Cage lifetimes of ionic liquids as studied by the magnetic field effect probe

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Magnetic field effects (MFEs) on the photoinduced hydrogen abstraction reaction of benzophenone with phenol were investigated in ionic liquids (ILs) with a short alkyl chain (N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide (TMPA TFSA)) and long alkyl chains ((N,N,N-trimethyl-N-octylammonium bis(trifluoromethanesulfonyl)amide (TMOA TFSA) and N-decyl-N,N,N-trimethylammonium bis(trifluoromethanesulfonyl)amide (DTMA TFSA)) by a nanosecond laser flash photolysis technique. In each ionic liquid, escaped radical yield of a benzophenone ketyl radical rapidly increased with increasing magnetic field strength (B) of 0 T < B ≤ 0.01 T. At 0.01 T < B ≤ 0.4 T, the escaped radical yield almost saturated in TMPA TFSA or gradually increased in TMOA TFSA and DTMA TFSA. At much higher fields of 0.4 T < B < 30 T, the yield gradually decreased, resulting in 10–15% decrease at 30 T. The observed MFEs can be explained by the hyperfine coupling and Δg mechanisms together with the relaxation mechanism. On the time profiles of the transient absorption observed for the benzophenone ketyl radical, MFEs were generated in the time range of 0 < t < 0.6 µs. The cage lifetimes of TMOA TFSA and DTMA TFSA were estimated to be at least 120 ns.

1. Introduction

Ionic liquids (ILs) are currently a promising new class of solvents in green chemistry, electrochemistry, and nanochemistry, because of their exceptional combination of properties: non-volatility, noncorrosiveness, nonflammability, stability to air and moisture, and designability, and provide new environments for chemical reactions.1–7 Although a number of studies on their structures and functions have been reported,8–15 the mechanistic insight into chemical reactions in ILs is still unclear because of the complex solvent structures in ILs. Especially, it has been reported that the ILs have nanoscale ordering structures as a result of the strong coulombic interactions and the aggregation of the nonpolar parts of ionic molecules.9–11 Such nanoscale ordering structure works as a cage in which viscosity may be different from the bulk viscosity (macroviscosity). One of the most attractive queries regarding the nanoscale ordering structures in ILs is the lifetime of the cage, which may be related to the unusual chemical properties of ILs such as electron transportation, polymerization, and formation of nanomaterials. To the best of our knowledge, however, the cage lifetime of ILs has not been reported.

Recently we have applied a strategy of the magnetic field effect probe (MFE probe) to study the nanoscale heterogeneous structures.16–21 Magnetic field interacts with the electron spin of radical pairs (RPs) generated by the photochemical reactions, and thus the spin conversion between singlet (S) and triplet (T) RPs is influenced by the magnetic fields. The yield of escaped radicals, therefore, shows appreciable magnetic field effects (MFEs).22–24 According to the RP mechanism of MFEs, the RP lifetime (τRP) should be longer than or comparable to the S–T spin conversion time (τS–T) and spin relaxation time (τrel): τRP ≥ τS–T, τrel. In other words, if MFEs are observed, one can estimate the RP lifetime.25,26 In many chemical reactions, viscous solvents and cages of micelle are extensively used for generating long-lifetime RPs. Nanoscale ordering structure of ILs also works as a cage, in which the local viscosity in the vicinity of the RPs (microviscosity) is somewhat small. In an IL N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide (TMPA TFSA), the cage radius and microviscosity in the cage were reported to be ~2 nm and 2–4 cP, respectively.19–20 In such a low microviscosity cage, the cage lifetime (τcage) should be longer than or comparable to the RP lifetime: τcage ≥ τRP. Thus the cage lifetime can be estimated from the RP lifetime by using the MFE probe.

In TMPA TFSA, we have observed the large MFEs for the photoinduced hydrogen abstraction reaction of benzophenone (BP) with thiophenol (PhSH) in the range of 0 T < B ≤ 28 T.16,17 In the reaction, RPs of a benzophenone
ketyl radical (BPH$^*$) and a phenylthiyl radical (PhS$^*$) were generated. However, the S–T spin conversion and spin relaxation times were too fast to estimate the RP lifetime from the MFEs. We focus on photoinduced hydrogen abstraction reaction of BP with phenol where a slower spin process is expected, and MFEs of the reaction were studied in TMPA TFSA and two other ILs having long alkyl chains: $N,N,N$-trimethyl-$N$-octylammonium bis(trifluoromethanesulfonyl)amide (TMOA TFSA) and $N$-decyl-$N,N,N$-trimethylammonium bis(trifluoromethanesulfonyl)amide (DTMA TFSA) (Chart 1).

