The Magnetic Field Effects on Photochemical Reactions in Ionic Liquids

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The magnetic field effects (MFEs) on photoinduced hydrogen abstraction reactions of benzophenone (BP) with thiophenol (PhSH) in the ionic liquids (ILs) *N,N,N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl) imide (TMPA TFSI), *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl) imide (P13 TFSI), and *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl) imide (PP13 TFSI) were investigated at 296 K by using a nanosecond laser flash photolysis technique under magnetic fields of 0−1.7 T. Large MFEs were observed for the first time in the ILs. In TMPA TFSI, the yield of the benzophenone ketyl radical gradually decreased with increasing magnetic field strength from 0 to 1.7 T, producing a 20% decrease at 1.7 T.

Introduction

Ionic liquids (ILs), which are considered to be one of the most promising new classes of solvents in green chemistry, have recently attracted a great deal of attention, because of their unusual chemical properties: nonvolatile, noncorrosive, non-flammable, stable in air and moisture, and designable.[1−6] Potential applications include their use as reaction media for organic reactions or in homogeneous catalysis, as novel extraction solvents, as liquid crystals, and as electrolytes for electrochemical reactions. From a green-chemistry prespective, ILs are ideally suited for use as solvents in photochemistry. However, there are few reports on the photochemical reactions in ILs. Hamaguchi et al. reported that the photoisomerization indeed proceeds in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF$_6$) with a rate much larger than that expected from its polarity and viscosity.[7] Jones et al.[8] reported photoreduction of benzophenone (BP) by amines in ILs, and McLean et al.[9] reported hydrogen abstraction from ILs by BP. The photoelectron transfer from ruthenium(II) tris(bipyridyl) to methylviologen in [bmim]PF$_6$ was also reported by McLean et al.[10] García et al. reported that a series of photochemical reactions in [bmim]PF$_6$ covering energy transfer, hydrogen transfer, and electron transfer was studied.[11] Samanta et al. reported the intermolecular excimer formation of 1,3-bis(1-pyrenyl)propane in four different 1-butyl-3-methylimidazolium salts.[12] Pagni et al. described photoinduced electron transfer of anthracene[13] and 9-methylanthracene[14] in ILs. In those reports, ILs are shown, to a large extent, to be suitable for use as solvents in many types of photochemical reactions. However, some results observed in ILs are quite different from those observed in conventional solvents.[7,9−11] The differences may be caused by local structure or some domains in the ILs, which have recently been proposed by Hamaguchi et al.,[15] Nishikawa et al.,[16] and Wishart et al.[17]

Magnetic field effects (MFEs) on the chemical reactions in conventional solvents have been studied extensively and constitute a rapidly developing field encompassing chemistry, physics, and biology.[18−20] This new branch is called *spin chemistry*.[19] Magnetic fields can interact with the electron spins of radical pairs generated in chemical reactions, and cause the spin conversion of radical pairs between singlet (S) and triplet (T$_m$, $m = 0, \pm1$) states. Thus, the lifetime of the radical pairs and the yield of the escaped radicals consequently show appreciable MFEs. Such MFEs can be interpreted by the radical pair mechanism and the triplet mechanism (RPM and TM). In the case of usual organic radicals, the MFEs can be interpreted by the RPM, in which four variants are known:[18,19] (1) The Δg mechanism (ΔgM) which is due to the difference between the isotropic g factors of two radicals in a pair. (2) The hyperfine coupling mechanism (HFCM) due to the isotropic hyperfine interaction between electron and nuclear spins. (3) The level-crossing mechanism (LCM) due to the crossing between the S and T$_{+1}$(or T$_{−1}$) levels. (4) The relaxation mechanism (RM) due to the anisotropic g tensor (δg), HFC (δHFC), and the spin−spin dipolar interactions of radical pairs. Because a confined system is necessary for a radical pair during the S−T spin conversion, MFEs are very sensitive to the environment around the radical pair. If ILs have a local structure like that of micellar solutions, large MFEs are expected to be observed. To date, however, there is no report of MFEs in ILs. Here, we report large MFEs in the photoinduced hydrogen abstraction reactions of benzophenone (BP) with thiophenol (PhSH) in ILs.

