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Reactions of Excited-State Benzophenone Ketyl Radical in a Room-Temperature Ionic Liquid

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Abstract

The photochemistry of benzophenone ketyl radical in the D_1 excited state, BPH(D_1), was studied by means of two-color dual-pulse laser flash photolysis (355 and 532 nm) in a room-temperature ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (Bmim-TFSA), and in methanol. Upon excitation with the 532-nm pulse, BPH(D_1) emitted strong fluorescence. The transient absorption and fluorescence spectra of BPH(D_1) were measured with nanosecond and sub-nanosecond time resolution, respectively. The observed Stokes shift was 1700 cm^{-1} in Bmim-TFSA, and this shift was close to that in acetonitrile. The fluorescence lifetime of BPH(D_1) was determined to be 5 ns in Bmim-TFSA, and again the value was close to that in acetonitrile. The rate constant of the reaction of BPH(D_1) with CCl_4 in Bmim-TFSA was determined to be $(2.1 \pm 0.4) \times 10^9\text{ M}^{-1}\text{ s}^{-1}$, which was 10 times the rate constant calculated on the basis of the bulk viscosity of Bmim-TFSA. The results are discussed in terms of the effective microscopic viscosity of the ionic liquid that was recently reported for the cage effect.

Introduction

Ionic liquids (ILs) are receiving much attention as potential green solvents for various chemical processes. Potential applications include their use as electrolytes for electrochemical reactions and as green reaction media for organic reactions including photochemical reactions and photoinduced electron-transfer reactions.¹⁻¹⁶ Because the photochemistry of benzophenone (BP) has been widely investigated in various organic solvents,¹⁷ comparing the dynamics of photoinduced reactions of triplet-state BP (BP(T₁)) and benzophenone ketyl radical (BPH) in ILs with the reaction dynamics in conventional organic solvents can provide information about the solvent characteristics of ILs. For example, Muldoon *et al.* found that the activation energy for hydrogen abstraction from imidazolium-based ILs (22 to 25 kJ/mol) by BP(T₁) is substantially higher than the energies observed in conventional solvents (13.7 kJ/mol in cyclohexane and 14.5 kJ/mol in toluene).¹⁸ The activation energy is independent of the anionic component (PF₆ or (CF₃SO₂)N) and the availability of the hydrogen atom at the 2-position of the imidazolium ring.

Recently Wakasa studied the effects of a magnetic field on photoinduced hydrogen-abstraction reactions of BP(T₁) with thiophenol in ILs.¹⁹ The yield of the ketyl radical decreased even when the intensity of the magnetic field was low. The high viscosity of ILs cannot be the reason for this large magnetic field effect, and Wakasa speculated that a cage effect may be important because a confined system is necessary for spin conversion. This speculation is consistent with the recent findings on local structure and domains in ILs, which are unique characteristics of ILs as condensed media. The importance of local structures has been discussed recently. For example, Hamaguchi's group used Raman spectral analysis to show for the first time that two distinct conformational structures of the imidazolium cation exist simultaneously in the IL state.^{20, 21} These investigators also obtained evidence of mesoscopic local structure in ILs by means of coherent anti-Stokes Raman scattering measurements.²² Iwata *et al.* investigated the importance of local structures in reaction dynamics by measuring the vibrational cooling rates of the excited state of *trans*-stilbene in ILs by picosecond time-resolved Raman spectroscopy.^{23,24} The local structure is manifested by the existence of structurally distinct domains of polarity and nonpolarity occupied by the charged (constituent ions) and uncharged parts (side chains) of ILs, respectively. The volumes and interconnectivity of these heterogeneous domains depend on the lengths of the aliphatic side

chains.²⁵⁻²⁷ The distribution of various solutes between the domains depends on the solute characteristics. Consequently, attempts to characterize the polarity of ILs using solvatochromic probes give disparate answers depending on the probe molecule used.²⁸

Many fast bimolecular reactions have been studied in ILs.²⁹⁻³⁷ In general, hydrodynamic approximation of the diffusion coefficient on the basis of the Stokes–Einstein equation is not applicable to diffusion-limited reactions in ILs. Several research groups have suggested that the faster translational diffusion in ILs is due to a large void volume produced by cations and anions.^{18, 34} Recently, Kimura’s group^{38, 39} measured diffusion coefficients of transient radicals in ILs using a transient grating method and found that the diffusion coefficient of BP in ILs is larger than that predicted by the Stokes–Einstein equation. These investigators measured the diffusion coefficients of BPH and BP in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (Bmim-TFSA) to be $(1.30 \pm 0.03) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $(3.40 \pm 0.09) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, respectively; that is, the diffusion coefficient of the ketyl radical (BPH) is about 1/3 that of the parent molecule (BP). Kimura et al. also found that the ratios of the diffusion coefficient of BP to that of BPH were larger in ILs (2.7–4.0) than in conventional organic solvents (1.4–2.3). The slow diffusion of BPH in ILs was discussed in terms of the fluctuation of the local electric field produced by the surrounding solvent ions.

