Kinetic Study of Thermal *Z* to *E* Isomerization Reactions of Azobenzene and 4-Dimethylamino-4′-nitroazobenzene in Ionic Liquids [1-R-3-Methylimidazolium Bis(trifluoromethylsulfonyl)imide with R = Butyl, Pentyl, and Hexyl]

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Abstract: Thermal *Z* to *E* isomerization reactions of azobenzene and 4-dimethylamino-4′-nitroazobenzene were examined in three ionic liquids of general formula 1-R-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (R = butyl, pentyl, and hexyl). The first-order rate constants and activation energies for the reactions of azobenzene measured in these ionic liquids were consistent with those measured in ordinary organic solvents, which indicated that the slow isomerization through the inversion mechanism with a nonpolar transition state was little influenced by the solvent properties, such as the viscosity and dielectric constant, of ionic liquids. On the other hand, the rate constants and the corresponding frequency factors of the Arrhenius plot were significantly reduced for the isomerization of 4-dimethylamino-4′-nitroazobenzene in ionic liquids compared with those for the isomerization in ordinary organic molecular solvents with similar dielectric properties. Although these ionic liquids are viscous, the apparent viscosity dependence of the rate constant could not be explained either by the Kramers–Grote–Hynes model or by the Agmon–Hopfield model for solution reactions. It is proposed that the positive and the negative charge centers of a highly polar rotational transition state are stabilized by the surrounding anions and cations, respectively, and that the ions must be rearranged so as to form highly ordered solvation shells around the charge centers of the reactant in the transition state. This requirement for the orderly solvation in the transition state results in unusually small frequency factors of 10^4–10^7 s^{-1}.

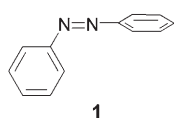**Keywords:** azobenzenes · ionic liquids · isomerization · kinetics

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Introduction

Ionic liquids have attracted much attention from chemists in various fields because of their unique physical and chemical properties, such as 1) fluidity over wide temperature ranges, 2) nonvolatility even in a vacuum, and 3) relatively large dielectric constants. In addition to these properties, some series of ionic liquids have been synthesized to exhibit a wide range of viscosity by varying the substituents on the cationic and/or anionic part of the molecule.[1–5] Although various types of organic/inorganic reactions in ionic liquids have been reported to date, systematic studies concerning the effect of the physical properties of ionic liquids on the reaction process are scarce.[6]

Thermal *Z* to *E* isomerization of substituted azobenzenes has been intensively studied in organic solvents,[7–13] and the mechanism has been examined in various media including supercritical CO_2.[14] It is known that the isomerization of

unsubstituted azobenzene (AB) proceeds through the inversion transition state **1**, in which one of the nitrogen atoms is sp hybridized. On the other hand, the reaction of push–pull-substituted azobenzenes, such as 4-dimethylamino-4′-nitroazobenzene (DNAB), takes place through two independent mechanisms: in nonpolar solvents, by inversion of one of the nitrogen atoms as in AB, and in polar solvents, by rotation around the N−N bond through the polarized transition state **2** (Scheme 1). In solvents such
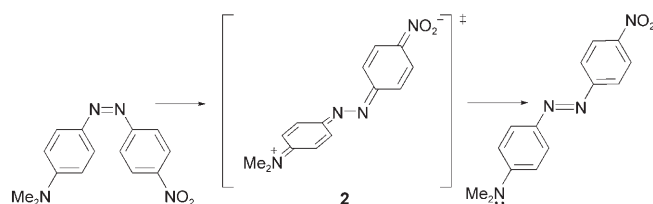
Scheme 1. The isomerization reaction of DNAB in polar solvents by rotation around the N−N bond through polarized transition state **2**.

as benzene, the two mechanisms compete with each other and a shift of the mechanism was identified by monitoring the temperature dependence of the activation energy.[12] These mechanisms were later supported by quantum-chemical calculations.[15]

In this study, we focus on the interaction between the solute and the ionic liquids for the Z to E isomerization reactions of AB and DNAB at different temperatures. The alkyl substituent on the imidazolium ring was varied to control the viscosity of the ionic liquids, while the dielectric properties were not largely altered.