Experimental Section

Materials. *N,N,N*-Trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl) imide (TMPA TFSI, Cica), *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl) imide (P13 TFSI, Cica), and *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl) imide (PP13 TFSI, Cica) were used as received. Thiophenol (PhSH, Cica) was purified by vacuum

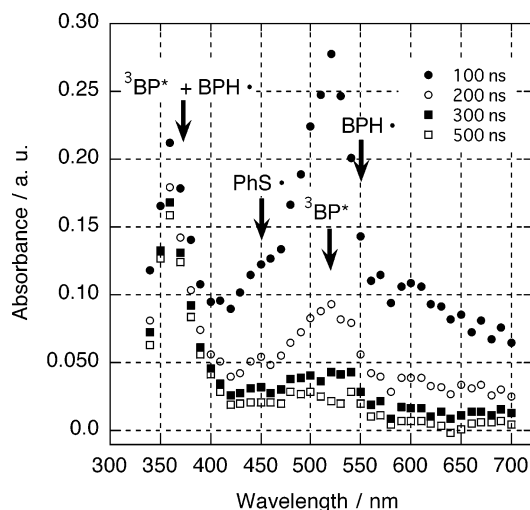* To whom correspondence should be addressed. E-mail: mwakasa@ chem.saitama-u.ac.jp.

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Figure 1. Transient absorption spectra observed at 296 K at delay times of 100, 200, 300, and 500 ns after laser excitation.

distillation. Benzophenone (BP, Cica) was recrystallized from methanol. The concentrations of BP and PhSH in the employed ILs were 2.0×10^{-2} and 1.2×10^{-1} mol dm^{-3}, respectively.

Nanosecond Laser Flash Photolysis. Laser flash photolysis experiments were carried out with an apparatus that was essentially the same as the apparatus described elsewhere.[21,22] The second harmonic (355 nm) of a nanosecond Nd:YAG laser (Quanta-Ray, INDY; 7 ns fwhm) was used as an excitation light source. The excitation light was introduced perpendicularly to the monitoring light. The transient absorption was recorded by a LeCroy WavePro 960 digitizing oscilloscope with a Hamamatsu R636 photomultiplier. The argon-bubbled solution in a quartz cell was placed at the center of an electromagnet. Magnetic fields (B) of up to 1.7 T were provided by a TOKIN SEE-10W electromagnet. Applied magnetic field was measured with a Lake-Shore model 421 gauss meter placed right next to the quartz cell.

Results and Discussion

Laser flash photolysis was performed in the ILs at 296 K. Time profiles of the transient absorption, $A(t)$, were measured at 520 nm in the presence of BP only, because the triplet excited state of BP has a triplet–triplet (T–T) absorption band at 520 nm.[23]

$$BP \xrightarrow{h\nu} {}^1BP^* \rightarrow {}^3BP^* \qquad (1)$$

Here, ${}^1BP^*$ and ${}^3BP^*$ represent the singlet and triplet excited states of BP, respectively. The decay of the $A(t)$ curves was very slow; the lifetimes of ${}^3BP^*$ observed in each solution were as follows: 19 μs (in TMPA TFSI), 10 μs (in P13 TFSI), and 10 μs (in PP13 TFSI). In conventional solvents, the lifetime of ${}^3BP^*$ is much shorter than those seen in the ILs: 3 μs (in benzene), 300 ns (in cyclohexane), and 5 ns (in 2-propanol).[21] Such short lifetimes of ${}^3BP^*$ are due to the reactions of ${}^3BP^*$ with conventional solvents. Thus, we concluded that the ILs employed in the present study are very inert in the reaction of the triplet excited state of BP and therefore suitable for use as solvents in the photochemical reactions of BP, which is one of the most important photochemical reagents.

