Electrolyte-Concentration and Ion-Size Dependence of Excited-State Intramolecular Charge-Transfer Reaction in (Alkylamino)benzonitriles: Time-Resolved Fluorescence Emission Studies

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Time-resolved studies with three intramolecular charge-transfer molecules 4-(1-azetidinyl)benzonitrile (P4C), 4-(1-pyrrolidinyl)benzonitrile (P5C), and 4-(1-piperidinyl)benzonitrile (P6C) in ethyl acetate in presence of LiClO$_4$ indicate that the average reaction time for LE → CT conversion increases at low electrolyte concentration and then decreases to become comparable and even lower than that in the pure solvent. Except for Mg^{2+}, the average reaction time decreases linearly with the ion size in perchlorate solutions of ethyl acetate. The observed electrolyte-concentration dependence of the average reaction time for these molecules agrees well with the predictions from the theory of Zwan and Hynes [*Chem. Phys.* **1991,** *152,* 169] in the broad barrier overdamped limit with barrier frequency, $\omega_b \approx 2 \times 10^{12}$ s^{-1}.

I. Introduction

In the preceding Article[1] we discussed the steady-state spectroscopic results of electrolyte-concentration and ion-size dependence of excited-state intramolecular charge-transfer reactions in three (alkylamino)benzonitrile derivatives. The presence of electrolyte in solution has been found to significantly affect the LE → CT conversion reaction in these molecules. The change in reaction free energy ($-\Delta G_r$) is also found to depend linearly on the cation size, provided the composite ion–solvent dynamics is fast enough to ensure the equilibrium.[2–5] Here we present the effects of electrolyte concentration on the rate of LE → CT conversion reaction in ethyl acetate where the concentration of LiClO$_4$ has been changed from 0.0 to 2.5 M. Dynamics of electrolyte solutions is expected to be very different from that of pure polar solvents because the ion-atmosphere relaxation and time-dependent ion–solute interaction dominate the ionic solution dynamics at low electrolyte concentrations.[2–5] At higher concentrations, the solution dynamics is even more complex due to the presence of triple ion, ion pairs (solvent shared and solvent separated), and other nonpolar ion–solvent composite species.[3–9] Several authors have already studied the dynamics of electrolyte solutions in solvents of varying polarity and found that electrolyte solution dynamics is characteristically different from that of the pure solvent.[2–5] For example, the average solvation time for a dipolar probe in acetonitrile[2] at room temperature is increased by a factor of ~17 000 upon addition of 0.1 M NaClO$_4$. Moreover, the average solvation time decreases by a factor of 6 as the salt concentration is increased from 0.1 to 1.0 M in the same electrolyte–solvent combination.[2] In solvents of low dielectric constants, such as in ethyl acetate, formation of triple ions, ion pairs, and other species will occur at concentrations relatively lower than that in acetonitrile.[10–11] Consequently, the dynamics and its effects on reactions are expected to be complex in electrolyte solutions of these solvents. It would therefore be interesting to investigate how the modified

solution dynamics affect the intramolecular charge-transfer reactions at different electrolyte concentrations in these solvents.

The reaction rate is affected in a more complex manner than the dynamical solvent modes because of the following reasons. The experimentally observed dynamics in electrolyte solutions is at least 1000 times slower than the microscopic time scale for barrier crossing, which is on the order of 1 ps even for a fairly broad-barrier reaction.[12–13] This means that the ion atmosphere remains out of equilibrium during barrier crossing. If we now assume that the TICT mechanism is valid for these molecules, this nonequilibrium ion atmosphere would exert more electrodynamic friction[12] on the twisting mode. Consequently, the TICT reaction rate will be substantially modified. Because the dynamics becomes faster with the increase in electrolyte concentration, the coupling between the reactive mode and the environment dynamics becomes further modified. This modification also contributes to the electrolyte-concentration dependence of the LE → CT conversion rate. As correctly pointed out in ref 12, experimental studies are required to determine the effects of such concentration-dependent nonequilibrium solvation. The present study is an attempt toward this direction.

In this Article we report results on the excited-state intramolecular charge-transfer reactions of 4-(1-azetidinyl)benzonitrile (P4C), 4-(1-pyrrolidinyl)benzonitrile (P5C), and 4-(1-piperidinyl)benzonitrile (P6C) in solution in the presence of electrolytes. The photoinduced intramolecular charge-transfer reaction in these molecules has been depicted in Schemes 1 and 2 of ref 1. We use the TICT model to analyze our data as done earlier.[14] Note that Rettig and co-workers[15–19] and Zachariasse et al.[20] have studied these compounds earlier. In fact, the latter group[20] has investigated the excited-state charge-transfer reaction in the above compounds containing three- to eight-membered rings and represented them as P*n*C series (*n* represents the number of atoms constituting the ring). However, studies of electrolyte effects on the rate of TICT reactions have not been performed before and such a study is reported here. The choice of ethyl acetate as the low-polarity solvent comes from its ability to dissolve a large amount of LiClO$_4$, which provides an op-

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portunity to study the effects of electrolyte on TICT reaction for a wide range of electrolyte concentrations. The cation-size dependence of the average reaction rate in ethyl acetate has also been investigated. It has been found that the theory developed by Zwan and Hynes (ZH) for studying isomerization reactions in electrolyte solutions[12] can be applied to understand the observed electrolyte-concentration dependence of reaction rate in these TICT molecules.