Experimental Section

Materials: All of the common organic solvents were purified as recommended.[16] AB (Wako Pure Chemical Ind.) was purified by sublimation, whereas DNAB (TCI) was recrystallized from toluene. 1-Chlorobutane, 1-chloropentane, and 1-chlorohexane (Tokyo Kasei Ltd.; GR grade) were dried over anhydrous MgSO$_4$ for several days before distillation. 1-Methylimidazole (Aldrich) was dried over sodium and distilled under reduced pressure. The ionic liquids were synthesized by modifying the reported methods.[2,4]

1-R-3-Methylimidazolium chloride (R = butyl, pentyl, and hexyl) was obtained by refluxing each solution of 1-methylimidazole in toluene (ca. 0.5 mol) and 1-chlorobutane, 1-chloropentane, or 1-chlorohexane (ca. 0.8 mol), respectively, at 112–113 °C under an argon atmosphere for 3 h. Each oily product was separated from toluene under reduced pressure. The yield was nearly 100 %. The bis(trifluoromethylsulfonyl)imide salts (ionic liquids) of each imidazolium cation were prepared by using the following method: Lithium bis(trifluoromethylsulfonyl)imide (0.09 mol) was added to a solution of 1-R-3-methylimidazolium chloride (0.08 mol) dissolved in distilled water (100 mL), and the mixture was left under reflux at 100 °C for 1 h. After cooling the mixture to room temperature, the organic layer was extracted by using dichloromethane (200 mL). The final products were obtained by removing dichloromethane under reduced

pressure. The ionic liquids, 1-R-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (R = butyl, pentyl, and hexyl) are abbreviated as B-IL, P-IL, and H-IL, respectively, throughout this article.

It was found that essentially colorless ionic liquids were obtained when the reactions were carried out with excess amounts of active charcoal. Treatment of the final products with charcoal did not significantly improve the purity of the ionic liquids: the purity was examined by using microanalysis as well as by the faint color exhibited by the impure product.

Because analyses using the Karl Fisher method revealed that the synthesized ionic liquids contained large amounts of water (typically 120 mmol kg^{-1} for 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), each ionic liquid was dried in a vacuum oven at 60 °C for 48 h; it was shown from the preliminary experiments to examine the optimum conditions for drying ionic liquids at 60 °C that synthesized B-IL contained 120 mmol kg^{-1} of water, which was reduced to 70 mmol kg^{-1} after 2 h, to ≈10 mmol kg^{-1} after 24 h, and to 5.0 mmol kg^{-1} after 48 h. The temperature of the oven was kept at 60 °C, because the drying procedure at temperatures higher than 80 °C caused partial decomposition, as observed by the coloring of B-IL. The amount of water in the treated ionic liquids was less than 5 mmol kg^{-1} for all of the ionic liquids used in this study. Further drying under the same conditions did not make a significant improvement.

B-IL: ^{1}H NMR ([D$_1$]chloroform): $\delta = 8.75$ (s, 1H; NCHN), 7.30 (m, $J = 1.5$ Hz, 2H; NCHCHN), 4.17 (t, $J = 7.4$ Hz, 2H; NCH$_2$), 3.94 (s, 3H; CH$_3$N), 1.85 (q, 2H; NCH$_2$CH$_2$), 1.36 (sext, $J = 7.5$ Hz, 2H; N-(CH$_2$)$_2$CH$_2$), 0.96 ppm (t, $J = 7.5$ Hz, 3H; CH$_3$CH$_2$); elemental analysis calcd (%) for C$_{10}$H$_{15}$N$_3$O$_4$S$_2$F$_6$: C 28.64, N 10.02, H 3.61; found: C 28.22, N 10.21, H 3.61.

P-IL: ^{1}H NMR ([D$_1$]chloroform): $\delta = 8.76$ (s, 1H; NCHN), 7.30 (m, 2H; NCHCHN), 4.16 (t, 2H; NCH$_2$), 3.94 (s, 3H; CH$_3$N), 1.87 (q, $J = 6.9$, 2H; NCH$_2$CH$_2$), 1.33 (m, $J = 7.9$ Hz, 4H; CH$_3$(CH$_2$)$_2$), 0.90 ppm (t, $J = 5.1$ Hz, 3H; CH$_3$CH$_2$); elemental analysis calcd (%) for C$_{11}$H$_{17}$N$_3$O$_4$S$_2$F$_6$: C 30.49, N 9.70, H 3.95; found: C 30.29, N 9.92, H 3.83.