In the present study, we conducted the first investigation of the reactions of excited-state BPH in Bmim-TFSA using two-color dual-pulse laser flash photolysis. Because the absorption maximum of BPH is located around 540 nm, measuring the reaction kinetics of excited-state BPH using a combination of third- and second-harmonic pulses of a Nd-YAG laser is not difficult. In organic solvents, many studies of the D_1 excited state of benzophenone ketyl radical, BPH(D_1), have been carried out by means of absorption and emission spectroscopies.⁴⁰⁻⁴⁴ The dipole moment of BPH(D_1) is estimated to be 7 D,⁴³ which indicates that BPH(D_1) is highly polarized. BPH(D_1) reportedly decays by radiative and nonradiative relaxations and by unimolecular and bimolecular chemical reaction processes.⁴¹⁻⁴⁴ Cleavage of the O-H bond of BPH(D_1), photo-ionization and formation of solvated electrons, and electron transfer from BPH(D_1) to BP have also been reported. These characteristics of BPH(D_1) are interesting enough to warrant studying them in the ionic milieu of ILs.

Experiments

N,N,N-trimethyl-*N*-propylammonium bis(trifluoromethylsulfonyl)amide (TMPA-TFSA) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (Bmim-TFSA) were purchased from Kanto Chemical Co. (stated purity > 98%), along with benzophenone (>98.5%), methanol (for fluorescence measurement, >99.7%), and CCl₄ (for fluorescence measurement, >99.75%). IL samples were prepared in 20-mL sample bottles and dried under vacuum at 60 °C, and then BP-containing IL samples with an initial BP concentration of ~15 mM were prepared. For kinetics measurements, aliquots of dried BP-containing IL samples were placed in screw-capped, 1-cm quartz cuvettes and dried again under vacuum at 60 °C prior to measurement. The final BP concentrations (10–11 mM) were determined with a UV absorption spectrophotometer (JASCO, V-570). Care was taken to dry the IL because water may accelerate the diffusion of ions. Water content was measured by means of Karl Fischer titration (Mettler Toledo, DL31). The concentrations of water were less than 40 ppm. The viscosity of the IL was measured with a viscometer (Brookfield, DV-II+Pro, CP-40).

Figure 1 shows experimental set-up for two-color dual-pulse laser flash photolysis with transient absorption measurements with nanosecond time resolution. The nanosecond transient absorption was measured with a double-pulse Nd-YAG laser (LOTIS TH, LS-2144DC) in which two independent Nd-YAG rods and Pockels cells were installed. The two Nd-YAG rods were excited by a single flash lamp. By changing the Q-switch trigger timing, the time delay between the laser pulses (channels 1 and 2) was controlled with 1-ns time resolution. A fundamental frequency pulse (1064 nm) from channel 1 was converted into a third-harmonic-frequency pulse (355 nm) through KTP and KDP crystals. The laser pulse from channel 2 was converted to a second-harmonic-frequency pulse (532 nm) through the KTP crystal. The typical output energies were about 25 and 50 mJ for the 355- and 532-nm pulses, respectively. The repetition rate of the Q-switch trigger of the laser was set to 0.5 Hz so that the sample was well mixed in the cuvette by a magnetic stirrer. Both laser pulses were merged at the front of the sample cell holder by means of dichroic mirrors. A 150-W xenon arc lamp was used as an analyzing light source, and the excitation laser pulses were perpendicular to the analyzing light. The excitation pulses irradiated the sample in the cuvette through a 6-mm circular mask, and the analyzing light passed through 3-mm circular masks. To measure kinetic traces, we used band-pass filters (OPTO-LINE, band width 10 nm) to select the analyzing wavelength. The kinetics data were normally measured at 500 nm because at this wavelength, the scattered light from the 532-nm laser was negligible. Transient signals were collected with a

fast silicon photodiode (Thorlabs, PDA10A, 150 MHz) and recorded on a 500-MHz oscilloscope (Tektronix, DPO 7054). Because ILs undergo photodegradation by UV irradiation⁴⁵, the sample and cuvette were renewed every 50 laser shots. We examined the effect of laser irradiation and photodegradation on the transient signal and found that there was no change in the transient signal even after about 100 shots. One transient absorption trace was obtained by averaging 5–6 signals.

For spectral measurements, a system consisting of a 300-mm monochromator (ACTON, SpectraPro 2358i) and a gated intensified charge-coupled device camera (Princeton Instruments, PI-MAX-II, UNIGENII) was used. The wavelength response of the detector was corrected by comparing the fluorescence spectrum of Coumarin 153 with a reported reference spectrum.⁴⁶ The analyzing light after the sample cell was collimated to the optical bundle fiber and transferred to the spectrometer. A UV-cutoff filter (420 nm) was placed before the sample.

We also measured the transient fluorescence intensity of BPH with subnanosecond time resolution; we used the third harmonic (355 nm) of an optical parametric oscillator (Spectra Physics, MOPO-SL) excited by a Nd³⁺:YAG laser (Spectra Physics, Pro-230-10) to generate BPH and the second harmonic oscillation (532 nm) of a sub-nanosecond laser (EKSPLA, SL-311, 150 ps) to excite the BPH. The delay time between the two laser pulses was adjusted with a digital delay generator (Stanford Research Systems, DG535). Emission from BPH(D₁) was detected with a Si photodiode (New Focus, 1601) after being dispersed with a monochromator. The observed wavelength was 600 nm. The signal from the detector was introduced into a digital oscilloscope (LeCroy, 6200A). The rise time of the overall system was about 400 ps.