We have used the kinetic framework discussed in ref 14 to analyze our experimental data reported in this Article. This means that the reaction is assumed to be in the rapid equilibration limit and a biexponential decay of intensity with time is expected. We mention here that the rapid equilibration limit may not be realized in electrolyte solutions because the solution dynamics is considerably slower. However, a biexponential function with two different time constants is found to be sufficient to fit the time-dependent intensity decay for all combinations with P4C and P5C. For P6C, however, a triexponential function is required to properly fit the intensity decays. The average reaction time constant falls off exponentially with electrolyte concentration and decreases linearly as z/r_{ion} (z being the valence on the ion) increases. At all electrolyte concentrations in ethyl acetate, the observed average reaction rate for these TICT molecules is found to be in good agreement with the prediction from the theory by Zwan and Hynes[12] in the broad barrier overdamped limit with barrier frequency, $\omega_b \approx 2 \times 10^{12}$ s^{-1}. The other parameters necessary for calculating the average rates from the ZH theory[12] are obtained from the relevant experiments.

The organization of the rest of the paper is as follows. Experimental details are given in the next section. Section III contains experimental results from our time-dependent studies of TICT reaction in ethyl acetate in presence of electrolyte. A comparison between experimental results and prediction from the ZH theory is presented in section IV. The Article then ends with concluding remarks in section V.

II. Experimental Details

Time-resolved emission studies have been performed using time-correlated single photon counting (TCSPC) instrument based on a picosecond Ti:sapphire laser with excitation light at wavelength (λ) at 293 nm (third harmonic). The detail of this instrumentation is discussed elsewhere[21] and hence only brief information will be given here. The emission fluorescence has been collected at magic angle at both LE and CT peak positions (of steady-state spectrum) with an emission band-pass of 8 nm. The effective resolution (full width at half-maximum) of the instrument response function (IRF) is approximately 50 ps. Subsequently, collected decays have been deconvoluted from the IRF and fitted to multiexponential function using an iterative reconvolution algorithm. Because such fitting enables one to capture decay kinetics with time constant as fast as ~10 ps with reasonable accuracy,[14] the rate data for P5C and P6C at higher electrolyte concentration might be trusted with some confidence. For a few cases, emission decays have been collected at two or three different emission wavelengths around the LE and CT peaks and average data have been shown for them. Note that in such cases the data associated with different wavelengths are found to vary *insignificantly* and hence are regarded as fluctuations. Therefore, these small variations do not seem to indicate any different relaxation process or different species involved.

Because the average solvation time is required for rate calculation from ZH theory, we have also measured average solvation time of a polarity probe in electrolyte solutions of ethyl acetate. Time-resolved emission spectra at each electrolyte concentration have been constructed from a series of 18−22 emission decays at equally spaced wavelengths across the steady-state emission spectrum of coumarin 153 (C153)[22] collected via time-correlated single photon counting (TCSPC) method by using a diode laser based system (Lifespec-ps, Edinburgh, U.K.). A diode laser is used to provide 409 nm light as excitation. The effective resolution (fwhm) of the instrument response function is ~75 ps. Note that this resolution might miss the relatively faster component of the solvent response in ethyl acetate in the presence of electrolyte but is expected to capture the long time dynamics well. The same instrumental setup has been used to collect emission decays of P4C at LE and CT peaks with 299 nm light as excitation. The effective resolution (fwhm) of the instrument response function with the 299 nm excitation source is ~450 ps. All the experiments have been performed at $T = 298.15 \pm 0.1$ K. Similar dynamical studies with acetonitrile and solvents with a higher dielectric constant have not been attempted because of the limited time resolution available to us. Note that the procedures for obtaining P4C, P5C, and P6C and other materials necessary for the experiments have been discussed in ref 1 and hence will not be repeated here.