2. Experimental

Materials

Benzophenone (BP) and phenol (PhOH) were recrystallized twice from methanol and hexane, respectively. TMPA TFSA was purchased from Kanto Chemical Co., Inc (Cica) and used as received. TMOA TFSA was purchased from Piotrek Co., Ltd. DTMA TFSA was synthesized from decyltrimethylammonium bromide and lithium bis(trifluoromethanesulfonyl)amide as described in the literature.$^{27}$ TMOA TFSA and DTMA TFSA were washed with deionized water and hexane individually 10 times, impurity remains were adsorbed by activated carbon, and dried under vacuum at room temperature for more than 24 h. The water contents in TMPA TFSA, TMOA TFSA, and DTMA TFSA used in the present work were 90–100 ppm. The concentrations of BP and PhOH in the employed ILs were $2.0 \times 10^{-2}$ and $1.1 \times 10^{-1}$ mol dm$^{-3}$, respectively.

The kinetic viscosity and density of each IL were measured by using a viscometer (Yamauchi VM-10A-L) and a density meter (Anton Paar DMA 5000), respectively. The viscosities ($\eta$) obtained from the kinetic viscosities and densities are summarized in Table 1.

### Table 1 Viscosities ($\eta$) of ionic liquids used in the present study and magnetic field effects on the yield of the escaped radical ($R(B) = Y(B)/Y(0 \ T)$) observed at 0.01, 0.4, 28 and 30 T

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>$\eta/\mathrm{cP}$</th>
<th>$R(0.01 \ T)$</th>
<th>$R(0.4 \ T)$</th>
<th>$R(28 \ T)$</th>
<th>$R(30 \ T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMPA TFSA</td>
<td>95</td>
<td>1.02</td>
<td>1.02</td>
<td>—</td>
<td>0.85</td>
</tr>
<tr>
<td>TMOA TFSA</td>
<td>219</td>
<td>1.02</td>
<td>1.06</td>
<td>—</td>
<td>0.91</td>
</tr>
<tr>
<td>DTMA TFSA</td>
<td>320</td>
<td>1.03</td>
<td>1.08</td>
<td>0.96</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ Obtained from the kinetic viscosities and densities at 293 K.

Nanosecond laser flash photolysis

Laser flash photolysis experiments were carried out using an apparatus that was essentially the same as the apparatus described elsewhere.$^{26,29}$ The third harmonic (355 nm) of a Nd:YAG laser (Quanta-Ray INDI) with a pulse width of 7 ns was used as an exciting light source. The probe light from a Xe short arc lamp (Perkin Elmer Optoelectronics Lx-300 or Ushio UXL-500D) with a custom-built pulse current generator was divided into two beams, creating a double-beam probe system. One beam was guided to a quartz sample cell by a quartz optical fiber (3M FT1.0-UMT) and passed through the cell. The other was detected directly. Both beams were guided by optical fibers to photomultipliers (Hamamatsu R636-10) through a monochromator (Oriel MS257 and Shimadzu SPG-120S, respectively). This double-beam probe system was constructed to accurately observe transient absorption by maintaining a flat baseline signal. In the present study, the baseline contained somewhat large noise contributions, which were generated from Q-switching of the laser and the pulsed trigger of the Xe lamp. Signal voltage from the photomultiplier was terminated by a 50 $\Omega$ resistor and was recorded by a digitizing oscilloscope (LeCroy Wave Pro 960, 2 GHz). A personal computer was used to control the apparatus and record data. Magnetic fields of up to 1.6 T were provided by an electromagnet (Tokin SEE-10W). The pulsed magnet having a room-temperature bore with a diameter of 20 mm and a length of 160 mm was used to provide the magnetic field up to 30 T. Pulsed magnetic fields were generated by supplying intense pulsed currents from a 10 mF capacitor bank of 125 kJ at 5 kV. The maximum field was 32.2 T at 3.5 kV. Applied magnetic field was measured with a gauss meter (Lake-Shore model 421, for the electromagnet) and a search coil (for the pulsed magnet) placed right next to the quartz cell. Argon-bubbled solutions in the quartz cell were placed at the center of the electromagnet or pulsed magnet. Laser flash photolysis measurements were carried out at 293 K.