$A(t)$ curves for BP and PhSH were measured in TMPA TFSI. Transient absorption spectra at delay times of 100, 200, 300, and 500 ns after laser excitation were measured in the wavelength range 340–700 nm (Figure 1). Here, transient
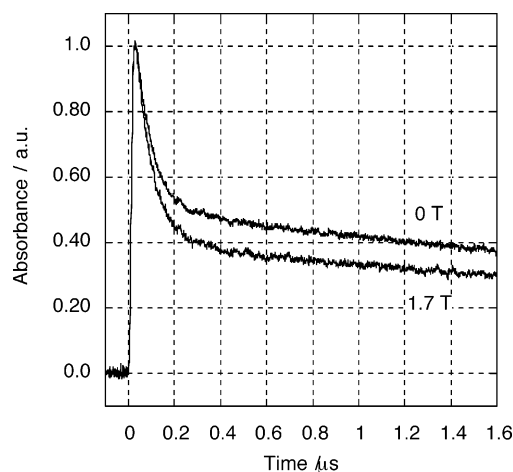

Figure 2. $A(t)$ curves observed at 380 nm for the hydrogen abstraction reaction of BP with PhSH in TMPA TFSI at 0 and 1.7 T.
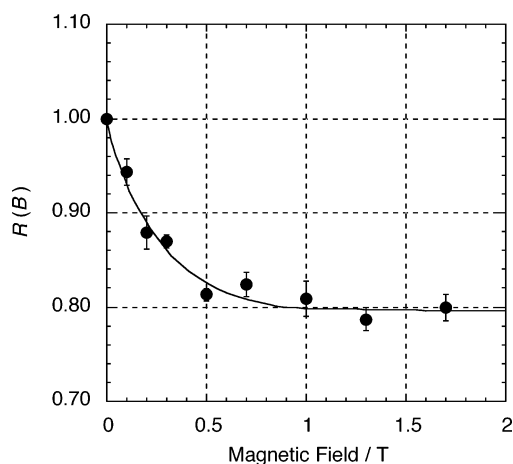

Figure 3. Magnetic field dependence of the yield of escaped BPH• ($R(B) = A(0.5 \mu s, B\ T)/A(0.5 \mu s, 0\ T)$) observed at 380 nm in TMPA TFSI.

absorption bands caused by the T–T absorption of ${}^3BP^*$ were observed at 360 and 520 nm;[23] they disappeared quickly with a lifetime of 85 ns. After the decay of the T–T absorption, the benzophenone ketyl radical (BPH•)[24] was observed at 380 and 550 nm and the phenylthiyl radical (PhS•)[25] at 450 nm. Similar transient absorption spectra were observed in P13 TFSI and PP13 TFSI. These results indicate that fast hydrogen abstraction of ${}^3BP^*$ from PhSH occurs in the ILs and that a triplet radical pair involving BPH• and PhS• is generated efficiently.

$$^3BP^* + PhSH \rightarrow {}^3(BPH\bullet\ \bullet SPh) \qquad (2)$$

Here, ${}^3(BPH\bullet\ \bullet SPh)$ represents the triplet radical pair of benzophenone ketyl and phenylthiyl radicals.

