Received: December 19, 2015 | Accepted: January 10, 2016 | Web Released: January 16, 2016 CL-151169

First Observation for Dynamic Solvent Effect in Ionic Liquids

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We observed pressure effects on the rate of thermal fading of colored chromene **1** photochemically generated from **2** in ionic liquids. The reaction rates were retarded with increasing pressure in [C$_4$-mim][CS], [bzl-mim][Tf$_2$N], and [mnp-mim][Tf$_2$N], whereas the reaction rate increased with pressures in [C$_4$-mim][Tf$_2$N]. These pressure-induced retardations, so-called dynamic solvent effects, result from the slow thermal fluctuations of solvents.

Keywords: Ionic liquid | Solvation behavior | Dynamic solvent effect

Room-temperature ionic liquids could be suitable and environmentally safer replacements for volatile, toxic, and flammable organic solvents, and ionic liquids have been used in the synthetic and catalytic reactions.[1] There are various reports about using ionic liquids as media for Friedel–Crafts,[2] Diels–Alder,[3] Heck,[4] hydrogenation,[5] and porphyrin preparation.[6] Properties of medium, such as polarity, viscosity, and hydrogen-bonding ability, affect the reaction rate in condensed phase.[7] Unlike ordinal molecular solvents, which build up with a single component, ionic liquids are composed of a cation and an anion. Furthermore, the size of a cation and an anion are relatively larger than that of molecular solvents. These features also play a key role in the solvation behavior of ionic liquids. The solvation dynamics of the dipole probe in ionic liquids or ionic deep eutectic solvents were investigated previously.[8] However, the solvation behavior of ionic liquids is still poorly understood in the electronic ground state because it is difficult to observe the solvent molecular movement around the substrates.

By combining high pressure and viscous molecular solvents, Asano et al. demonstrated that the thermal isomerization of molecules in their electronic ground state are retarded with an increase in pressure (dynamic solvent effect).[9] In general, ionic liquids have higher viscosity than molecular solvents. Herein, we firstly examined the observation of the dynamic solvent effect on thermal isomerization in the electronic ground state in ionic liquids.

We selected the thermal cyclization of a colored hexadienone from 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran as a probe reaction in ionic liquids (Figure 1). The thermal cyclization reaction is an appropriate probe for discussing the solvation behavior in ionic liquids because the reaction has been studied in detail in molecular solvents.[10] Hexadienone **1** was photochemically generated in situ from **2** and its decay was followed spectrophotometrically. The experiments were carried out according to the literature.[11]

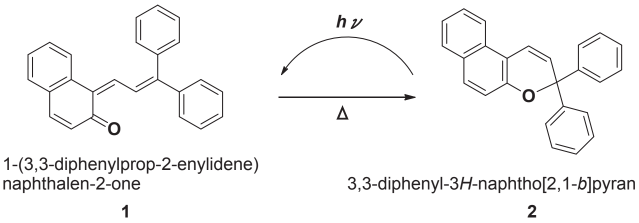

Figure 1. Photo and thermal isomerization between **1** and **2**.

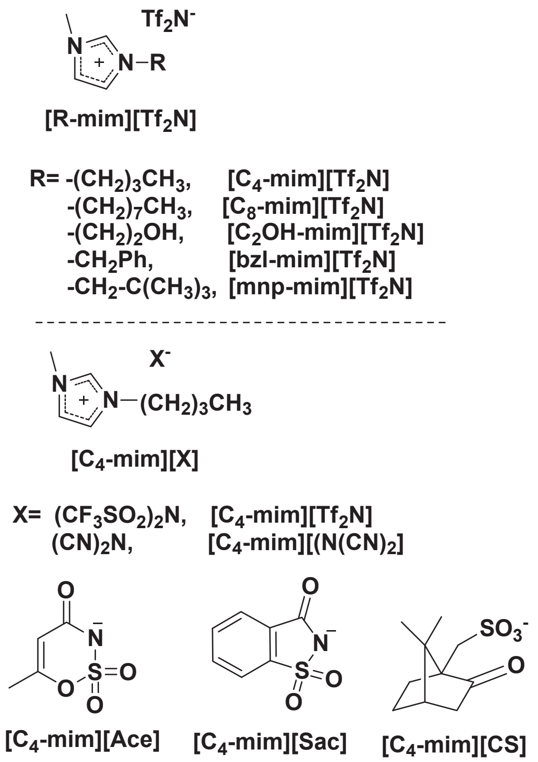

Figure 2. The structure of ionic liquids.