3. Results and discussions

Reaction scheme

The following reactions are believed to occur by the photo-excitation of BP in the presence of PhOH.$^{30-34}$

$$
\begin{align*}
\text{BP} + h\nu (355 \text{ nm}) \rightarrow & \text{1} \text{BP*} \rightarrow \text{3} \text{BP*} & \quad (1) \\
\text{3BP*} + \text{PhOH} \rightarrow & \text{3(1)BP* } \text{•} \text{OPh} & \quad (2) \\
\text{3(1)BP* } \text{•} \text{OPh} \xrightarrow{B} & \text{1(1)BP* } \text{•} \text{OPh} & \quad (3) \\
\text{1(1)BP* } \text{•} \text{OPh} \xrightarrow{\text{k}_{\text{rec}}} & \text{recombination products} & \quad (4) \\
\text{1,3(1)BP* } \text{•} \text{OPh} \xrightarrow{\text{k}_{\text{esc}}} & \text{escaped radicals} & \quad (5)
\end{align*}
$$
Here, $^1\text{BP}^*$ and $^3\text{BP}^*$ represent the singlet and triplet excited states of BP, respectively. BPH* and $^0\text{OPh}$ represent the benzophenone ketyl and phenoxyl radicals, respectively. $^1$(BPH* $^0\text{OPh}$) and $^3$(BPH* $^0\text{OPh}$) denote singlet and triplet RPs, respectively, that are composed of BPH* and $^0\text{OPh}$. Upon laser excitation of BP, $^3\text{BP}^*$ is immediately generated via the fast intersystem crossing of $^1\text{BP}^*$ (eqn (1)). The triplet RP of BPH* and $^0\text{OPh}$ is formed by a hydrogen abstraction reaction of $^3\text{BP}^*$ with PhOH (eqn (2)). The spin conversion and relaxation processes between triplet and singlet RPs can be affected by the magnetic field ($B$) (eqn (3)). The singlet close-neighboring RPs recombine to form the recombination products with a rate constant $k_{\text{rec}}$ (eqn (4)), whereas radicals escape from the singlet and triplet RPs with a rate constant $k_{\text{esc}}$ (eqn (5)).

### Measurements of transient absorption

The laser flash photolysis of BP ($2.0 \times 10^{-2}$ mol dm$^{-3}$) with PhOH ($1.1 \times 10^{-1}$ mol dm$^{-3}$) in the ILs was performed at 293 K. Time profiles of the transient absorption ($A(t)$) were measured in the wavelength range of 310–700 nm. Transient absorption spectra observed in TMPA TFSA at delay times of 0.01, 0.10, 0.20, and 1.00 µs after laser excitation are shown in Fig. 1. A transient absorption peak due to the triplet–triplet (T–T) absorption of $^3\text{BP}^*$ was observed at 520 nm. This peak decayed quickly, with a decay rate constant of T–T absorption ($k_{T-T}$) of $6.17 \times 10^6$ s$^{-1}$ ($\tau_{T-T} = 162$ ns), and the decay was accelerated with increasing PhOH concentration. Following the disappearance of the T–T absorption, the transient absorption attributed to BPH* was observed at 545 nm, and absorption characteristic of $^0\text{OPh}$ was also observed at 400 nm. Similar results were also observed in TMOA TFSA and DTMA TFSA.

Fig. 2 shows the PhOH concentration dependence of the decay rate constant ($k$) observed for $^3\text{BP}^*$ at 520 nm in TMPA TFSA. A good linear relationship was observed between $k$ and PhOH concentration. From the slope of this plot, the rate constant for the hydrogen abstraction reaction of $^3\text{BP}^*$ with PhOH was determined to be $5.8 \times 10^7$ s$^{-1}$ mol$^{-1}$ dm$^3$, which is almost the same as that observed in acetonitrile ($7.0 \times 10^7$ s$^{-1}$ mol$^{-1}$ dm$^3$) although the viscosities are quite different: 95 cP for TMPA TFSA and 0.34 cP for acetonitrile. This result indicates that the present hydrogen abstraction is not the diffusion-controlled reaction.