Results and Discussion

Hydrogen abstraction by BP in the triplet excited state, BP(T₁), is known to generate BPH in organic solvents such as cyclohexane, toluene, and alcohols. However, studies of the reaction of BP(T₁) in ILs are limited.^{18, 19, 38} In TMPA-TFSA, the lifetime of BP(T₁) is reported to be 19 μ s, which is substantially longer than the lifetimes in cyclohexane (300 ns), 2-propanol (5 ns), and benzene (3 μ s).¹⁹ In contrast, the lifetime of BP(T₁) in Bmim-TFSA has been reported to be 3 μ s. These results suggest that TMPA-TFSA is unreactive with BP(T₁) and that Bmim-TFSA is substantially more reactive with BP(T₁) than TMPA-TFSA. It has been suggested that BP(T₁)

abstracts a hydrogen atom from the 2-position of the imidazolium ring of Bmim-TFSA.¹⁸

In Fig. 2, transient absorption spectra after the excitation of BP with a 355-nm pulse in (a) TMPA-TFSA and in (b) Bmim-TFSA are shown. Comparison of these two spectra with previously reported spectra in methanol and acetonitrile^{17, 42-44} clearly indicates that the spectra observed in TMPA-TFSA until 10 μ s after the pulse can be attributed to BP(T_1); in contrast, the spectra observed in Bmim-TFSA at 4 μ s after the pulse clearly indicate the formation of BPH. The spectra in Bmim-TFSA are consistent with the spectrum recently measured in Bmim-PF₆ by Nishiyama *et al.*³⁸ Therefore, as previously suggested,^{18,19} hydrogen abstraction is slow in TMPA-TFSA.

Because BPH was produced in Bmim-TFSA, we examined BPH in the D_1 excited state generated with a 532-nm laser pulse in Bmim-TFSA. Upon excitation with the 532-nm pulse, BPH emitted fluorescence from the D_1 state (Fig. 2b). The fluorescence spectrum was measured 20 μ s after the 355-nm pulse with a 3-ns gate width and was fitted by a log-normal function. The peak of the spectrum was 594 nm. Because the absorption maximum was located around 539.5 nm, the Stokes shift, ν_{Stokes} , of BPH in Bmim-TFSA was determined to be 1700 cm^{-1} . The present results are compared with previously reported results in several organic solvents in Table 1; the absorption maximum in the visible region $\lambda_{\text{Abs}}^{\text{max}}$, the fluorescence maximum $\lambda_{\text{Fluo}}^{\text{max}}$, ν_{Stokes} , the energy gap between the fully equilibrated D_1 and D_0 states of BPH $\Delta E(D_1 - D_0)$, and the fluorescence lifetimes τ_f of BPH(D_1) are listed in the table. It has been reported⁴³ that the relationship between the Dimroth $E_T(30)$ parameter⁴⁹ and ν_{Stokes} is linear in organic solvents except for 2-propanol and methanol, as shown in Fig. 3. The line in Fig. 3 shows the correlation between ν_{Stokes} and $E_T(30)$ with the alcohol data excluded. Because ν_{Stokes} of BPH was measured to be 1700 cm^{-1} in Bmim-TFSA, $E_T(30)$ for Bmim-TFSA was determined to be 45.3 kcal/mol from the correlation. This value is close to the value for acetonitrile. In contrast, it has been reported that $E_T(30)$ for Bmim-TFSA is 50–52 kcal/mol.⁵⁰ When we used 52 kcal/mol as $E_T(30)$, ν_{Stokes} of BPH was calculated to be 2084 cm^{-1} , which represents a 384 cm^{-1} difference from the measured value.

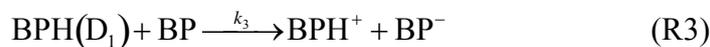
One possible reason for the difference in ν_{Stokes} may be a blue shift of the fluorescence spectra if the solvation dynamics of Bmim-TFSA around the excited BPH(D_1) are slow compared to the excited-state lifetime of BPH(D_1).⁵¹⁻⁵⁸ The dipole moment of BPH(D_0) is estimated to be 1.71 D, whereas the dipole moment of BPH(D_1) is estimated to be 7.0 D.⁴³ The

large dipole moment of BPH(D₁) suggests that BPH(D₁) is highly polarized in the excited state. Therefore a relatively large change in solvation structure may be required after the excitation of BPH(D₀). However, if the solvation dynamics of Bmim-TFSA are not fast enough to form a stable solvation structure during the lifetime of BPH(D₁), a blue shift of the fluorescence spectra of BPH(D₁) may result. The solvation time for Bmim-TFSA obtained by means of a C153 probe is reported to be 0.28 ns at 298 K.^{59, 60} If the fluorescence lifetime of BPH(D₁) in Bmim-TFSA is comparable to or shorter than the solvation time, slow solvent relaxation may explain the difference between the measured and estimated ν_{Stokes} values. To evaluate this possibility, we measured the fluorescence lifetime of BPH(D₁) using the two-laser synchronized system. BPH(D₀) was formed by irradiation of BP with a nanosecond laser pulse (355 nm), and then a picosecond laser pulse (532 nm) was used to excite the BPH(D₀). The fluorescence signal from BPH(D₁) in Bmim-TFSA is shown in Fig. 4. The lifetime in Bmim-TFSA was found to be 5.0 ± 0.04 ns, which is the same as the lifetime in acetonitrile (Table 1, entries 6 and 7). These results indicate that the fluorescence lifetime of BPH(D₁) in Bmim-TFSA was too long to support the above-mentioned hypothesis.