III. Results and Discussion

A. Average Reaction Rates: Electrolyte-Concentration Dependence. Time-resolved emission decay measurements have been performed with P4C, P5C and P6C molecules in ethyl acetate containing $LiClO_4$ in concentrations ranging from 0.1 to 2.5 M. We have used 0.5 M solutions of perchlorate salts containing Li^+, Mg^{2+}, Ca^{2+}, Na^+, Sr^{2+}, and $({}^tBu)_4N^+$ in ethyl acetate to investigate the cation-size dependence of the average reaction rate in these TICT molecules. This choice of cations provides an order of magnitude spread over crystallographic ionic radius (~0.7 Å for Li^+ to ~5 Å for $({}^tBu)_4N^+$).[2] As already discussed, a time-dependent biexponential function has been found to fit emission decays containing P4C and P5C in all electrolyte concentrations in ethyl acetate. For P6C, however, a triexponential function is required for properly fitting the collected decays. An example of such a fit is shown in Figure 1 for P4C in a 0.1 M $LiClO_4$ solution of ethyl acetate, and the fit parameters are listed. This shows that a biexponential function is sufficient to describe the observed emission decay as the residual does not contain any nonrandom pattern[24] and the "*goodness of fit parameter*" (χ^2) is close to 1.

The biexponential fit parameters for the electrolyte-concentration-dependent LE emission decays obtained for P4C and P5C in $LiClO_4$ solutions of ethyl acetate are summarized in Table 1. Note that all the decays can be fitted to biexponential functions even in the presence of electrolyte at all concentrations and therefore the decay kinetics for P5C in electrolyte solutions conforms to the classical two-state reversible reaction mechanism as described by Maroncelli and co-workers in ref 14. We mention here that the collected emission decays at wavelengths near CT emission peaks could also be fitted to biexponential functions with the same or similar time constants as found for the corresponding LE decays. For example, for P5C in the presence of 0.1 M $LiClO_4$ in ethyl acetate, fitting of the CT emission decay with no constraints produces time constants 46 ps (rise time) and 2149 ps with $\chi^2 = 1.33$. This time constant (rise time) is thus very similar to the fast time constant (decay time, 62 ps) of the LE decay, indicating that these time constants are essentially associated with the average reaction rate.[14] When the rise time is fixed to the fast decay
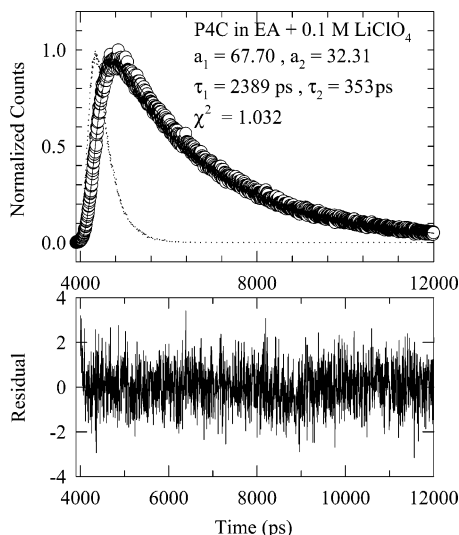
11526 *J. Phys. Chem. A, Vol. 111, No. 45, 2007*

Pradhan and Biswas

Figure 1. Representative LE emission decay of P4C in ethyl acetate in presence of 0.1 M LiClO$_4$. The data are represented by circles, and the fit through the data is the solid line. The instrument response function (IRF) is shown by the dashed line. The fit (biexponential) results are also provided in the upper panel. The LE peak count is ~4000. Residuals are shown in the lower panel (±5 full scale).

TABLE 1: Electrolyte-Concentration Dependence, Fit Parameters for the LE Emission Decays in LiClO$_4$ Solutions of Ethyl Acetate

P4C

conc (M)	τ_1 (ps)	τ_2 (ps)	a_1	a_2	χ^2
0.0	2916	274	76.4	23.6	1.054
0.1	2389	353	67.70	32.31	1.032
0.25	1796	333	61.11	38.89	1.056
0.5	1209	326	57.02	42.98	1.022
0.75	940	320	51.12	48.88	1.137
1.0	842	308	43.46	56.54	1.09
1.5	714	277	30.84	69.16	1.092
2.0	660	263	23.33	76.67	1.056
2.5	655	238	15.43	84.57	1.033

P5C

conc (M)	τ_1 (ps)	τ_2 (ps)	a_1	a_2	χ^2
0.0	2867	54	11.7	88.3	1.34
0.10	1912	66	9.9	90.9	0.99
0.25	1315	52	6.8	93.2	1.05
0.5	1076	48	3.7	96.3	1.09
1.0	1241	47	1.3	98.7	1.03
1.5	1090	33	0.7	99.3	1.04
2.0	1251	33	0.5	99.5	0.91
2.5	1506	31	0.4	99.6	1.01