H-IL: ^{1}H NMR ([D$_1$]chloroform): $\delta = 8.79$ (s, 1H; NCHN), 7.29 (m, 2H; NCHCHN), 4.17 (t, 2H; NCH$_2$), 3.95 (s, 3H; CH$_3$N), 1.86 (m, 2H; NCH$_2$CH$_2$), 1.32 (m, 6H; CH$_3$(CH$_2$)$_3$), 0.88 ppm (t, $J = 6.9$ Hz, 3H; CH$_3$CH$_2$); elemental analysis calcd (%) for C$_{12}$H$_{19}$N$_3$O$_4$S$_2$F$_6$: C 32.21, N 9.39, H 4.28; found: C 32.69, N 9.49, H 4.65.

Measurements: Sample solutions were prepared by using a vacuum line to avoid contamination with water, and sealed after deaeration. Concentrations of the azobenzenes in each sample solution were determined spectrophotometrically. Amounts of water in each sample solution were determined by using a Mitsubishi Kasei KA-07 Karl Fisher apparatus after each measurement by breaking the sample cells: it was found that the amount of water in each solution was typically less than 2.74 mmol kg^{-1} for R = butyl, 4.12 mmol kg^{-1} for R = pentyl, and 5.00 mmol kg^{-1} for R = hexyl, thus indicating that contamination with water was successfully avoided by using this sampling method.

Z isomers of AB and DNAB were prepared by irradiating the samples with light ($\lambda > 350$ by using a UV-cutoff filter) with sufficient agitation by using a Ushio high-pressure Hg lamp (1000 W) for 30 min. During the irradiation, the temperature of the sample solutions was controlled by using thermostatted water, so as to make the measurements of the thermal Z to E isomerization possible immediately after irradiation. Kinetic measurements of the isomerization of the azobenzenes were carried out by measuring the absorption change of the n–π* transition-band maxima at $\lambda \approx 440$ and ≈ 480 nm for AB and DNAB, respectively, by utilizing a JASCO V-570 spectrophotometer with a thermostatted cell compartment. The temperature of the sample solutions was controlled to within ±0.2 °C by means of the circulation of the thermostatted water. All the reactions were found to clearly be of first order, and such an example of the absorbance change corresponding to the Z to E thermal isomerization of AB in B-IL is shown in Figure 1. ^{1}H NMR signals were measured by using a Bruker AMX-400WB spectrometer at 400 MHz.
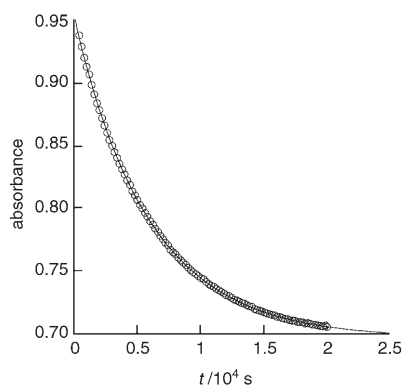
Figure 1. Absorbance change at $\lambda = 438$ nm for the reaction of azobenzene in B-IL. $[AB] = 9.12 \times 10^{-4}$ mmol kg^{-1}, $T = 318.0$ K.
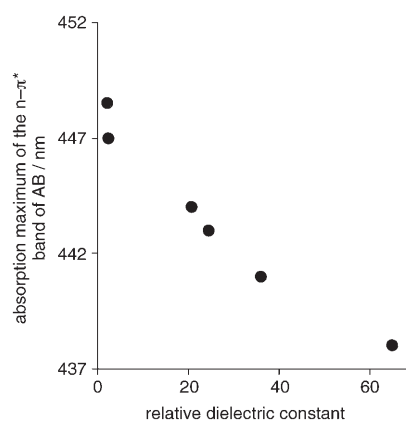

Figure 2. Relationship between the position of the n–π* band maximum of azobenzene and the dielectric constant of organic solvents.