### Magnetic field effects on the reaction of $^3\text{BP}^*$ and PhOH

The MFEs on the yield of escaped BPH* were measured in each IL at magnetic fields of 0–30 T. Typically, Fig. 3–5 show time profiles of the transient absorption, $A(t)$, observed at 545 nm in the absence and presence of magnetic fields of 0, 28, and 30 T in TMPA TFSA ($\eta = 95$ cP), TMOA TFSA ($\eta = 219$ cP), and DTMA TFSA ($\eta = 320$ cP) at 293 K. Each $A(t)$ curve has a decay component ($0 < t < 0.6$ µs) and an almost constant component (0.6 µs $\leq t$). The decay component is ascribable to the decay of RPs, and the constant component is ascribable to the escaped BPH*. As shown in Fig. 3–5, the observed $A(t)$ curves were clearly affected by the magnetic fields, but the B- and $\eta$-dependencies on the MFEs were somewhat complicated. The MFEs observed are summarized as follows: (1) At the low magnetic field of 0.4 T, the RP lifetime ($\tau_{\text{RP}}$) and the yield of the escaped radical ($Y$) increased and the magnitude of the MFE increased with increasing $\eta$. (2) At the high magnetic fields of 28 and 30 T, $\tau_{\text{RP}}$ and $Y$ decreased and the magnitude of the MFE decreased with increasing $\eta$. (3) The MFEs were generated in the time range of several hundreds of ns after laser excitation of BP. (4) After the delay time of 0.6 µs, the magnitude of the MFEs remained nearly constant as the escaped BPH*.

Since the reversion of MFEs; increase in $Y$ at low fields but decrease at high fields was observed, the $B$-dependence of $Y$ is obtained as the relative yield, $R(B) = Y(B)/Y(0\text{T}) = A(1.0 \mu s, B \text{T})/A(1.0 \mu s, 0 \text{T})$. The $A(1.0 \mu s)$ value is proportional to the escaped radical yield for a given magnetic field ($Y(B)$). Fig. 6 shows $R(B)$ observed at magnetic fields of up to 30 T in TMPA TFSA, TMOA TFSA, and DTMA TFSA. In each IL, the $R(B)$ value rapidly increased with increasing $B$ in the range of 0 T $\leq B \leq 0.01$ T. At 0.01 T $< B \leq 0.4$ T, $R(B)$ almost
Fig. 3  $A(t)$ curves observed in TMPA TFSA at 545 nm in the absence and presence of magnetic fields of (a) 0.4 T and (b) 30 T.

Fig. 4  $A(t)$ curves observed in TMOA TFSA at 545 nm in the absence and presence of magnetic fields of (a) 0.4 T and (b) 30 T.

Fig. 5  $A(t)$ curves observed in DTMA TFSA at 545 nm in the absence and presence of magnetic fields of (a) 0.4 T and (b) 28 T.
saturated in TMPA TFSA or gradually increased in TMOA TFSA and DTMA TFSA. At much higher fields of 0.4 T < B ≤ 30 T, R(B) gradually deceased in all ILs. The R(B) values observed at 0.01, 0.4, 28, and 30 T are listed in Table 1.

Mechanism of magnetic field effects

The observed MFEs can be classified by several mechanisms as follows:22–24 (1) the hyperfine coupling mechanism (HFCM), which is due to the isotropic hyperfine interaction between electron and nuclear spins; (2) the Δg mechanism (ΔgM), which is due to the difference between the isotropic g factors of two radicals in a RP; (3) the relaxation mechanism (RM), which is due to the anisotropic g tensor (Δg), HFC (ΔHFC), and the spin–spin dipolar interactions of RPs. The rapid increase in R(B) observed at 0 T < B ≤ 0.01 T as shown in Fig. 6a is ascribable to the HFCM. The MFEs due to the HFCM are caused by the blocking of S–T spin conversion. Since the present hydrogen abstraction reaction of BP and PhOH occurs through the triplet excited state forming the triplet RPs, the blocking of S–T spin conversion causes the increase in escaped radical yield. The rate constant of S–T spin conversion by the HFCM (kHFCM) is given by22–24

\[ k_{\text{HFCM}} = (1/2)g\mu_B B_{1/2}/h \]  

(6)

Here, g and μB are the g-values of the free electron (2.00231) and the Bohr magneton, respectively. B_{1/2} is the effective hyperfine coupling (Weller’s half-field of the saturation) in the RP, which can be expressed by40

\[ B_{1/2} = 2(B_1^2 + B_2^2)/(B_1 + B_2) \]  

(7)

\[ B_i = \left\{ \sum k a_i k (J_k + 1) \right\}^{1/2} \]  

(8)