P6C

conc (M)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	a_1	a_2	a_3	χ^2
0.0	2918	453	15	19.3	4.8	75.9	1.14
0.1	2068	562	15	10.5	3.7	85.8	1.06
0.25	1920	567	15	6.3	4.9	87.8	1.03
0.5	1930	632	15	2.7	6.8	90.5	0.91
1.0	2050	502	15	1.6	3.9	93.5	1.05
1.5	2194	464	15	1.2	3.7	95.1	1.05
2.0	2329	480	15	1.1	3.0	95.9	1.16
2.5	2827	535	15	0.8	2.4	96.8	1.19

time constant observed for the corresponding LE emission decay (62 ps), the same fit produces 2142 ps as the long time constant with $\chi^2 = 1.36$. Addition of a third exponential did not produce a better fit. It is therefore interesting to note that addition of electrolyte has not induced any deviation from the behavior (biexponential) observed earlier for P4C and P5C in pure ethyl acetate.[14]
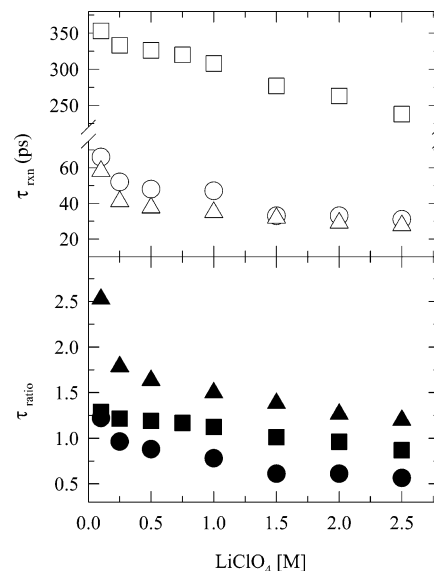

Figure 2. Electrolyte (LiClO$_4$)-concentration dependence of average reaction time (τ_{rxn}^{avg}) in ethyl acetate. Upper panel: τ_{rxn}^{avg} for P4C is represented by squares, for P5C by circles, and for P6C by triangles. Note that τ_{rxn}^{avg} has been calculated from the relevant fit parameters by using eq 1 of the text. Lower panel: The ratio between average reaction times obtained in presence and absence of electrolyte ($\tau_{ratio} = \tau_{rxn}^{avg}(M)/\tau_{rxn}^{avg}(M{=}0)$) is shown as a function of electrolyte concentration in ethyl acetate. The value of $\tau_{rxn}^{avg}(M{=}0)$ for P6C is taken from ref 14. The representations by the filled symbols are the same as those by their open counter-parts in the upper panel.

As discussed earlier, the LE emission decays of P6C in LiClO$_4$ solutions in ethyl acetate require triexponential functions to adequately fit the time-dependent decays. The fit results are also summarized in Table 1. Note that the smallest time constants (15 ps) in these decays have been fixed to get reasonable fit. The CT emission decays are still described by a sum of two exponentials. However, the time constants do not match with the LE time constants. This is similar to what has been described in ref 14 as "type III" systems while studying TICT reactions with P6C in neat solvents. These reactions have been explained in terms of time-dependent reaction rate involved in LE → CT conversion. Therefore, the decay kinetics of P6C in electrolyte solutions is similar to what have already been found in neat solvents.[14]

The average reaction time has been calculated from the collected LE emission decay using the following relation:[14]

$$\tau_{rxn}^{avg} = \frac{\sum_{i=1}^{n-1} a_i \tau_i}{\sum_{i=1}^{n-1} a_i} \tag{1}$$

where a_i and τ_i are the fractional amplitudes and time constants observed in n-exponential fit. The electrolyte (LiClO$_4$)-concentration-dependent average reaction time (τ_{rxn}^{avg}) for P4C, P5C, and P6C molecules in ethyl acetate are shown in the upper panel of Figure 2. The ratios between the average reaction time constants in the presence and absence of LiClO$_4$ in ethyl acetate ($\tau_{ratio} = \tau_{rxn}^{avg}(M)/\tau_{rxn}^{avg}(M{=}0)$) as a function of electrolyte concentration are shown in the lower panel of Figure 2. Note that the average reaction time is larger at lower electrolyte concentrations than in pure ethyl acetate. Further addition of electrolyte in ethyl acetate decreases the average reaction time.[25] At 2.5
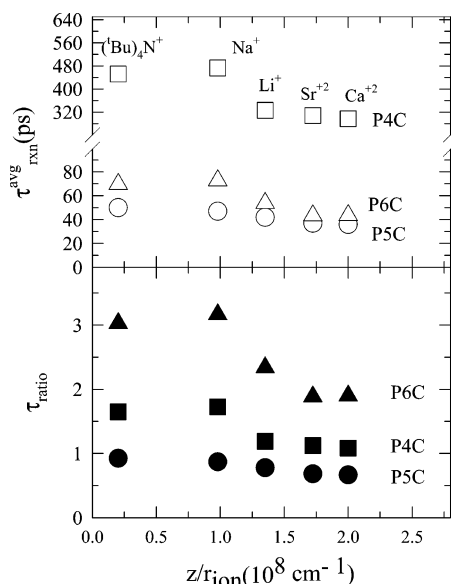
Charge-Transfer Reaction in (Alkylamino)benzonitriles