Another possible reason for the difference in the ν_{Stokes} values may be a specific interaction of Bmim-TFSA, especially the 2-position of the imidazolium ring, with the zwitterionic betaine dye used as the probe molecule for the measurement of $E_{\text{T}}(30)$; the H atom at the 2-position of imidazolium is known to participate in hydrogen bonding.⁶¹ As can be seen in Fig. 3, the ν_{Stokes} values in hydrogen-bonding solvents, such as 2-propanol and methanol, deviated from the relationship observed for other organic solvents. It has been suggested that 1-methyl-3-alkylimidazolium cations can act as weak hydrogen-bond donors because of the weakly acidic C(2)-H hydrogen atom on the heterocyclic ring. Replacement of the C(2)-H atom with an alkyl group results in a substantial decrease in $E_{\text{T}}(30)$.⁶² For example, $E_{\text{T}}(30)$ for 1,2-dimethyl-3-butylimidazolium-TFSA is 48.6 kcal/mol, which is close to the estimated value in the present study. Recently, Kawai *et al.* studied the solvation of BPH in ILs by evaluating the hyperfine coupling constant of the hydroxyl proton by means of time-resolved electron paramagnetic resonance measurements.⁶³ The hyperfine coupling constant of the hydroxyl proton depends on Gutmann's donor number of the anions, whereas the constants of phenyl α -protons are essentially the same for these ILs. Kawai *et al.* speculated that the electron-donating character of the anions is important in the solvation in ILs through the anion-OH group. The relatively long fluorescence lifetime of BPH(D₁) in Bmim-TFSA

suggests that the interaction between BPH(D₁) and Bmim-TFSA was weak. The fluorescence lifetime in methanol, in which hydrogen bonding may be important, was much shorter than that in other, non-hydrogen-bonding solvents. The strong interaction between BPH(D₁) and solvent may have increased nonradiative relaxation, which shortened the fluorescence lifetime. Because the fluorescence lifetime in Bmim-TFSA was the same as that in acetonitrile, the interaction of BPH(D₁) with Bmim-TFSA may have been similar to that with acetonitrile, as previously suggested by non-equilibrium molecular dynamics simulations.⁶⁴

The transient kinetics of the excited state of BPH were examined in methanol and Bmim-TFSA (Fig. 5a, b). The transient signals were monitored at 500 nm, and CCl₄ was added as a reaction partner for the excited state of BPH. BPH(D₀) formed by excitation with a 355-nm pulse was excited with a 532-nm pulse at 1 μs (in methanol) or 20 μs (in Bmim-TFSA) after the 355-nm pulse. When the sample containing CCl₄ was irradiated with the 532-nm laser pulse, the transient absorption signal displayed an instrument-limited decrease, and the decrease of absorption did not recover within the lifetime of BPH(D₀). As the concentration of CCl₄ was increased, the amount of the permanent bleaching increased. Therefore the bleaching can be attributed to the reaction of BPH(D₁) with CCl₄. BPH(D₁) reportedly decays through radiative and nonradiative relaxations and through unimolecular and bimolecular chemical reaction processes.⁴¹⁻⁴⁴ Reported unimolecular chemical reaction processes include O–H bond cleavage and photoionization of BPH(D₁). After the photoionization, a solvated electron may be formed. For the bimolecular reaction of BPH(D₁), an electron transfer reaction from BPH(D₁) to BP has been suggested.⁴⁴ After considering these reaction paths, we propose the following reactions to explain the permanent bleaching that we observed:



where k_1 , k_2 , k_3 , and k_4 are the rate constants for the respective reactions. Though we cannot yet specify the product P obtained from reaction R4, an electron-transfer reaction from BPH(D₁) to CCl₄ is one possibility. Because reaction R1 re-produces BPH(D₀) after the excitation of BPH(D₀), this reaction cannot contribute to the bleaching of BPH(D₀). In contrast, because reactions R2, R3, and R4 do not re-produce BPH(D₀), these reaction result in signal bleaching. Therefore, the following relationship between the observed bleaching and the above reactions

can be established:

$$\frac{(\text{Abs}_0 - \text{Abs}_t)}{F \times \text{Abs}_0} = \frac{k_2[\text{BPH}(\text{D}_1)] + k_3[\text{BPH}(\text{D}_1)][\text{BP}] + k_4[\text{BPH}(\text{D}_1)][\text{CCl}_4]}{k_1[\text{BPH}(\text{D}_1)] + k_2[\text{BPH}(\text{D}_1)] + k_3[\text{BPH}(\text{D}_1)][\text{BP}] + k_4[\text{BPH}(\text{D}_1)][\text{CCl}_4]} \quad (1)$$

where Abs_0 and Abs_t are the absorbances immediately before and after the 532-nm pulse, respectively, and F is a constant that depends on experimental conditions such as laser intensity and quantum efficiency for the formation of $\text{BPH}(\text{D}_1)$ upon 532-nm irradiation of $\text{BPH}(\text{D}_0)$. Though fitting the bleaching amount using k_1 – k_4 and F may be possible, we improved the fitting reliability by determining F by means of the following method. When the concentration of CCl_4 is high enough that $k_4[\text{CCl}_4] \gg (k_2 + k_3[\text{BP}])$, eqn (1) can be written as

$$\frac{\text{Abs}_0}{\text{Abs}_0 - \text{Abs}_t} = \frac{1}{F} + \frac{k_1}{F \times k_4[\text{CCl}_4]} \quad (2)$$

Therefore, at high CCl_4 concentrations, F and k_1/k_4 can be determined from a plot of $\text{Abs}_0/(\text{Abs}_0 - \text{Abs}_t)$ versus $1/[\text{CCl}_4]$. The relationship between these two quantities was linear at high CCl_4 concentrations, and the F values in methanol and Bmim-TFSA were determined to be 0.71 ± 0.06 and 0.72 ± 0.08 , respectively.