Results and Discussion

Shift of the n–π* transition band in various solvents including ILs: Reports on the dielectric properties of ionic liquids are limited, because of 1) the uncertainty in the measurements that originates from the relatively high dielectric constants of this type of fluid, and 2) the nonexistence of established formulae that describe the dielectric properties of molten salts other than the qualitative theory postulated by Doucet.[17] Dielectric constants have been reported only for molten ethylammonium nitrate,[18] a molten Ca(NO$_3$)$_2$/KNO$_3$ mixture,[19] molten trioctylammonium chloride,[20] and molten nitrate salts of alkali metals.[21] Weingartner reported that the relative dielectric constant of molten ethylammonium nitrate was small (27.1 at 15 °C) and decreased monotonically to 22.2 at 80 °C, although measurements of dielectric properties were difficult at a low frequency. It is also known that the Walden product, the product of viscosity and conductivity of a fluid, is almost constant for this ionic liquid.[18]

In our study, we utilized a rather classical method for the rough estimation of the relative dielectric constants of ionic liquids: the shift of the n–π* transition band of AB was monitored in various organic solvents and in the ionic liquids. It has been known that the n–π* band shifts toward the shorter wavelength region in polar solvents, because the electronic configuration in the ground sate is more stabilized compared with the π* excited state. The results are shown in Figure 2 and Tables 1 and 2: the n–π* band maximum was monotonically blueshifted on increasing the relative dielectric constant of the solvent. In addition, the position of the band maximum was not sensitive to temperature (22 to 60 °C). From these results, the relative dielectric constants for B-IL, P-IL, and H-IL were determined to lie in the range of 15 to 20. This range of dielectric constant is consistent with the value for ethylammonium nitrate at room temperature.[18] The reason for such small dielectric constants of these ionic liquids may be attributed to the formation of ion pairs that have a longer lifetime than the dielectric relaxation (ca. 10^{-10} s at room temperature[18]), or to the low mobility of the large cations with asymmetric structures.

Table 1. Absorption maximum of the n–π* band of azobenzene in ionic liquids at various temperatures.

T [°C]	λ_{max}(n–π*) [nm]		
	B-IL	P-IL	H-IL
60	443	445	
55	444	445	445
50	444	443	443
45	442	445	442
23–40	442	443	443

Table 2. Absorption maxima of the n–π* and π–π* bands of azobenzene in organic solvents at 25 °C.

	ε_{rel}[a]	λ_{max}(n–π*) [nm]	λ_{max}(π–π*) [nm]
1,4-dioxane	2.209	448.5	318
toluene	2.381	447	320
acetone	20.56	444	
ethanol	24.55	443	316.5
acetonitrile	35.94	441	316
propylene carbonate	64.92	438	319

[a] Relative dielectric constant.

Z to E isomerization of AB in B-IL, P-IL, and H-IL: The results for the thermal Z to E isomerization of AB examined in ionic liquids are summarized in Tables 3 and 4. The

Table 3. Rate constants[a] and kinetic parameters observed for Z to E isomerization of azobenzene in three ionic liquids at various temperatures.

B-IL, $[AB] = 9.12 \times 10^{-4}$ mol kg^{-1}

T [K]	310.2	315.0	319.5	324.2	328.9
k [s^{-1}]	3.82×10^{-6}	6.63×10^{-6}	1.11×10^{-5}	1.69×10^{-5}	2.97×10^{-5}

P-IL, $[AB] = 1.00 \times 10^{-3}$ mol kg^{-1}

T [K]	310.9	315.5	319.8	323.9	327.6
k [s^{-1}]	3.30×10^{-6}	6.69×10^{-6}	1.24×10^{-5}	1.91×10^{-5}	3.49×10^{-5}

H-IL, $[AB] = 9.54 \times 10^{-4}$ mol kg^{-1}

T [K]	310.6	315.6	319.8	324.0	329.4
k [s^{-1}]	4.77×10^{-6}	7.73×10^{-6}	1.29×10^{-5}	2.15×10^{-5}	3.51×10^{-5}

[a] Typical errors for the rate constants at each temperature were within 2 % for two runs.

Table 4. Activation energies and frequency factors for the isomerization reaction of azobenzene in ionic liquids.

Ionic liquid	E_a [kJ mol^{-1}]	A [s^{-1}]
B-IL	89.5 ± 2.1 (91.6 ± 2.0)[a]	4.8×10^9 (1.1×10^{10})[a]
P-IL	104.5 ± 3.1 (117 ± 3.0)[a]	1.3×10^{12} (1.4×10^{14})[a]
H-IL	94.4 ± 4.7	3.5×10^{10}

[a] Data obtained in ionic liquids that contain ≈ 100 mmol kg^{-1} of water are shown in the parentheses.