The $A(t)$ curves at 0 and 1.7 T observed at 380 nm have fast and slow decay components (Figure 2): we ascribe the fast component to the T–T absorption of ${}^3BP^*$ and the slow one to the escaped BPH•. As is clearly seen in this figure, the yield of escaped BPH• is appreciably affected by the field. The lifetime of T–T absorption was measured to be 85 ns—this is the fast component; the slower component of the absorption, $A(0.5 \mu s, B\ T)$, is proportional to the yield of the escaped radical, $Y(B\ T)$. Thus, the ratio $R(B) = Y(B\ T)/Y(0\ T) = A(0.5 \mu s, B\ T)/A(0.5 \mu s, 0\ T)$ gives the MFE on the yield of the escaped BPH•. $R(B)$ decreased with increasing B; $R(1.7\ T)$ reached 0.80 ± 0.02 (Figure 3). This means that the yield of BPH• decreased with increasing magnetic fields; a field of 1.7 T produced a 20%
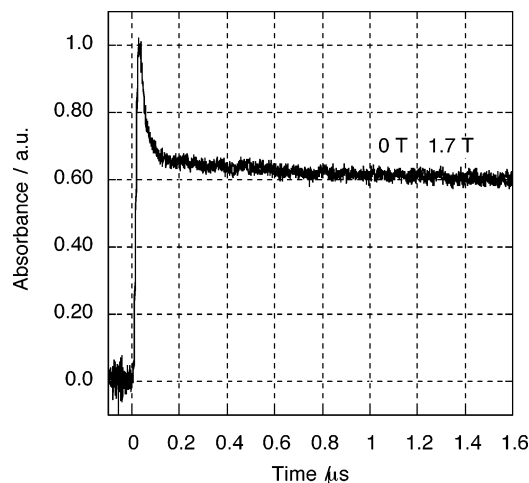
Figure 4. $A(t)$ curves observed at 550 nm for the hydrogen abstraction reaction of BP with PhSH in a mixed solvent of cyclohexanol and 2-methyl-1-propanol (100:1, $\eta = 54.8$ cP) at 0 and 1.7 T.

decrease. Similar magnetic field dependence on the $R(B)$ values was observed in P13 TFSI and PP13 TFSI. The obtained $R(1.7$ T) values in P13 TFSI and PP13 TFSI were 0.81 ± 0.02 and 0.75 ± 0.02, respectively. The observed $R(B)$ values are as large as those observed in conventional solvents at an ultrahigh magnetic field of 30 T.[26,27] This is the first time that such large MFEs have been observed in ILs.

In our previous paper,[22,26,27] the $R(1.7$ T) values observed for the same reaction in conventional solvents decreased with increasing solvent viscosity ($\eta \leq 3.3$ cP (2-methyl-1-propanol)) and the MFEs could be explained by using the Δg mechanism of the RPM. It might be thought that the large MFEs observed in this experiment would be explained by using the same mechanism because of the high viscosities of the ILs ($\eta = 56.7$ cP (P13 TFSI), 72.6 cP (TMPA TFSI), and 137 cP (PP13 TFSI)). To clarify the contribution of the viscosity, we measured the $A(t)$ curves of the same reaction using a mixed solvent of cyclohexanol and 2-methyl-1-propanol (100:1, $\eta = 54.8$ cP). Although the solvent viscosity was similar to that of P13 TFSI, surprisingly, no MFE was observed at 1.7 T (Figure 4). Thus, the large MFEs observed in the present study could not be explained by the high viscosity of the ILs alone.

What is the other important factor causing such large MFEs? Because a confined system is necessary for a radical pair during the S−T spin conversion, we consider the cage effect to be more important than viscosity. If ILs have a local structure like micellar solutions, the large MFEs can be explained by the cage effect.[28] In fact, local structure or some domains in ILs were recently reported by Hamaguchi et al.,[15] Nishikawa et al.,[16] and Wishart et al.[17] To examine the cage effect of the ILs, we are currently carrying out temperature dependent measurements of the MFEs and time-resolved electron spin resonance (ESR) measurements.

Conclusions

MFEs on the photoinduced hydrogen abstraction reactions of benzophenone with thiophenol in ILs were studied for the first time. The ILs employed in the present study (TMPA TFSI, P13 TFSI, and PP13 TFSI) are very inert in the reaction of the triplet excited state of BP and suitable for use as solvents in the photochemical reactions of BP. Large MFEs on the yields of the escaped benzophenone ketyl radical were observed. The MFEs observed in the present study could not be explained by the high viscosity of the ILs alone. A local structure such as micellar solutions was suggested.