Eqn (1) can be rewritten as

$$\frac{\text{Abs}_0}{\text{Abs}_0 - \text{Abs}_t} = \frac{1}{F} \left[\frac{k_1/k_4}{(k_2 + k_3[\text{BP}])/k_4 + [\text{CCl}_4]} + 1 \right] \quad (3)$$

Using the F values determined above, k_1/k_4 and $(k_2 + k_3[\text{BP}])/k_4$ were determined by least-squares fitting of the data (Fig. 6, Table 2); the k_1/k_4 values were determined to be $(7.9 \pm 0.9) \times 10^{-2}$ M in methanol and $(9.4 \pm 1.6) \times 10^{-2}$ M in Bmim-TFSA. Because the k_1 values were estimated to be 4×10^9 and 2×10^8 s⁻¹ from the lifetimes of $\text{BPH}(\text{D}_1)$ in methanol and Bmim-TFSA, respectively, the k_4 values in methanol and Bmim-TFSA were determined to be $(5.1 \pm 0.6) \times 10^{10}$ and $(2.1 \pm 0.4) \times 10^9$ M⁻¹ s⁻¹, respectively. These values suggest that the reaction of $\text{BPH}(\text{D}_1)$ with CCl_4 was diffusion limited. The diffusion-limited rate constant k_{diff} based on the hydrodynamic approximation (the Stokes–Einstein equation) is given by³⁰⁻³⁵

$$k_{\text{diff}} = 8000RT/3\eta \quad (4)$$

where η is viscosity (in Pa s), and R is the gas constant (8.314 J K⁻¹ mol⁻¹). Using the viscosity of Bmim-TFSA, we calculated the reaction rate to be 1.2×10^8 M⁻¹ s⁻¹, which is 1/10 the measured rate constant. A limitation on using the Stokes–Einstein equation for estimating diffusion-limited reaction rates has been discussed previously. For example, McLean *et al.* studied the quenching of the triplet state of BP by naphthalene in imidazolium-based ILs⁹ and

found that the reaction rates were nearly 10 times the rates predicted by eqn (4). This result suggests that the diffusion coefficient we calculated from the bulk viscosity of ILs was not necessarily correct.

An alternative way to estimate the diffusion-limited rate constant is to calculate it with the Smoluchowski equation:³⁹

$$k_{\text{diff}} = 4\pi D_{\text{AB}} r_{\text{AB}} \quad (5)$$

where D_{AB} is a mutual diffusion coefficient for the reactants, and r_{AB} is the reaction distance. The diffusion coefficient of BPH(D₀) in Bmim-TFSA has been determined previously by a transient grating method,^{38,39} but there is no value for BPH(D₁). When we assumed D_{AB} to be twice the diffusion coefficient of BPH(D₀), and the reaction distance to be sum of van der Waals radii of BPH(D₀) (0.4 nm)^{38,39} and CCl₄ (0.17 nm),⁶⁵ the calculated diffusion-limited rate constant was $1.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. This value is still far from the measured rate constant. Therefore our assumption about D_{AB} was not adequate for estimating the reaction rate of BPH(D₁) with CCl₄ in Bmim-TFSA. To estimate the reaction rate using eqn (5), we would have to have the actual diffusion coefficients of BPH(D₁) and CCl₄ in Bmim-TFSA. In general, the translational diffusion of a small molecule in ILs is known to be much faster than predicted by the Stokes–Einstein equation. For example, the diffusion coefficients of CO measured in ILs are 10 to 50 times the values predicted by the viscosity of ILs.³⁸ In addition, the diffusion coefficient of BPH(D₀) is reported to be exceptionally slow³⁸ and is close to the value predicted by the Stokes–Einstein equation. Therefore, as the molecular size of CCl₄ is small, the diffusion coefficient of CCl₄ in Bmim-TFSA can be expected to be much faster than the values predicted by the Stokes–Einstein equation.

Recently Wakasa¹⁹ suggested that a cage effect may be more important than viscosity in explaining the large magnetic field effects (MFE) on abstraction of a hydrogen atom from thiophenol by BP in ILs. If there is local structure in ILs, as there is in micellar solutions, the large MFE can be explained by the cage effect. The presence of local structure or domains in ILs has been previously reported.^{20-27, 66-68} Wakasa et al. recently reported that the sphere cage model well reproduces the observed MFE.⁶⁹ A nanoscale heterogeneous structure with a cage radius of 1.8 nm and an effective viscosity in the cage of 1–2 mPa s has been found. Using an effective viscosity of 2 mPa s, we calculated a diffusion-limited rate constant of $3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ from eqn (4). This value is close to the rate constant measured in the present study. Therefore the reaction rate of BPH(D₁) with CCl₄ in Bmim-TFSA may be explained by considering the

effective microscopic viscosity.