Here, a_i is the isotropic HFC constant of the kth nuclei in the radical (i = 1, 2). J_k is the nuclear spin. Using the reported hyperfine coupling constants of BPH^{41} and *OPh^{42} kHFCM in the absence of magnetic field was estimated to be 1.9 × 10^8 s^-1. In the presence of magnetic fields, the triplet sublevel splits into three levels (T_0, T_+1, and T_-1) by means of the Zeeman interaction, and S–T_+1 and S–T_-1 spin conversions are obstructed. Thus the S–T spin conversion rate (k_{S–T}) decreases with increasing B and reaches a value that is one third of that observed in zero field. Thus k_{S–T} (= (1/3)k_{HFCM}) is estimated to be 0.6 × 10^7 s^-1. Since the obstruction of the spin conversions S–T_+1 and S–T_-1 occurs at higher magnetic fields of the HFC, the increase in R(B) is saturated at those fields. The half-field of the saturation (B_{1/2}) for the present RP was calculated by eqn (7) and (8) to be 2.2 mT.40–42 From the observed R(B) value of TMPA TFSA, the rapid increase in R(B) reached its maximum at 4–6 mT, which might be the saturation field for the HFCM. Therefore, B_{1/2} was roughly estimated to be 2–3 mT. This estimated value agrees well with the calculated value of 2.2 mT. These results indicate that the rapid increase in R(B) observed at 0 T < B ≤ 0.01 T can safely be explained by the HFCM.

As shown in Fig. 6b, the gradual decease in R(B) was observed at 0.4 T < B ≤ 30 T in all ILs. According to the ΔgM, the escaped radical yield (Y) from a triplet precursor can be given as follows:43,44

\[ Y = 1 - \frac{1}{3} \Lambda \sqrt{q/2} + \sqrt{q} \]  

(9)

\[ q = \Delta g T B d^2/(2h(D_1 + D_2)) \]  

(10)

Here, Λ is a constant for the degree of diffusion controlled reaction. Δg is the difference of the isotropic g values, and d is the distance of the closest approach estimated as the sum of the averaged radii (d_i) of radicals. D_i is the diffusion constant, and it can be given by the Stokes–Einstein relation:

\[ D_i = kT/6\pi\eta d_i \]  

(11)

Since \sqrt{q} is much smaller than 2, R(B) can approximately be represented as follows:

\[ R(B) = Y(B)/Y(0 T) = 1 - 1/6\Lambda \sqrt{\Delta g T B d^2/2h(D_1 + D_2)} \]  

(12)

It is therefore well known that the MFE due to the ΔgM shows a good linear relationship between R(B) and B^{1/2}.22,24,29,43,44

Fig. 6 Magnetic field dependence of R(B) observed at 545 nm for escaped BPH^* in TMPA TFSA (η = 95 cP), TMOA TFSA (η = 219 cP), and DTMA TFSA (η = 320 cP) at the magnetic field range of (a) 0 T ≤ B ≤ 1.7 T and (b) 0 T ≤ B ≤ 30 T at 293 K. Inset: plots of R(B) against B^{1/2} at 0 T ≤ B ≤ 30 T.
In Fig. 6b (inset), the $R(B)$ values are plotted against $B^{1/2}$. The plots have good linear relationships at high fields. Thus the MFEs observed at $0.4 \, \text{T} < B \leq 30 \, \text{T}$ can qualitatively be explained by the $\Delta gM$. The rate constant of S–T spin conversion by the $\Delta gM$ ($k_{\Delta gM}$) is given by:

$$ k_{\Delta gM} = (1/2)\Delta gMB/h $$

Here, $\Delta g$ is the difference between the g-values of two radicals. The $k_{\Delta gM}$ value at 0 T is zero, but this value increases proportionally with increasing $B$. Since $\Delta g$ was estimated to be 0.0020 from the reported g-values of BPH$^*$ (2.0030) and *OPh (2.0050), $k_{\Delta gM}$ at 30 T was calculated to be $2.6 \times 10^8 \, \text{s}^{-1}$. From these calculations, we can estimate the overall S–T spin conversion ($k_{S-T}$) at $0.4 \, \text{T} < B \leq 30 \, \text{T}$ as follows:

$$ k_{S-T} = (1/3)k_{\Delta gM} + (1/3)k_{\text{HFCM}} $$

Thus $k_{S-T}$ dramatically decreases from $1.9 \times 10^8$ to $0.6 \times 10^8 \, \text{s}^{-1}$ at 0 T to 0.4 T by the HFCM and then increases with increasing $B$ to reach $9.3 \times 10^8 \, \text{s}^{-1}$ at 30 T by the $\Delta gM$. These calculations indicate that the escaped radical yield increases at low fields but decreases at high fields. The present MFEs can be interpreted by the HFCM and the $\Delta gM$ except at $0.01 \, \text{T} < B \leq 0.4 \, \text{T}$.

