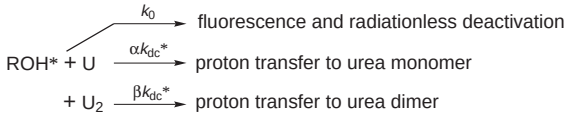
Combining eqs 8 and 9; and expanding the square root[17] in the resulting equation yields

$$[\mathrm{U}] = [\mathrm{U}]_0 - 2K[\mathrm{U}]_0^2 \tag{10}$$

and

$$[\mathrm{U}_2] = K[\mathrm{U}]_0^2 \tag{11}$$

4.4. A Kinetic Model. If the proton-transfer reaction of ROH* is fully diffusion-controlled and both urea monomers and urea dimers are assumed to accept the proton, the decay of ROH* can be described as follows:



Using r_B for the dimer to be 3.1 Å (calculated with the assumption that the volume of the urea dimer is approximately twice that of the urea monomer), k_{dc}* for the dimer calculated from eq 2 is about 3% smaller than k_{dc}* for the urea monomer. This decrease is considered to be negligible, and therefore, k_{dc}* of monomer and dimer are considered to be the same. On the basis of the above-mentioned reaction scheme, the fluorescence decay of ROH* may be expressed by:

$$\frac{1}{\tau} = k_0 + \alpha k_{dc}^*[\mathrm{U}] + \beta k_{dc}^*[\mathrm{U}_2] \tag{12}$$

where $k_0 = 1/\tau_0$ is the fluorescence quenching constant, τ is the fluorescence lifetime of the probe, and α and β are proton accepting efficiencies of urea monomers and dimers, respectively. The value of β can be taken as unity if every encounter between ROH* and urea dimers leads to a proton transfer, i.e., 100% proton accepting efficiency. Substitution of eqs 10 and 11 in eq 12 and rearranging results in

$$\frac{\frac{1}{\tau} - \frac{1}{\tau_0}}{k_{dc}^*} = \alpha[\mathrm{U}]_0 + (\beta - 2\alpha)K[\mathrm{U}]_0^2 \tag{13}$$

The left-hand side of eq 13 represents the proton acceptor concentration, since the proton-transfer rate, rate $= 1/\tau - 1/\tau_0$, is given by the proton transfer of the bimolecular diffusion-controlled rate constant, k_{dc}*, and the effective concentration of proton acceptor, i.e.

$$\text{rate} = k_{dc}^*[\text{acceptor}] \tag{14}$$

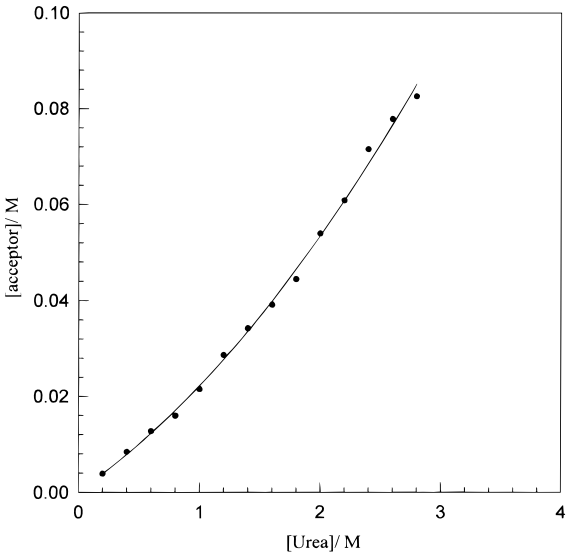


Figure 7. Plot of the proton acceptor concentration versus the original concentration of urea in methanol at 25 °C. Solid line indicates the fit to eq 15.

and therefore

$$[\text{acceptor}] = \alpha[\mathrm{U}]_0 + (\beta - 2\alpha)K[\mathrm{U}]_0^2 \tag{15}$$