The value of k_4 is 100 times ($k_2 + k_3[\text{BP}]$) in Bmim-TFSA, and ($k_2 + k_3[\text{BP}]$) in Bmim-TFSA is 1/10 that in methanol (Table 2). Therefore the contribution of reaction paths for the dissociation and ionization of BPH(D₁) may be minor compared to the contributions of the reaction of BPH(D₁) with CCl₄ and the relaxation to the ground state in Bmim-TFSA. In contrast, the photo-excitation of BPH in polar solvents is known to lead to the formation of solvated electrons.⁴³⁻⁴⁴ In the present study we found no experimental evidence for the formation of solvated electrons in Bmim-TFSA. Even if an electron had been ejected from BPH, the electron would have immediately been scavenged by the Bmim cation, as we previously reported.^{36, 70} Therefore, the contribution of solvated electrons in the present reaction system was probably negligible. However, the ejection of an electron from the excited BPH into ILs is an interesting possibility. We previously examined photo-excitation of solvated electrons in TMPA-TFSA.⁷¹ After the photo-excitation of the solvated electrons at 532-nm, we observed permanent bleaching of the solvated electrons. The permanent photo-bleaching may have been due to formation of quasi-free electrons, which are highly mobile in the IL. We are planning to study the present reaction system in ILs in which solvated electrons are stable.

Conclusion

Two-color dual-pulse (355- and 532-nm) laser flash photolysis was used to study the D₁ excited state of benzophenone ketyl radical, BPH(D₁). The transient absorption spectra of the ketyl radical and the fluorescence spectrum of BPH(D₁) were measured in Bmim-TFSA. The Stokes shift in Bmim-TFSA was 1700 cm⁻¹, and this value was close to that in acetonitrile despite the fact that the dielectric constant of Bmim-TFSA (11.52) is substantially smaller than that of acetonitrile (36). This result suggests importance of local heterogeneous structure in Bmim-TFSA. Local heterogeneous structure results from structurally distinct domains of polarity and nonpolarity occupied by the charged and uncharged parts of the constituent ions, respectively, and BPH may be localized around the polar domain rather than the nonpolar domain.

The reaction of BPH(D₁) was examined for the first time in IL Bmim-TFSA by means of two-color dual-pulse laser flash photolysis. The fluorescence lifetime of BPH(D₁) in Bmim-TFSA was determined to be 5 ns. After excitation of the ketyl radical with 532-nm light, permanent bleaching due to the reaction with CCl₄ was observed. The rate of the reaction of

BPH(D₁) with CCl₄ was 10 times that expected from the hydrodynamic approximation. In contrast, the measured rate constant in Bmim-TFSA was well reproduced when the effective viscosity in a nanoscale heterogeneous structure was considered. This result confirms the importance of local heterogeneous structure in Bmim-TFSA in chemical reactions.

Through the present work, we felt that a new type of experiment for evaluating the excitation-wavelength dependence of electron-transfer reactions may provide interesting information about ILs. As pointed out by Annapureddy and Margulas,⁵⁴ if the lifetime of an excited state is shorter than the time required for solvent relaxation, the electron-transfer rate may depend on the excitation wavelength. These investigators suggested that ILs provide a tool for manipulating the outcome of chemical reactions simply by tuning the initial excitation wavelength, and that ILs offer an extra degree of control of chemical reactivity. We believe that excited-state BPH may be a good candidate for testing their suggestion, and we are now planning to carry out this experiment at low temperature to make solvation slower than the lifetime of the excited state.

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Table 1. Absorption and fluorescence maxima and Stokes shifts of BPH in several solvents

Solvent	ϵ	$\lambda_{\text{Abs}}^{\text{max}}$ (nm)	$\lambda_{\text{Fluo}}^{\text{max}}$ (nm)	ν_{Stokes} (cm^{-1})	$\Delta E(D_1 - D_0)$ (eV)	τ_f (ns)
1 cyclohexane	2	541 ^a	564.9 ^a	780 ^b	2.20 ^b	2.0 ^a
2 toluene	2.4	540 ^a	571.6 ^a	1020 ^b	2.17 ^b	2.8 ^a
3 MTHF	7.6	548 ^a	590.6 ^a	1320 ^b	2.10 ^b	1.8 ^a
4 2-propanol	20	547 ^a	595.6 ^a	1490 ^b	2.08 ^b	0.49 ^a
5 methanol	33	544 ^a	593.3 ^a	1530 ^b	2.09 ^b	0.26 ^a
6 acetonitrile	36	530 ^a	582.1 ^a	1688 ^b	2.13 ^b	4.7 ^a
7 Bmim-TFSA	11.52 ^c	540	594	1700	2.09	5.0 \pm 0.04 ^d

^a Data from ref. 43, ambient temperature. ^b Calculated from $\lambda_{\text{Abs}}^{\text{max}}$ and $\lambda_{\text{Fluo}}^{\text{max}}$ in this study. ^c Data from refs. 47 and 48. ^d At 296 K.

Table 2. Fitting parameters in eqn (3).