Next, differences observed in $R(B)$ in TMPA TFSA, TMOA TFSA, and DTMA TFSA are considered in detail. The significant differences are summarized as follows: (1) as shown in Fig. 6b (inset), the magnitude of the MFEs observed at high field decrease with increasing macroviscosity of ILs, although the slope of the plots showed no significant change; (2) as shown in Fig. 6a, $R(B)$ almost saturated in TMPA TFSA but gradually increased in TMOA TFSA and DTMA TFSA at $0.01 \, \text{T} < B \leq 0.4 \, \text{T}$. These differences may be explained by the increase in macroviscosity of the ILs from 95 cP (TMPA TFSA) to 320 cP (DTMA TFSA) causing the strong cage effect. As reported previously, ILs have a nanoscale heterogeneous structure. In the case of TMPA TFSA, a cage radius is estimated to be $\sim 2 \, \text{nm}$, and the cage effect is not so large.

However, every slope of the plots in Fig. 6b (inset), where the $B$-dependence of MFEs is ascribable to the $\Delta gM$, is almost the same. As indicated by eqn (11) and (12), if the macroviscosity becomes higher, the slope should be larger giving the larger MFEs. Thus the smaller MFEs observed at high field in TMOA TFSA and DTMA TFSA are explained by the higher macroviscosity, suggesting that the macroviscosities of TMOA TFSA and DTMA TFSA are almost the same as of TMPA TFSA (2–4 cP), while it can be explained by the increase of the cage effect. In strong cages such as micellar solutions, it is well known that the MFEs due to the RM are usually not observed at the same time, because of their different spin conversion rates of $10^6$ and $10^8 \, \text{s}^{-1}$, respectively. Thus, TMOA TFSA and DTMA TFSA may have at least two domains with weak (for the $\Delta gM$) and strong (for the RM) cage effects. For more quantitative analysis of the mechanism, theoretical calculations using the stochastic Liouville equation (SLE) are necessary, but these are beyond the scope of the present study.

### Cage lifetimes of ionic liquids

In the present study, since appreciable MFEs were observed in TMPA TFSA, TMOA TFSA and DTMA TFSA, the RP lifetime ($\tau_{RP}$) is certainly longer than or comparable to the S–T spin conversion time ($\tau_{S-T}$) and spin relaxation ($\tau_{rel}$) time: $\tau_{RP} \geq \tau_{S-T}$, $\tau_{rel}$. In all ILs, similar slopes of the MFEs due to the $\Delta gM$ were observed as shown in Fig. 6b (inset). This result indicates that TMOA TFSA and DTMA TFSA have a low microviscosity cage such as TMPA TFSA. As mentioned in the Introduction, in a low microviscosity cage, the cage lifetime ($\tau_{cage}$) should be longer than or comparable to the RM lifetime: $\tau_{cage} \geq \tau_{RP}$. Thus the cage lifetime of TMPA TFSA, TMOA TFSA and DTMA TFSA can be estimated from the S–T spin conversion and spin relaxation times.

In the case of TMPA TFSA, MFEs due to the HFCM and $\Delta gM$ were observed. The $k_{S-T}$ value dramatically decreased from $1.9 \times 10^8$ to $0.6 \times 10^8 \, \text{s}^{-1}$ at 0 T to 0.4 T by the HFCM and then increased with increasing $B$ to reach $9.3 \times 10^8 \, \text{s}^{-1}$ at 30 T by the $\Delta gM$. Thus the RP lifetime of TMPA TFSA is roughly estimated from the smallest $k_{S-T}$ value at 0.4 T to be $17 \, \text{ns} \,(= 1/k_{S-T})$. It is concluded that the cage lifetime of TMPA TFSA is at least $17 \, \text{ns} \, (\tau_{cage} \geq \tau_{RP} \geq \tau_{S-T})$. The RP lifetimes of TMOA TFSA and DTMA TFSA are expected to be much longer than $17 \, \text{ns}$, because MFEs due to the RM associated with $\tau_{rel}$ were observed. If the RP lifetime is as long as $\tau_{rel}$ which is usually several tens of ns to sub-μs, a generation of MFE should be observed. To investigate the generation of MFE, $\Delta A(t)$ $(= A(B, t) - A(0, t))$ curves were obtained using $A(t)$ curves observed at 0.4 T, because MFEs due to the RM were observed at 0.4 T. The obtained $\Delta A(t)$ curves are plotted in Fig. 7.