According to eq 15, a plot of the acceptor concentration versus the initial concentration of urea should be nonlinear. This is shown in Figure 7, where experimentally determined acceptor concentrations (see also Table 1) show a second-order nonlinear curve as a function of $[U]_0$ with a regression coefficient of 0.999. From the fit of the curve, the value of α is determined to be 0.0175. This indicates that about 1.75% of the encounters between ROH* and urea monomers in methanol actually lead to proton transfer. The second coefficient $(\beta - 2\alpha)K$, obtained from the fit, is about 4.58×10^{-3} L/mol. Keeping the proton accepting efficiency of the urea dimers, β, equal to unity allows us to estimate the equilibrium constant, K, for the formation of urea dimers from the coefficient of the second term in eq 15 and it is found to be 0.00119 L/mol. Putting this value of K into eqs 10 and 11, the ground-state concentrations of urea monomers and the urea dimers may be calculated. As the molar volume of urea at very low concentration in methanol is known (i.e., 37 cm^3/mol), one may determine the apparent molecular volume of the urea at any original concentration of urea in methanol by using

$$\bar{V}_m = \frac{n_1 V_{m_1} + n_2 V_{m_2}}{n_1 + n_2} \tag{16}$$

where V_{m_1} is the molar volume of the urea monomer, V_{m_2} is the molar volume of the urea dimer ($\cong 2V_{m_1}$), n_1 is moles of urea monomer, n_2 is moles of urea dimer, and $\bar{V}_m$ is the apparent molar volume of urea. Hence, eq 16 may be used to check the presumption of the proton accepting efficiency β of urea dimers being equal to unity. For instance, when the original concentration of urea is 2.0 M, the concentration of urea monomers and dimers respectively are about 1.99 and 0.00476 M and the apparent molar volume at this particular concentration is about 37.09 cm^3/mol. This value is not in good agreement with the literature value, which is 38.8 cm^3/mol at 2.0 M urea.[14] This disagreement points to the fact that not every encounter may lead to proton transfer. Hence, the proton accepting efficiency

of the urea dimer β must be less than unity, which suggests that the presumption for the proton transfer of ROH* to a urea dimer in methanol being a fully diffusion-controlled reaction may not be true.

We, therefore, try to get the equilibrium constant, *K*, for the formation of urea dimers from the literature in order to calculate the proton acceptor efficiency of urea dimers in methanol. According to the data of Hamilton and Stokes,[14] the dependence of the apparent molar volume of urea on concentration is not exactly a linear relationship. However, for the concentration range over which we have measured the lifetime of the ROH*, it is nearly linear. Thus, eq 16 may be rewritten, taking the total volume of the solution to be approximately independent of the urea concentration.

$$\bar{V}_m = \frac{\frac{n_1}{V_{\text{total}}} V_{m_1} + \frac{n_2}{V_{\text{total}}} V_{m_2}}{\frac{n_1 + n_2}{V_{\text{total}}}} \tag{17}$$

or

$$\bar{V}_m = \frac{[\text{U}]V_{m_1} + 2[\text{U}_2]V_{m_1}}{[\text{U}] + [\text{U}_2]} \tag{18}$$

Substituting of eqs 10 and 11 into eq 18 results in

$$\bar{V}_m = V_{m_1} \frac{1}{1 - K[\text{U}]_0} \tag{19}$$

which can eventually be approximated to

$$\bar{V}_m \approx V_{m_1}(1 + K[\text{U}]_0) \tag{20}$$

From the linear fit of the data obtained from ref 14 to eq 20, the slope is found to be approximately 0.882, and thus *K*, obtained from eq 20, is around 0.0238 L/mol. Using this value of *K* and the coefficient in eq 15, β is found to be about 0.227, indicating that about 23% of the total encounters between the probe and the urea dimers result in the proton transfer in methanol. On the basis of the work of Lee et al.,[13] who investigated the chemical structure of urea in water, we speculate that the hydrogen bonding between methanol and urea monomers or dimers, respectively, may also affect the proton accepting efficiencies α and β.