Table 5. Rate constants[a] observed for Z to E isomerization of DNAB in three ionic liquids at various temperatures.[b]

B-IL, [DNAB] $= 3.02 \times 10^{-5}$ mol kg^{-1}

T [K]	280.9	284.2	288.7	290.4	293.3
$k \times 10^3$ [s^{-1}]	3.86 ± 0.02	4.99 ± 0.01	6.55 ± 0.03	7.82 ± 0.03	8.78 ± 0.02

P-IL, [DNAB] $= 2.01 \times 10^{-5}$ mol kg^{-1}

T [K]	280.9	284.2	288.7	290.4	293.3
$k \times 10^3$ [s^{-1}]	0.94 ± 0.04	1.18 ± 0.03	1.89 ± 0.02	2.15 ± 0.03	2.51 ± 0.03

H-IL, [DNAB] $= 2.01 \times 10^{-5}$ mol kg^{-1}

T [K]	284.1	288.7	293.4	297.9	307.1
$k \times 10^3$ [s^{-1}]	1.06 ± 0.02	1.40 ± 0.03	1.76 ± 0.03	2.15 ± 0.04	3.93 ± 0.03
T [K]	316.7	320.9	324.8		
$k \times 10^3$ [s^{-1}]	6.35 ± 0.07	7.58 ± 0.05	9.01 ± 0.15		

[a] Standard deviations given are for up to four runs). [b] Activation parameters obtained from these data are shown in Table 6.

rate constants (k) were comparable to the reported values for common organic solvents and the activation energies, $E_a = 90$ (B-IL), 104 (P-IL), and 95 kJ mol^{-1} (H-IL), were also in the range of reported values for ordinary organic solvents, that is, 84–104 kJ mol^{-1}.[8,22,23] Neither the rate constants nor the activation parameters in Tables 3 and 4 show a clear correlation with the viscosity of the ionic liquids, 52 (B-IL), 57 (P-IL), and 60 cP (H-IL), at 25°C. The reaction became faster on increasing the chain length on the imidazolium ring, probably reflecting a small decrease of the polarity of the medium.[24] Therefore, it is reasonable to conclude that the thermal Z to E isomerization of AB was not influenced by the viscosity of the medium and that the reaction can be safely described by the ordinary transition-state theory (TST) even in these ionic liquids.

Z to E isomerization of DNAB in B-IL, P-IL, and H-IL: The results for the thermal Z to E isomerization of 4-dimethylamino-4′-nitroazobenzene (DNAB) examined in B-IL, P-IL, and H-IL are summarized in Table 5. The Arrhenius plots were linear and therefore no significant change in the reaction pathway was indicated in the temperature range examined in this study. Summarized in Table 6 are the kinetic parameters reported for the Z to E isomerization of DNAB in various solvents, together with the relative dielectric constants (ε_{rel}) and viscosities (η) of each solvent. In Figure 3, the plots of the activation energy and the rate constant of DNAB against the relative dielectric constant of the solvents at 25°C are shown. It is seen that the rate constants measured in the ionic liquids at 25°C are close to those observed in solvents with relatively small dielectric constants, such as hexane, benzene, 1,4-dioxane, pentane, and tetrachloromethane, although the estimated relative dielectric con-

stants for these ionic liquids are as large as 15 to 20: the rate constants measured for molecular solvents that have similar dielectric constants to those of the ionic liquids are unequivocally larger. Such large rate constants observed in dipolar solvents have been explained by the dominance of the rotation mechanism in which the nitrogen–nitrogen π bond is heterolytically cleaved and the reaction is effected by rotation around the remaining N−N bond.[7–12] It is evident from Table 6 that the frequency factors (A) are very small for the reactions in ionic liquids, although the activation energies are in the range of those (42–52 kJ mol^{-1}) re-

Table 6. Kinetic parameters reported for the Z to E isomerization of DNAB in various solvents at 25°C.