Note Added after ASAP Publication. This paper was published ASAP on July 21, 2007. A value listed in the caption of Figure 4 was changed. The updated paper was reposted on July 27, 2007.

References and Notes

(1) Seddon, K. R. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351.
(2) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
(3) Wasserscheid, P.; Kein, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.
(4) Sheldon, R. *Chem. Commun.* **2001**, 2399.
(5) Dupont, J.; Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667.
(6) Ohno, H. *Electrochemical aspects of ionic liquids*; John Wiley & Sons, Inc.: Hoboken, NJ, 2005.
(7) Ozawa, R.; Hamaguchi, H. *Chem. Lett.* **2001**, *30*, 736.
(8) Reynols, J. L.; Erdner, K. R.; Jones, P. B. *Org. Lett.* **2002**, *4*, 917.
(9) Muldoon, M. J.; McLean, A. J.; Gordon, C. M.; Dunkin, I. R. *Chem. Commun.* **2001**, 2364.
(10) Gordon, C. M.; McLean, A. J. *Chem. Commun.* **2000**, 1395.
(11) Álvaro, M.; Ferrer, B.; Gracía, H.; Narayana, M. *Chem. Phys. Lett.* **2002**, *362*, 435.
(12) Karmakar, R.; Samanta, A. *Chem. Phys. Lett.* **2003**, *376*, 638.
(13) Hondrogiannis, G.; Lee, C. W.; Pagni, R. M.; Mamantov, G. *J. Am. Chem. Soc.* **1993**, *115*, 9828.
(14) Lee, C. W.; Winston, T.; Unni, A.; Pagni, R. M.; Mamantov, G. *J. Am. Chem. Soc.* **1996**, *118*, 4919.
(15) Hamaguchi, H.; Ozawa, R. *Adv. Chem. Phys.* **2005**, *131*, 85.
(16) Nishikawa, K.; Wang, S.; Katayanagi, H.; Hayashi, S.; Hamaguchi, H.; Koga, Y.; Tozaki, K. *J. Phys. Chem. B* **2007**, *111*, 4894.
(17) Funston, A. F.; Fadeeva, A. F.; Wishart, J. F.; Castner, E. W., Jr. *J. Phys. Chem. B* **2007**, *111*, 4963.
(18) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.
(19) Nagakura, S; Hayashi, H.; Azumi, T. *Dynamic Spin Chemistry*; Kodansha-Wiley: Tokyo, New York, 1998.
(20) Hayashi, H.; Sakaguchi, Y.; Wakasa, M. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 773.
(21) Hamasaki, A.; Sakaguchi, Y.; Nishizawa, K.; Kido, G.; Wakasa, M. *Mol. Phys.* **2006**, *104*, 1765.
(22) Wakasa, M.; Hayashi, H. *J. Phys. Chem.* **1996**, *100*, 15640.
(23) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1968**, *15*, 1.
(24) Sakaguchi, Y.; Hayashi, H.; Nagakura, S. *J. Phys. Chem.* **1982**, *86*, 3177.
(25) Jeschke, G.; Wakasa, M.; Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem.* **1994**, *98*, 4069.
(26) Wakasa, M.; Nishizawa, K.; Abe, H.; Kido, G.; Hayashi, H. *J. Am. Chem. Soc.* **1998**, *120*, 10565.
(27) Wakasa, M.; Nishizawa, K.; Abe, H.; Kido, G.; Hayashi, H. *J. Am. Chem. Soc.* **1999**, *121*, 9191.
(28) In sodium dodecylsulfate (SDS) micellar solutions, similar MFEs on the hydrogen abstraction reactions of xanthone with *p*-aminothiophenol[29] and benzophenone with thiophenol[30] were previously reported.
(29) Wakasa, M.; Nakamura, Y.; Sakaguchi, Y.; Hayashi, H. *Chem. Phys. Lett.* **1993**, *215*, 631.
(30) Wakasa, M.; Sakaguchi, Y.; Hayashi, H. *Chem. Lett.* **1994**, *23*, 49.