J. Phys. Chem. A, Vol. 111, No. 45, 2007 **11527**

Figure 3. Ion-size dependence of average reaction time (τ_{rxn}^{avg}) for P4C (squares), P5C (circles), and P6C (triangles) in ethyl acetate solutions of 0.5 M perchlorate salts. The upper panel shows the variation of τ_{rxn}^{avg} as a function of ionic potential in 0.5 M perchlorate salt solutions in ethyl acetate containing (^{t}Bu)$_4^+$, Na$^+$, Li$^+$, Sr^{2+}, and Ca^{2+}. Equation 1 is used to obtain τ_{rxn}^{avg} from the relevant fit parameters. Data for (^{t}Bu)$_4^+$ are obtained by using tetrahydrofuran solution due to solubility restriction in ethyl acetate. Note that τ_{rxn}^{avg} in presence of Mg^{2+} is not included as it shows large deviation. τ_{rxn}^{avg} (in ps) for P4C, P5C, and P6C in the presence of Mg^{2+} are 429, 39, and 74, respectively.

M LiClO$_4$ in ethyl acetate, the average reaction time reduces by almost a factor of 2 for P4C and P5C from those at 0.1 M. This indicates that the reaction proceeds at an average rate approximately *twice* as fast in ethyl acetate containing 2.5 M LiClO$_4$ as that at 0.1 M. The enhancement of the reaction rate at higher electrolyte concentration in solution may originate from the concentration-induced enhancement of the solvation rate.[2−5] The reaction is slowed down at low electrolyte concentrations because the friction experienced by the twisting mode due to ion-dipole interaction is larger than the solvation stabilization of the product (CT state in this case). At larger electrolyte concentrations, the ion pair dominates, which is dipolar in nature and therefore solvation processes become faster. Moreover, formation of an ion pair reduces the friction (mainly the dielectric part of it) as the dipole−dipole interaction is weaker than the ion−dipole interaction and therefore the reaction proceeds at a faster rate.

However, for P6C (lower panel of Figure 2), the ratio between the reaction time constants determined in the presence and absence of LiClO$_4$, remains always above 1. This indicates that the reaction rate in P6C is slowed down by LiClO$_4$ at all concentrations in ethyl acetate. At the lowest electrolyte concentration, the reaction in P6C is slowed down by a factor of ~2.5 whereas that in P4C and P5C is only slowed by 1.2. The following reasons may be responsible for the observed differences. Effects of electrolyte on reaction in P6C may be more pronounced due to the higher dipole moment that couples strongly with the various ionic and dipolar species present in the electrolyte solution. The barrier height in P6C may also be altered differently by the presence of ions and ion pairs. Becauase the average reaction rate for P6C in pure ethyl acetate is 2.5 times faster than P5C, we may also have missed a considerable part of the initial fast decay due to the limited time

TABLE 2: Ion-Size Dependence, Fit Parameters for the LE Emission Decays in 0.5 M Perchlorate Solutions of Eethyl Acetate

				P4C		
salt	conc (M)	τ_1 (ps)	τ_2 (ps)	a_1	a_2	χ^2
(^{t}Bu)$_4$NClO$_4$	0.5	2619	452	25.34	74.66	1.053
NaClO$_4$	0.5	2033	473	28.42	71.58	1.197
LiClO$_4$	0.5	1209	326	57.02	42.98	1.022
Sr(ClO$_4$)$_2$	0.5	903	308	13.06	86.94	1.089
Ca(ClO$_4$)$_2$	0.5	765	296	26.78	73.22	1.073
Mg(ClO$_4$)$_2$	0.5	1894	429	39.49	60.51	1.120

				P5C		
salt	conc (M)	τ_1 (ps)	τ_2 (ps)	a_1	a_2	χ^2
(^{t}Bu)$_4$NClO$_4$	0.5	2494	50	2.9	97.1	1.297
NaClO$_4$	0.5	1686	47	2.6	93.4	1.055
LiClO$_4$	0.5	1076	42	3.7	96.3	1.09
Sr(ClO$_4$)$_2$	0.5	1042	37	0.8	99.2	1.093
Ca(ClO$_4$)$_2$	0.5	912	36	0.8	99.2	0.963
Mg(ClO$_4$)$_2$	0.5	1136	39	2.7	97.3	0.969

				P6C				
salt	conc (M)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	a_1	a_2	a_3	χ^2
(^{t}Bu)$_4$NClO$_4$	0.5	3803	368	15	5.2	14.7	80.1	1.072
NaClO$_4$	0.5	2391	490	15	3.9	11.7	84.4	1.197
LiClO$_4$	0.5	1912	615	13	2.6	6.6	90.6	0.898
Sr(ClO$_4$)$_2$	0.5	1926	327	15	2.2	8.9	88.9	1.104
Ca(ClO$_4$)$_2$	0.5	1675	325	15	1.6	9.1	89.3	1.012
Mg(ClO$_4$)$_2$	0.5	2867	642	15	1.9	9.3	88.8	1.327

resolution available to us. This will induce some error by putting extra weight artificially on the slower component of the triexponential fit function and hence on the average reaction time. However, the reaction in P6C becomes *doubly* fast at 2.5 M LiClO$_4$ than at 0.1 M in ethyl acetate which has also been observed for P4C and P5C.