In order to exhibit the effect of anion and cation structures of the ionic liquids on a dynamic solvent effect, the ionic liquids employed in this study can be categorized into two groups, as shown in Figure 2. [R-mim][Tf$_2$N] are composed of the alkylimidazolium cations with various substituents and the Tf$_2$N anion. [bmim][X] are composed of the 1-butyl-3-methyllimidazolium cation and different type of anions. These ionic liquids were prepared according to the published procedures,[12] and preparation details are shown in Supporting Information.

Figure 3 illustrates the pressure dependence of the reaction rate in [R-mim][Tf$_2$N], which have different imidazolium cations. Open plots represent the results in the molecular solvents. The reaction was moderately accelerated by a pressure

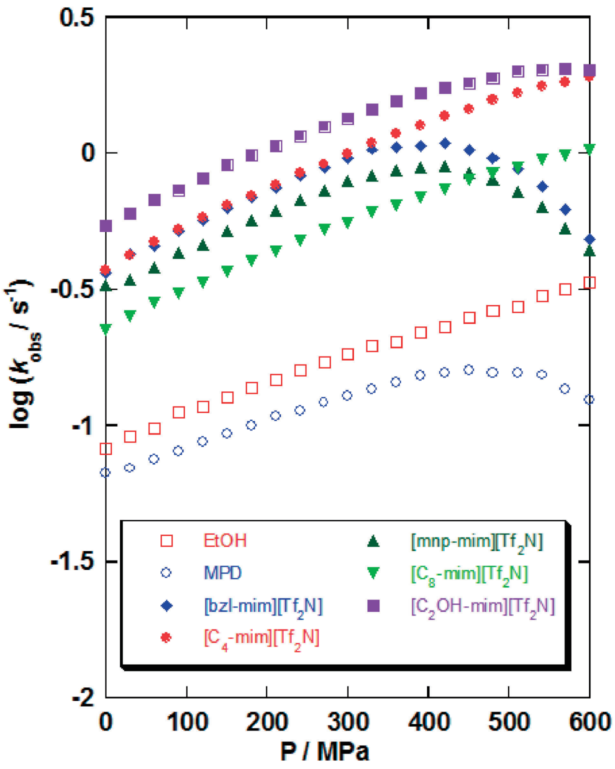

Figure 3. Pressure dependence of the cyclization rate (k_{obs}/s^{-1}) of **1** in [R-mim][Tf_2N] and molecular solvents (EtOH and MPD) at 25 °C.

increase in ethanol. On the other hand, the reaction rate was retarded with an increase in pressure in 2-methyl-2,4-pentanediol (MPD). The difference between ethanol and MPD shows slow solvent fluctuations of the MPD under high pressure and it is a typical example of dynamic solvent effects. The reaction rate increased with increasing pressure because of a negative activation volume.[9] However, a further increase in pressure resulted in a retardation. The viscosity of viscous solvents such as MPD is increased by high pressure and the increase of viscosity makes the solvent reorganization slow. In this case, the transition state theory (TST) is invalid, and the reaction was retarded by pressure. The closed plots represent the reaction in [R-mim][Tf_2N]. In [bzl-mim][Tf_2N] and [mnp-mim][Tf_2N] containing benzyl and methylneopentyl groups, respectively, the dynamic solvent effects were observed at higher pressures. [mnp-mim][Tf_2N] has a branching structure as well as MPD. It is reasonable to surmise that the branching structure of [mnp-mim][Tf_2N] give a high viscosity at high pressure as well as MPD, and the retardation of the reaction was observed. In case of [bzl-mim][Tf_2N], it is surmised that the increasing pressure exerts an effect on the formation of the π–π stacking interaction among the benzyl group of the cations, and such a rigid π–π interaction increased the viscosity of [bzl-mim][Tf_2N].

Figure 4 illustrates the pressure dependence of the reaction rate in [C_4-mim][X], which have different anions. In the ionic liquids containing the bulky anion such as Asc$^-$, Sac$^-$, and CS$^-$, the dynamic solvent effects were observed. The bulky anion structures of these ionic liquids play a critical role on the dynamic solvent effect. In particular, the viscosity of [C_4-mim][CS] is very high (1.9×10^4 cP at 25 °C, 0.1 MPa). Although we cannot evaluate the viscosity of ionic liquids at high pressure, it is surmised that [C_4-mim][CS] become more viscous at high pressure. Then, it seems to surmise that the reaction rate in [C_4-mim][CS] was decelerated considerably. The pressure effect based on TST may be extrapolated to TST-invalid viscosities if the reaction mechanism is the same at all pressures. This extrapolation provides an estimate for the rate constant expected from TST, k_{TST}. The k_{TST} values in [C_4-mim][CS] at higher pressures were estimated by extrapolations of the lower-pressure data. Isobaric activation energies from k_{TST} are almost the same in all pressures (73.0 kJ mol^{-1} at 0.1 MPa and 72.3 kJ mol^{-1} at 600 MPa). Therefore, it seems reasonable to conclude that the pressure effects in [C_4-mim][CS] at higher pressures are not a static effect.