The lower proton accepting efficiency than diffusion-controlled observed in both acceptors may as well be attributed to the requirement of a geometric arrangement for both the probe and the acceptor to have the necessary bond breaking and formation in favor of proton transfer. At lower concentrations of urea, the contribution of the urea monomer in proton transfer is significant because the concentration of the monomers is about 40 times higher than that of the dimers. An increasing contribution to proton transfer from the urea dimer is observed at higher concentrations of urea. The overall proton transfer dynamics is believed to be greatly affected by the transfer to urea dimers since they accept protons about 13 times more efficiently than urea monomers in methanol. Urea dimer molecules seem to stabilize both the proton and the aromatic moieties (RO^- *) to a larger extent than urea monomers in methanol.

5. Conclusion

Taking into account viscosity changes, our experimental observation that the proton acceptor concentration increases nonlinearly with the original concentration of urea in methanol is explained by assuming both urea monomers and dimers to be proton acceptors. Urea forms dimers in methanol.[14] Fitting our data to apparent molar volumes as reported in the literature[14] suggests that the proton accepting efficiency of the dimer is about 13 times higher than that of the monomer. However, it is about a quarter of the maximum accepting efficiency as calculated from a fully diffusion-controlled proton transfer. As mentioned in our introduction, the involvement of higher-order clusters in the proton transfer becomes more and more evident. Our experimental investigations support these findings. However, our work also suggests that these clusters cannot be simply loosely attached molecules; rather these clusters must be, for instance, dimers with proper chemical structures.[13] In solutions of urea in methanol up to 2.8 M, higher-order oligomers with possibly even higher proton accepting efficiencies, including the stabilization of both proton and anion, are not observed.

Acknowledgment. Support from the King Fahd University of Petroleum and Minerals is gratefully acknowledged. We thank Professor M. Hauser for providing us the sodium salt of 4-hydroxy-1-naphthalenesulfonic acid. We also thank Professor F. Al-Adel and Dr. A. Al-Arfaj for their support to make this work successful.

References and Notes

(1) Lee, J.; Griffin, R. D.; Robinson, G. W. *J. Chem. Phys.* **1985**, *82*, 4920.
(2) Suwaiyan, A.; Al-Adel, F.; Hamdan, A.; Klein, Uwe K. A. *J. Phys. Chem.* **1990**, *94*, 7423.
(3) Tolbert, L. M.; Harvey, L. C.; Lum, R. C. *J. Phys. Chem.* **1993**, *97*, 13335.
(4) Htun, M. T.; Suwaiyan, A.; Klein, U. K. A. *Chem. Phys. Lett*. **1995**, *243*, 71.
(5) Huppert, D.; Kolodney, E.; Gutman, M.; Nachliel, E. *J. Am. Chem. Soc*. **1982**, *104*, 6949.
(6) Tolbert, L. M.; Haubrich, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 10593.
(7) Kim, S. K.; Li, S.; Berstein, E. R. *J. Chem. Phys.* **1991**, *95*, 3119.
(8) Kim, S. K.; Wang, J. K.; Zewail, A. H. *Chem. Phys. Lett.* **1994**, *228*, 369.
(9) Kim, S. K.; Breen, J. J.; Willberg, D. M.; Peng, L. W.; Heikal, A.; Syage, J. A.; Zewail, A. H. *J. Phys. Chem.* **1995**, *99*, 7421.
(10) Douhal, A.; Lahmani, F.; Zewail, A. H. *Chem. Phys.* **1996**, *207*, 477.
(11) Politi, M. J.; Chaimovich, H. *J. Solution Chem.* **1989**, *18*, 1055.
(12) Lee, J. *J. Am. Chem. Soc*. **1989**, *111*, 427.
(13) Lee, C.; Stahlberg, E. A.; Fitzgerald, G. *J. Phys. Chem.* **1995**, *99*, 17737 and references therein.
(14) Hamilton, D.; Stokes, R. H. *J. Solution. Chem.* **1972**, *1*, 213.
(15) Henson, R. M. C.; Wyatt, A. H. *J. Chem. Soc., Faraday Trans. 2*, **1974**, *71*, 669.
(16) Laidler, K. J. *Chemical Kinetics*, 3rd. ed.; Harper Collins Publishers: New York, 1987; Chapt. 6.
(17) Bronstein-Semendjajew. *Handbook of Mathematics*, 6th ed.; Verlag Harri Deutsch and Frankfurt/Main: Zurich and Moscow, 1956.