B. Average Reaction Rates: Cation-Size Dependence. The cation-size-dependent data obtained after fitting the LE emission decays for P4C, P5C, and P6C in the presence of 0.5 M perchlorate salts in ethyl acetate are summarized in Table 2. The effects of cation size on emission decays are quite evident from this table. As mentioned earlier, a sum of two exponentials is required to fit the emission decays of P4C and P5C for all the ions studied here and a third exponential is required to adequately fit the P6C decays. The average reaction times (τ_{rxn}^{avg}), obtained from these fits by using eq 1, are shown in Figure 3, which describes the effects of ion size on TICT reactions in these molecules. For the three molecules, the average reaction time, τ_{rxn}^{avg}, decreases in a similar manner as z/r_{ion} increases. For P4C and P6C, however, the effects of ion size on τ_{rxn}^{avg} are stronger than that for P5C. It is interesting to note that the average reaction rate becomes larger for ions possessing higher values of z/r_{ion}. This is counterintuitive in the sense that larger z/r_{ion} is expected to exert stronger dielectric friction on twisting and therefore the rate should be smaller (conversely, τ_{rxn}^{avg} larger). Solvation dynamics studies in 1.0 M perchlorate solutions containing different cations in acetonitrile have shown that the average solvation time increases as z/r_{ion} increases.[2] This is explained in terms of larger binding strength between the probe and ions possessing higher z/r_{ion} values. For TICT reactions, the stronger binding is likely to stabilize more the CT state. This may be one of the reasons for the observed enhancement of the average reaction rate ($1/\tau_{rxn}^{avg}$) with z/r_{ion}.

IV. Zwan−Hynes Theory: Comparison with Experiments

Here we discuss the essential part of the theory proposed by Zwan and Hynes (ZH)[12] to compare our experimental results with the prediction of this theory. In ZH theory, isomerization reaction in a dipolar molecule dissolved in electrolyte solution of dipolar solvent has been studied after connecting the electrical friction on reactive mode with the solvation dynamics in electrolyte solutions. Their model assumes an ion atmosphere around a dipolar solute and the solvent as a structureless continuum. Subsequently, this is solved for dilute solutions of electrolytes containing ions of low valence in solvents of moderate to large dielectric constants. We have used the expressions derived for studying the broad barrier and over-damped reactions to explore the applicability of ZH theory[12] in our systems. This is done with the assumption that the twisting in TICT processes will experience the friction in the same manner as the rotating moiety during isomerization reaction in electrolyte solutions. In addition, because these molecules possess low activation barriers ($3-4$ k_BT),[14] the reaction involving these molecules are assumed to be broad-barrier and overdamped. The ZH theory provides the following expression for transmission coefficient,[12] κ_r ($=k/k_{TST}$) for *broad barrier* reactions with barrier frequency, ω_b

$$\kappa_r = \left[\kappa_r + \frac{\zeta_0}{I\omega_b} + \frac{1}{I\omega_b}\int_0^\infty dt\, e^{-\omega_b\kappa_r t}\delta\zeta_I(t)\right]^{-1} \quad (2a)$$

where ζ_0 and $\delta\zeta_I$ are, respectively, the solvent (collisional and dielectric) and ion-atmosphere contributions to the total friction experienced by the reactive mode. I denotes the moment of inertia and is calculated from the reduced mass of the rotating moiety.

Reactions involving broad barriers are likely to be over-damped and the ZH theory obtains the following expression for calculating the transmission coefficient in this limit[12]

$$\kappa_r = \left[\frac{\zeta_0}{I\omega_b} + \frac{1}{I\omega_b}\int_0^\infty dt\, e^{-\omega_b\kappa_r t}\delta\zeta_I(t)\right]^{-1} \quad (2b)$$

with

$$\delta\zeta_I(t) = \delta\zeta_I(t=0)\exp(-t/\tau_s) \quad (3)$$

The ion-atmosphere friction at $t = 0$, $\delta\zeta_I(t=0)$, can then be calculated from the static dielectric constant (ϵ_0) of the solvent, dipole moment of the solute (μ), and its cavity radius (a) by using the relation[12]

$$\delta\zeta_I(t=0) = \frac{\mu^2}{a^3}\left[\frac{2(\epsilon_0-1)}{2\epsilon_0+1} + \frac{3\epsilon_0 y}{(2\epsilon_0+1)(2\epsilon_0+1+\epsilon_0 y)}\right] \quad (4)$$

where y is related to the inverse Debye screening length (κ) as follows[12]

$$y = (1+\kappa a)^{-1}(\kappa a)^2 \qquad \kappa^2 = \frac{4\pi N_A e^2}{1000\epsilon_0 k_B T}\sum_i z_i^2 c_i \quad (5)$$