The MFEs observed in TMOA TFSA and DTMA TFSA are generated in the time range of $0 < t < 0.6 \, \text{μs}$. The rise times were roughly estimated to be $200–300 \, \text{ns}$. These values are two times longer than the lifetime of the T–T absorption $(= \text{generating time of the RPs})$. If the cage is ineffective, the generation of the MFEs should be simultaneous with the generation of the RPs. Thus the present results indicate that the TMOA TFSA and DTMA TFSA have measurable cage lifetime. The RPs are formed with the rate constant of $k_{T-T}(= 1/\tau_{T-T})$, following generation of the MFEs with the lifetime of $\tau_{RP}(= 1/k_{RP})$. Since $k_{T-T}$ is not so larger than $k_{RP}$, the generation of the MFEs is convoluted with $\tau_{T-T}$ and $\tau_{RP}$.
calculated with the parameters of (a) simulated curves obtained from eqn (15). Black and yellow lines are TFSA at 0.4 T, and (b) DTMA TFSA at 0.4 T. Red lines show step reaction as follows:

Here \( a \) are nonlinear least squares method with eqn (15). The fitting parameters are \( a_0 \) and \( k_{\text{RP}} \). The simulated curves (red lines) are depicted in Fig. 7 together with the calculated curves with \( \tau_{\text{RP}} = 0 \text{ ns (black lines) and 250 ns (yellow lines).} \) The \( k_{\text{T-T}} \) and \( \tau_{\text{RP}} \) values are listed in Table 2. Although the observed \( \Delta A(t) \) curves are very noisy, the \( \tau_{\text{RP}} \) values of TMOA TFSA and DTMA TFSA were obtained to be 121 and 124 ns, respectively. Since the microviscosity of the ILs is considered to be 2–4 cP as mentioned in the previous section, it is concluded that the obtained \( \tau_{\text{RP}} \) values indicate the cage lifetimes of the ILs (\( \tau_{\text{cage}} \geq \tau_{\text{RP}} \geq \tau_{\text{rel}} \)).

Therefore, \( \Delta A(t) \) is represented by the rate equation for the step reaction as follows:

\[
\Delta A(t) = a_0 \left( 1 + \frac{k_{\text{T-T}} e^{-k_{\text{T-T}} t} - k_{\text{RP}} e^{-k_{\text{RP}} t}}{k_{\text{RP}} - k_{\text{T-T}}} \right)
\]  

(15)

Here \( a_0 \) represents a factor of magnitude of the MFE. The \( k_{\text{T-T}} \) values were experimentally obtained from the decay of \( ^3\text{BP}^* \) observed at 610 nm to avoid contribution of BPH*. The \( \Delta A(t) \) curves were simulated by the Levenberg-Marquardt nonlinear least squares method with eqn (15). The fitting parameters are \( a_0 \) and \( k_{\text{RP}} \). The simulated curves (red lines) are depicted in Fig. 7 together with the calculated curves with \( \tau_{\text{RP}} = 0 \text{ ns (black lines) and 250 ns (yellow lines).} \) The \( k_{\text{T-T}} \) and \( \tau_{\text{RP}} \) values are listed in Table 2. Although the observed \( \Delta A(t) \) curves are very noisy, the \( \tau_{\text{RP}} \) values of TMOA TFSA and DTMA TFSA were obtained to be 121 and 124 ns, respectively. Since the microviscosity of the ILs is considered to be 2–4 cP as mentioned in the previous section, it is concluded that the obtained \( \tau_{\text{RP}} \) values indicate the cage lifetimes of the ILs (\( \tau_{\text{cage}} \geq \tau_{\text{RP}} \geq \tau_{\text{rel}} \)).