Solvent	k_1/k_4 (M)	$(k_2 + k_3[\text{BP}])/k_4$ (M)	F	η (mPa s)
Methanol	$(7.9 \pm 0.9) \times 10^{-2}$	$(7.4 \pm 0.5) \times 10^{-3}$	0.71 ± 0.06	0.56
Bmim-TFSA	$(9.4 \pm 1.6) \times 10^{-2}$	$(7.1 \pm 4.9) \times 10^{-4}$	0.72 ± 0.08	58

Figure Captions.

Fig. 1. Experimental set-up for two-color dual-pulse laser flash photolysis.

Fig. 2. Transient spectra of BP after 355-nm excitation in (a) TPA-TFSA and (b) Bmim-TFSA. The spectra were taken at 1.7- μ s intervals after the 355-nm pulse. The fluorescence spectrum of BPH(D₁) measured 10 μ s after the 355-nm pulse is also shown in (b).

Fig. 3. Relationship between Stokes shift and $E_T(30)$. The numbers in the figure correspond to the entry numbers in Table 1. The solid line is the fit obtained using data for solvents 1, 2, 3, and 6 only.

Fig. 4. Kinetic trace of fluorescence intensity of BPH(D₁) monitored at 600 nm in Bmim-TFSA.

Fig. 5. Transient absorption signal monitored at 500 nm in (a) methanol and (b) Bmim-TFSA. After the 532-nm pulse irradiation, permanent bleaching was observed. The inset in (b) is a measurement with a high time resolution after 532-nm pulse irradiation.

Fig. 6. Relationship between normalized photo-bleaching and CCl₄ concentration: (Δ) methanol, (\bullet) Bmim-TFSA. Solid lines are fitting results for eqn (3).

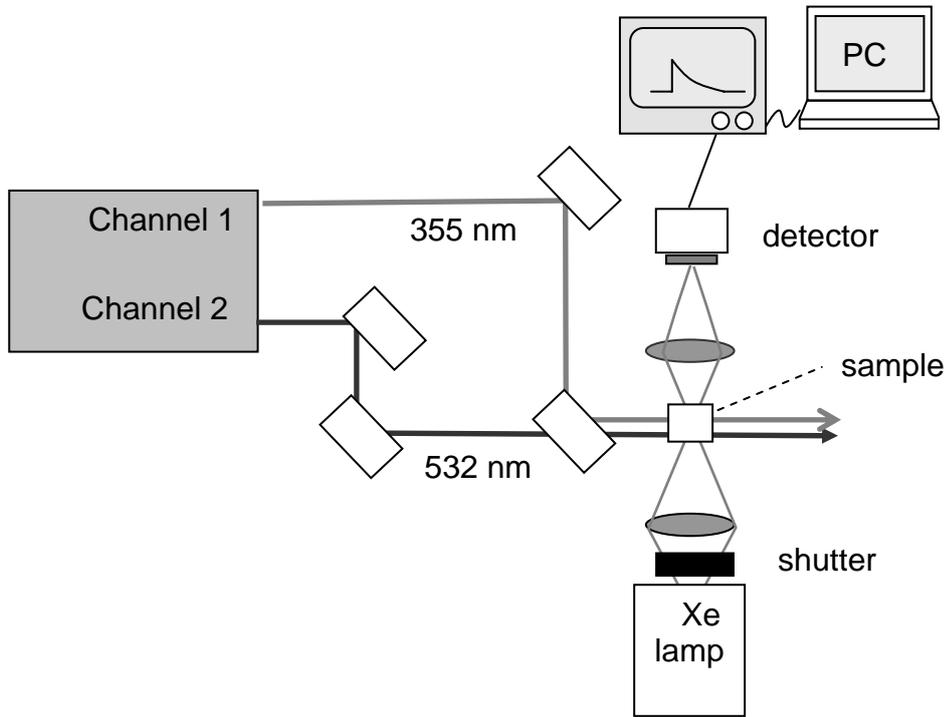


Fig. 1.