Here N_A is the Avogadro number, k_B is Boltzmann's constant, e is the electronic charge, and c_i and z_i are concentration (M) and valence of the ith ionic species. The average solvation time, τ_s, is connected to the spectral response function, $S(t)$ by the relation:[22] $\tau_s = \int_0^\infty dt\, S(t)$. In our calculation, τ_s for ethyl acetate in the presence of various concentrations of LiClO$_4$ has been obtained from the experimentally determined spectral response
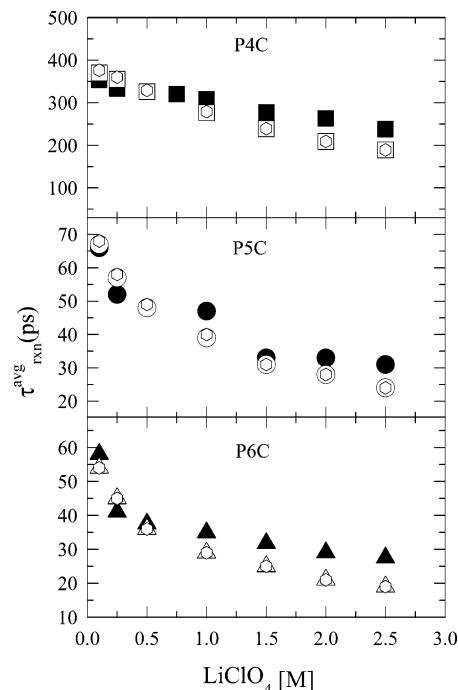

Figure 4. Comparison between experimentally obtained average reaction times (τ_{rxn}^{avg}) at different electrolyte concentrations and those predicted by the theory of van der Zwan and J. T. Hynes for P4C (upper panel, squares), P5C (middle panel, circles), and P6C (lower panel, triangles). The experimental data are shown by the filled symbols, and the predictions are denoted by the open symbols. The hexagons denote the calculation of the rate in the broad-barrier limit given by eq 2a in the text. The ZH predictions in the broad-barrier over-damped limit are calculated by using eq 2b and are shown by squares (P4C, upper panel), open circles (P5C, middle panel), and open triangles (P6C, lower panel). For the three molecules, calculations are done by using a single value of $\omega_b = 2 \times 10^{12}$ s^{-1}.

function, $S(t)$ by following the time-dependent fluorescence Stokes shift of a polarity probe dissolved in solution.[23] $\zeta_0 = 6\eta_0(4\pi R^3/3)$, with η_0 and R being the solvent viscosity and radius of the rotating moiety, respectively. Once these quantities are determined and ω_b is fixed, κ_r can be obtained by solving eqs 2a and 2b self-consistently. Finally, the rate (k) is calculated by using the relation[12]

$$k = \kappa_r \frac{k_B T}{h}\exp(-\Delta G^*/k_B T) = \kappa_r \nu_R \exp(-\Delta G^*/k_B T) \quad (6)$$

where the activation barrier (ΔG^*) is obtained from the change in reaction free energy ΔG_r (which, in turn, is determined from eq 1 given in ref 1) by using the correlation,[26] $\Delta G^* \approx \alpha\Delta G_r$ with α values reported in ref 14.

We now use eqs 2a and 2b to compute the electrolyte-concentration-dependent transmission coefficients (κ_r) in broad barrier and broad barrier overdamped limits for reactions in P4C, P5C, and P6C. Subsequently, the rate (k) is obtained by using eq 6. The computed results ($1/k$) are shown in Figure 4 where the upper panel represents the results for P4C, the middle panel the results for P5C, and the lower panel the results for P6C. The theoretical results are computed with $\omega_b \sim 2 \times 10^{12}$ s^{-1}. No other fitting parameters have been used for calculating the rate from the ZH theory.[12] We also show the experimental results (τ_{rxn}^{avg}) in the same figure for comparison. The agreement between the theory and experiment is surprisingly good for these TICT molecules. The deviation in larger electrolyte concentration may have originated from the partial neglect of the ion-pair effects on reaction rate.