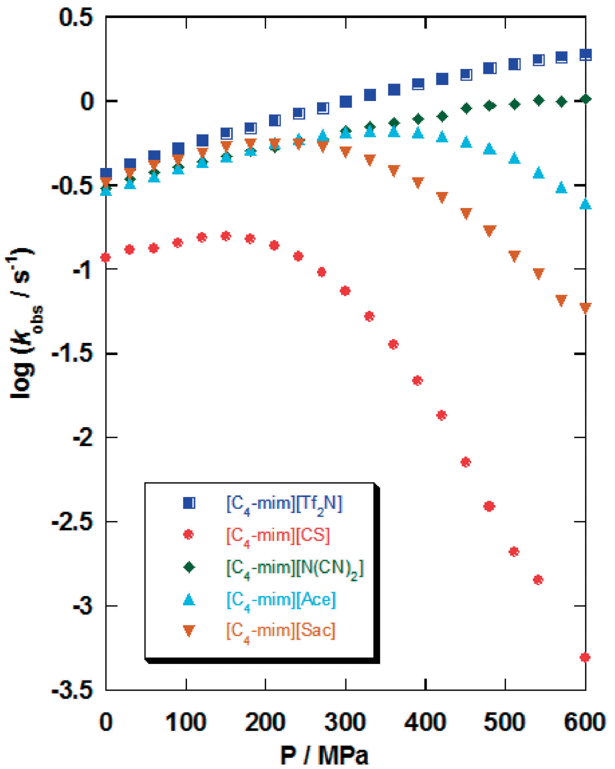

Figure 4. Pressure dependence of the cyclization rate (k_{obs}/s^{-1}) of **1** in [C_4-min][X] at 25 °C.

Table 1. Activation volume of thermal fading of colored chromene **1** to **2** in ionic liquids at 25 °C

Ionic liquids	$\Delta V_0^{\ddagger}$/cm^3 mol^{-1}
[C_4-mim][CS]	−6.4
[C_4-mim][$N(CN)_2$]	−8.4
[C_4-mim][Sac]	−11
[C_4-mim][Tf_2N]	−10
[mnp-mim][Tf_2N]	−10
[bzl-mim][Tf_2N]	−11

Finally, we discuss the activation volume ($\Delta V_0^{\ddagger}$/cm^3 mol^{-1}) in each ionic liquid (Table 1). The activation volume of thermal fading of colored chromene **1** to **2** is defined as a difference between the partial molar volumes of the activated complex and the reactant. The estimated activation volumes were almost the same levels in all ionic liquids except for [C_4-mim][CS]. Only [C_4-mim][CS] gave a small negative activation volume. There are two factors that can change the volume. First, a loss of internal freedom of motion with cyclization decreases the volume. Second, the polarity of the reactant is decreased in the cyclization pathway and the volume of the reactant is increased because of desolvation. The second factor is closely related to the solvation. Therefore, an extremely sterically bulky CS anion desolvates around **1** and such a large desolvation gave the small negative activation volume. The CS anion is an O-base anion, whereas the Sac anion is an N-base anion. The interaction of the O-base anion with chromene is weaker than that of the isomerization N-base anion. The difference between the O-base and N-base anions may affect the desolvation of the chromene.

In conclusion, the reaction rates in [bzl-mim][Tf_2N], [mnp-mim][Tf_2N], [C_4-mim][Sac], [C_4-mim][Ace], and [C_4-mim][CS] were retarded with increasing pressure. Such pressure-induced retardations, the so-called dynamic solvent effects, are the results of slow solvent thermal fluctuations caused by high viscosities. The bulky structures and aromatic ring of the ionic liquids caused high viscosity under the high pressure. The activation volumes of thermal cyclization of **1** show almost the same levels in all ionic liquids except for [C_4-mim][CS], which gave a small negative activation volume. It is reasonable to assume that the desolvation around **1** was effectively increased by the ionic liquids containing a bulky ion like a CS anion. In order to elucidate the difference of solvation behavior between [C_4-mim][CS] and other ionic liquids in detail, we conducted further experiments by using chromene derivatives with different polar substituents.

This work was supported by JSPS KAKENHI Grant Numbers 25810109, 26600028, 15K05598 and JST A-STEP Number AS242Z02498M.

Supporting Information is available on http://dx.doi.org/10.1246/cl.151169.

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