Solvent	ε_{rel}	η [cP]	E_a [kJ mol^{-1}][a]	A [s^{-1}][b]	k [s^{-1}][a]
cyclohexane	2.023[c]	0.898	88.3	1.2×10^{14}	0.04
hexane	1.880	0.2985	83.7	1.3×10^{12}	0.002
benzene	2.275	0.6028	102.0	3.5×10^{15}	0.0108
1,4-dioxane	2.209	1.439[d]	108.4	3.4×10^{16}	0.0142
tetrahydrofuran	7.58	0.460	48.1	1.6×10^8	0.513
o-dichlorobenzene	9.93	1.324	52.3	1.2×10^9	0.692
acetone	20.70	0.3040	46	6.8×10^8	2.5
ethanol	24.55	1.078	49.0	8.8×10^9	17.39
methanol	32.70	0.5445	48.1	1.6×10^{10}	47.03
N,N-dimethylformamide	36.71	0.802	42	4.1×10^8	50
dimethylsulfoxide	46.68	1.996	38	9.1×10^8	120
B-IL	≈ 17.5	52[e]	45.6 ± 2.5	1.4×10^6	0.00922[f]
P-IL	≈ 17.5	57[e]	56.9 ± 3.3	1.2×10^7	0.00350[f]
H-IL	≈ 17.5	60[e]	41.0 ± 0.8	1.2×10^4	0.00225[f]
pentane	1.844[c]	0.225			0.00271
tetrachloromethane	2.24[c]	1.038[d]			0.0027
toluene	2.379	0.5516			0.0111
chlorobenzene	5.621	0.757			0.162
diethyl ether	4.335[c]	0.237			0.0152
chloroform	4.806[c]	0.5413			0.180
dichloromethane	8.93	0.4117			0.90
pyridine	12.40[c]	0.884			3.0
1,2-dichloroethane	10.36	0.7823			1.48
2-propanol	19.92	2.1297			8.22
cyclohexanone	18.3[c]	2.0197			8.35
formamide	111[c]	3.302			1640
glycerol triacetate[d]	6.0[c]	16.9	49.8	6.6×10^8	3.34

[a] From references [7] and [8]. [b] Frequency factors for Arrhenius plot. [c] At 20°C. [d] At 15°C. [e] From reference [1]. [f] This work.
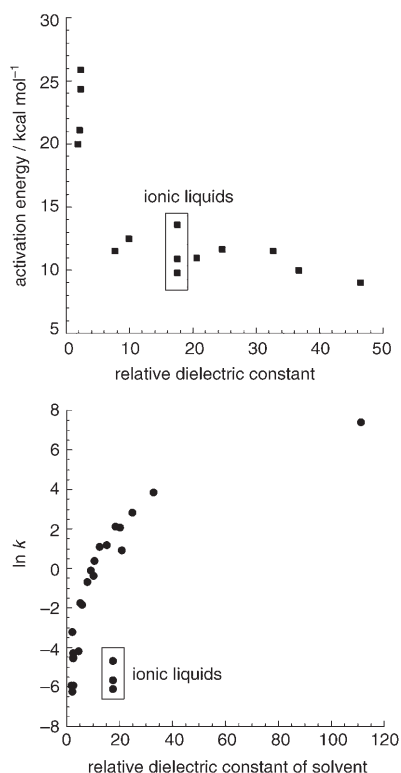
Figure 3. Activation energy (top) and ln k (bottom) for the isomerization reaction of DNAB in various solvents plotted against the relative dielectric constant of the solvents.
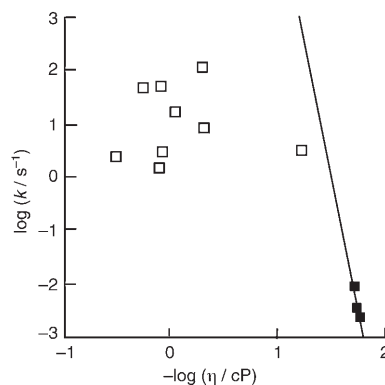

Figure 4. Plots of the logarithmic value of the isomerization rate constant against the logarithmic value of the viscosity of the solvents. Only data for molecular solvents (□) with similar dielectric constants to those of the ionic liquids (■) were used.

ported for the reactions in solvents with relative dielectric constants of 10 to 30, such as acetone, ethanol, methanol, and so forth. It should be noted that no significant decrease of the frequency factor was observed for the slow isomerization reaction of AB through the inversion mechanism in these ionic liquids.