Table 2  Rate constant of \( ^3\text{BP}^* \) decay (\( k_{\text{T-T}} \)) and RP lifetime (\( \tau_{\text{RP}} \)) in TMOA TFSA, TMOA TFSA, and DTMA TFSA

<table>
<thead>
<tr>
<th>Ionic liquids</th>
<th>( k_{\text{T-T}} \times 10^6 \text{ (s)} )</th>
<th>( \tau_{\text{RP}} \text{ (ns)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMOA TFSA</td>
<td>( 6.17 \times 10^6 ) (162)</td>
<td>( \geq 177 )</td>
</tr>
<tr>
<td>TMOA TFSA</td>
<td>( 6.37 \times 10^6 ) (157)</td>
<td>121</td>
</tr>
<tr>
<td>DTMA TFSA</td>
<td>( 6.77 \times 10^6 ) (148)</td>
<td>124</td>
</tr>
</tbody>
</table>

* Experimentally obtained from the decay of \(^3\text{BP}^*\) observed at 610 nm to avoid contribution of BPH*. Calculated from the singlet–triplet spin conversion rate at 0.4 T due to the HFCM and \( \Delta g \).

The \( \tau_{\text{cage}} \) values observed for TMOA TFSA and DTMA TFSA are much larger than that estimated in TMA TFSA from the singlet–triplet spin conversion rate due to the HFCM and \( \Delta g \). Such lengthening of the cage lifetime may be explained by the increase of cage effects with increasing macroviscosity. Very recently, we reported the cage effects of ILs by the SLE analysis with the solvent separated radical pair (SSRP) model.47 In ILs with short alkyl chains: 1-ethyl-3-methyl-imidazolium tetrafluoroborate (Emim BF\(_4\), \( \eta = 45 \text{ cP})\), N-methyl-N-propyl-pyrrolidinium bis(trifluoromethanesulfonyl)amide (P13 TFSA, \( \eta = 56 \text{ cP})\), TMOA TFSA (\( \eta = 73 \text{ cP})\), and N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)amide (PP13 TFSA, \( \eta = 137 \text{ cP})\), MFEs on the photoinduced hydrogen abstract reactions of BP and PhSH were studied. The SLE analysis suggested that the viscosity effective for the SSRP increased with increasing macroviscosity, but the viscosity for the other RPs (\( \eta_{\text{SSRP}} \)) did not show any change. Here, \( \eta_{\text{SSRP}} \) indicates the viscosity in the cage and \( \eta_{\text{SSRP}} \) for the boundary of the cage. Thus the ratio \( \eta_{\text{SSRP}}/\eta_{\text{RP}} \) implies the magnitude of the cage effect.48 In the report, the cage effects were found to increase with increasing macroviscosity from Emim BF\(_4\) to PP13 TFSA.47

The extensive studies on the nanoscale ordering structures of ILs have been reported8–15 however, the cage lifetime has not been reported until now. To the best of our knowledge, this is the first report on the cage lifetime of ILs. The observed cage lifetime of \( \geq 120 \text{ ns for TMOA TFSA and DTMA TFSA is rationalized by the spin relaxation time caused by the anisotropic HFCM.22–24} \) Although the microviscosities of TMOA TFSA and DTMA TFSA are fairly different, the observed RP lifetimes are almost the same. This result indicates that the obtained RP lifetime is limited by the spin relaxation time (\( \tau_{\text{rel}} \)) and microviscosities of TMOA TFSA and DTMA TFSA should be similar. The difference of magnitude of the MFEs due to the RM between TMOA TFSA and DTMA TFSA may be explained by the increase of the cage effects. If the spin relaxation time is the same, the strong cage effect enhances the MFEs because of the decrease of the escaped radicals.

**Conclusion**

MFEs on the photoinduced hydrogen abstract reactions of benzophenone with phenol in the ILs having the long alkyl chains were investigated by the nanosecond laser flash photolysis. The MFEs observed showed anomalous \( \eta \)-dependence: (1) at low magnetic fields, the escaped radical yield (\( Y \)) increased and the magnitude of the MFE increased with increasing \( \eta \). (2) At high magnetic fields, \( Y \) decreased and the magnitude of the MFE
decreased with increasing $\eta$. The observed MFEs can be explained by the hyperfine coupling and $\Delta g$ mechanisms together with the relaxation mechanism. The MFEs were generated in the time range of several hundreds of ns after laser excitation. Upon analyzing the generation profiles of the MFEs, the cage lifetimes of ILs were observed for the first time. The observed cage lifetime of $\geq 120$ ns for TMOA TFSA and DTMA TFSA is rationalized by the spin relaxation time caused by the anisotropic HFC ($\Delta g_{\text{HFC}}$). Such long cage lifetime can be explained by the increase of the cage effects with increasing macroviscosity.

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**References**