Charge-Transfer Reaction in (Alkylamino)benzonitriles

J. Phys. Chem. A, Vol. 111, No. 45, 2007 **11529**

The observed agreement between the experimentally determined electrolyte-concentration-dependent average reaction time and the predictions from the ZH theory is rather interesting and warrants the following comments. First, the ZH theory has been developed to study isomerization dynamics in electrolyte solutions that involve *only* the rotation of the polar moiety through the solution. Simultaneous charge transfer with rotation has not been dealt with in the ZH theory. However, if the intramolecular charge transfer becomes very fast compared to the rotational time scale, then the situation becomes similar, as envisaged in the ZH theory. Second, the inputs required to calculate the average reaction time have been obtained from the relevant experiments and hence contain effects of ion, triple ion, ion pair, and other species implicitly. This may be another reason for the calculated reaction time constants tallying so well with the experimental data obtained for (LiClO$_4$ + ethyl acetate) solution where ion pairs and higher order aggregates are expected to dominate.

V. Conclusion

Time-resolved fluorescence emission studies in ethyl acetate containing LiClO$_4$ reveal a moderate to strong electrolyte-concentration dependence of average reaction rate for LE → CT conversion in P4C, P5C, and P6C. The average reaction time (average rate) is found to decrease (increase) for all these molecules as the concentration of LiClO$_4$ is increased. The average reaction times for P4C and P5C are found to be even smaller in solutions of higher electrolyte concentration than that in pure ethyl acetate, which may be attributed to the interplay between the electrolyte−solute interaction and the effects due to the increased dielectric constant.[2−5] The average reaction time for P6C does not fall below that in pure solvent at higher electrolyte concentration, even though it decreases with electrolyte concentration. It could very well be that the average reaction time for P6C also becomes smaller at high electrolyte concentration than in pure ethyl acetate. Because the reaction rate in P6C in pure ethyl acetate is much faster than that in P5C, a good portion of the initial fast decay of P6C at higher electrolyte concentration might have been missed due to the limited time resolution (∼50 ps) available to us. As a result, the average reaction time obtained at higher LiClO$_4$ concentration involves larger uncertainty as it derives contributions incorrectly from the relatively slower decay components. Time-resolved studies also reveal that the average reaction time decreases linearly with z/r_{ion} provided the data for Mg^{2+} are not included in the correlation. It is to be mentioned here that similar linear correlation has been found in the steady-state studies of these TICT molecules[1] and also in the studies of dynamics in electrolyte solution[2] using several nonreactive solvation probes.[2] As indicated in these studies,[1,2] the deviation of Mg^{2+} and other ions with larger values of z/r_{ion} from the observed linearity arises because the time-dependent rearrangement of the environment surrounding the photoexcited probe (reactive or nonreactive) is considerably slowed down in the presence of such ions and hence the ion−solvent composite dynamics is not complete within the average excited-state lifetime of the probe.

We have also calculated the electrolyte-concentration-dependent average reaction time in ethyl acetate for the three molecules by using a theory proposed by Zwan and Hynes using $\omega_b \sim 2 \times 10^{12}$ s^{-1} in the broad barrier and broad-barrier overdamped limits.[12] All other parameters in our calculation have been obtained from the relevant experiments. For all the molecules studied here, the calculated average reaction times are found to be in semiquantitative agreement with experiments at all electrolyte concentrations. Note here that a better time resolution than employed here may slightly alter the values of the electrolyte-concentration-dependent average solvation time used here for the calculation. This means that a different value of ω_b may be required. However, a reasonable value of ω_b can capture the electrolyte-concentration dependence of average reaction rate for these TICT molecules in ethyl acetate where ion pairing and higher order aggregation phenomena dominate. It has been shown in the works of Zwan and Hynes[12] that a semiquantitative description of isomerization reaction in electrolyte solutions of weakly polar solvent (such as ethyl acetate) can be obtained provided the time-dependent dielectric friction is supplied from relevant experiments. Even though this extension involves approximation, the use of experimental data takes care of the effects of ion pairing and other complex species which is probably responsible for the observed agreement between theory and experiments.

We mention that effects of electrolyte on TICT reactions in higher dielectric constant solvents require further studies to gain a clear understanding of how ion pair and other multiple ionic species modulate reaction rates in solvents of differing polarity. Electrolyte-concentration dependence of reaction rate in very dilute electrolyte solutions (<0.1 M) would be useful to understand how ion and ion pair affect TICT reaction *differently* in electrolyte solutions of high- and low-polarity solvents. These studies would supply valuable data for developing theories which should be able to treat the simultaneous intramolecular charge transfer and rotation and connect to the fluorescence Stokes' shift dynamics. Anion dependence (of the electrolyte) may also be interesting, as anions are known to interact differently with the medium than the positively charged ions. One should also investigate what kind of association between an ion and a TICT molecule leads to the change in reaction rate. Computer simulation studies can be helpful to answer many of these questions. Effects of electrolyte on intramolecular charge-transfer reaction in molecules where twisting is heavily restricted could also be very interesting. TICT reactions in confined polar solvent pool may also be exciting as dynamics is very different here. Some of the studies mentioned above are already in progress and we hope to report them soon.[27−28]

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