Log–log plots of the rate constant against the viscosity for relatively polar molecular solvents ($10 < \varepsilon_{rel}$) and for ionic liquids are illustrated in Figure 4. Clearly, the rate constant shows little correlation with the viscosity for common organic solvents. In the ionic liquids, however, the reaction was markedly slower and log k seems to be linearly correlated with log η. The activation energy of viscous flow (E_a^v) was roughly estimated by using the reported viscosities at various temperatures for B-IL to give $E_a^v = 41 \pm 7$ kJ mol^{-1}, which may be compared with the activation energy of the isomerization reaction of DNAB in this fluid, that is, $E_a = 46 \pm 6$ kJ mol^{-1}. Therefore, it is tempting to attribute this retardation of the isomerization to slow thermal fluctuations of the cations and the anions surrounding the reactant. However, neither the Kramers–Grote–Hynes model[25–27] nor the more comprehensive Agmon–Hopfield-type models[28–36] can rationalize these retardations because the slope of the plot, -10, was much larger than the value predicted by these models, $0 < -$slope < 1. In addition, the isomerization of DNAB had been found to enter the Kramers' "high viscosity region" only when the viscosity exceeded 10^4 cP

($= 10$ Pa s).[37,38] It also has to be pointed out that in this "diffusion-controlled" region, the reaction was characterized by nonlinear Arrhenius plots with large downward deviations at low temperatures,[37,38] while the plots were linear in B-IL, P-IL, and H-IL.

A change of the mechanism from the rotation in polar molecular solvents to the nitrogen inversion in the ionic liquids can also be rejected on the basis of the activation parameters shown in Table 6. The slow isomerization in the ionic liquids was caused by smaller frequency factors whereas similarly slow isomerization in nonpolar molecular solvents was a result of large activation energies. There is little question that the reaction proceeded via the highly polar rotational activated complex **2** (Scheme 1) in the ionic liquids.

All of these experimental results indicate that the very small rate constants observed in the ionic liquids were not caused by the large macroscopic viscosity (52–60 cP at 25°C decreasing to ca. 20 cP at 40°C). In other words, the reaction is still in the TST-valid region in the present ionic liquids and the results must be interpreted on the basis of "solvation equilibria" in the initial and the transition states. In the initial state, specific interactions between the reactant Z isomer and the surrounding ions is not as strong as those in the transition state, because the reactant does not carry any formal charges. In such a case, the main role of the solvent is to provide a cavity that hosts the reactant. In the transition state, on the other hand, newly formed positive and negative charge centers must be stabilized by contact with the anion(s) and the cation(s), respectively. Though we do not know exactly how the ions are oriented around each charge center, random arrangements should not result in the maximum stabilization. The cationic and anionic parts of each ionic liquid must be placed at fairly strict positions with suitable orientations, around the Me$_2$N$^+$= and the =NO$_2^-$ atomic groups. We therefore conclude that each cationic and anionic part of the ionic liquid independently solvates the polarized structure of DNAB in the transition state and the counterions have to be positioned, again in a relatively strict manner, next to the nearest neighbors of

each cationic/anionic part. A longer carbon chain on the imidazolium ring would have imposed further restrictions for the arrangement of the ions and influenced the rate of the isomerization through the frequency factor. The failure to observe any strong retardations of the isomerization of AB in the ionic liquids implies the importance of the electrostatic interactions in the highly polar rotational transition state **2**. In the inversion transition state of AB (**1**), the interactions between the surrounding ions and the reactant are not as strong as those in **2** and looser and less strict arrangements of the ions (ionic liquids) would suffice to produce optimum solvation: considerably larger frequency factors were observed for the reactions of AB as a result.

Conclusion

The present results unequivocally demonstrate the importance of electrostatic solute–solvent interactions in ionic liquids. In a reaction where the polarity of the transition state does not differ greatly from that of the reactant, ionic liquids behave more or less in the same manner as the ordinary molecular liquids. On the other hand, if a reactant increases its polarity during the activation process, an exhaustive rearrangement of the solvation environment, which includes fairly strict positioning and orientations of the cations and anions around the charge centers of the activated complex, has to take place so as to allow the polar transition state to be stabilized, and this, in turn, results in the retardation of the reaction and a smaller frequency factor. In other words, a large charge density on $-NO_2$ in the transition state induces the cationic parts of the ionic liquid to restructure the hydrogen-bonding network that had been partly destroyed by the dissolution of the azobenzenes. The importance of the hydrogen-bonding network for understanding the physical properties of ionic liquids was previously pointed out by Dupont in his recent review.[39]

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