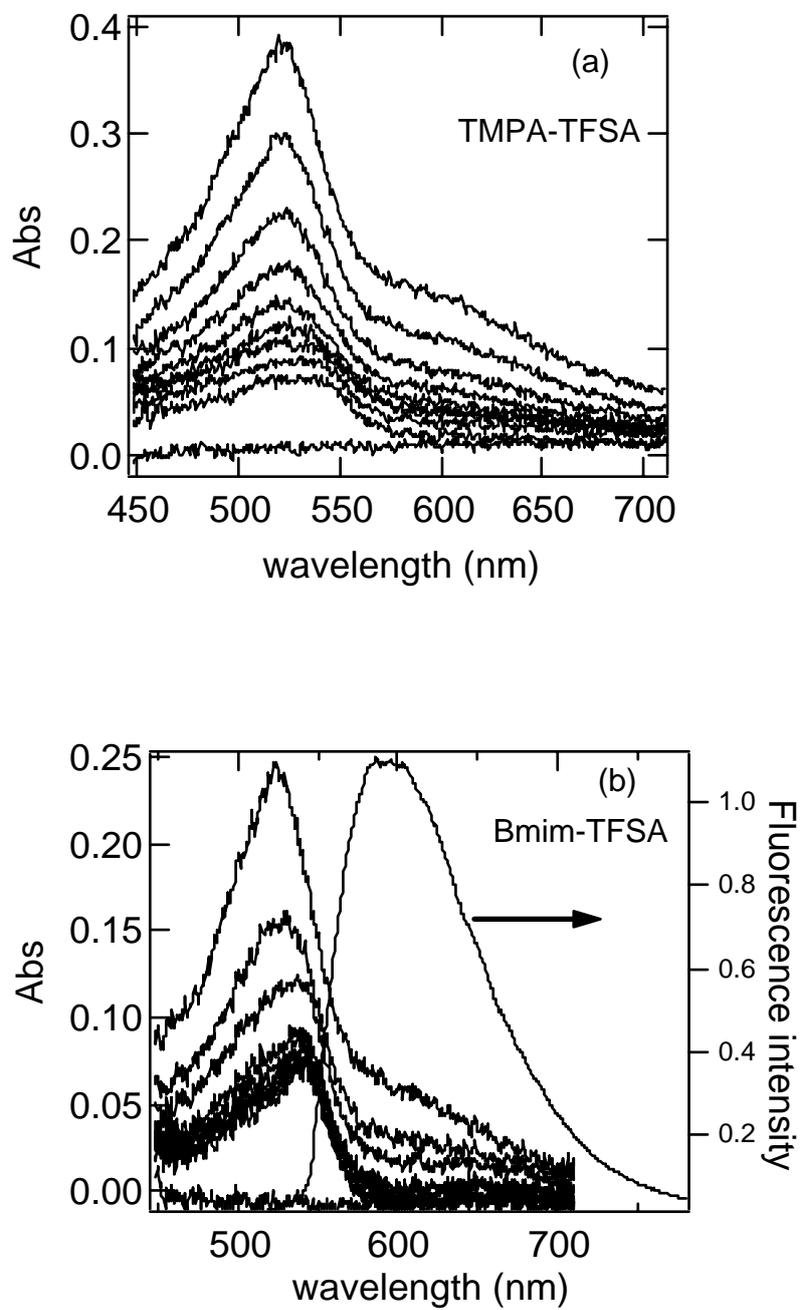


Fig. 2.

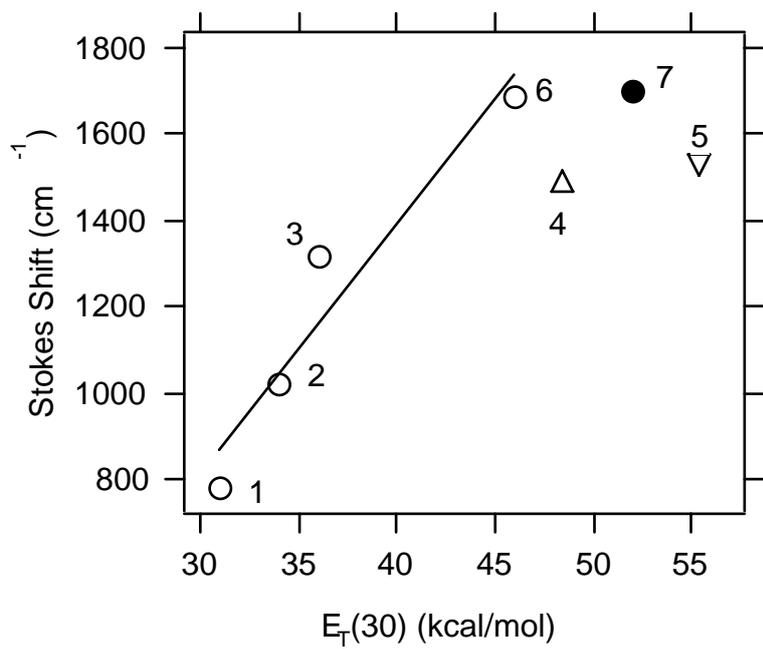


Fig. 3.

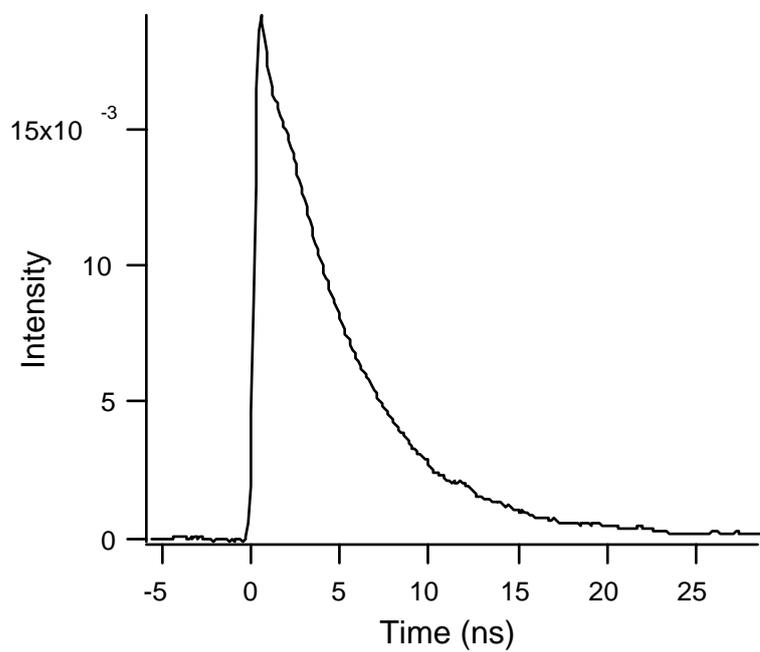


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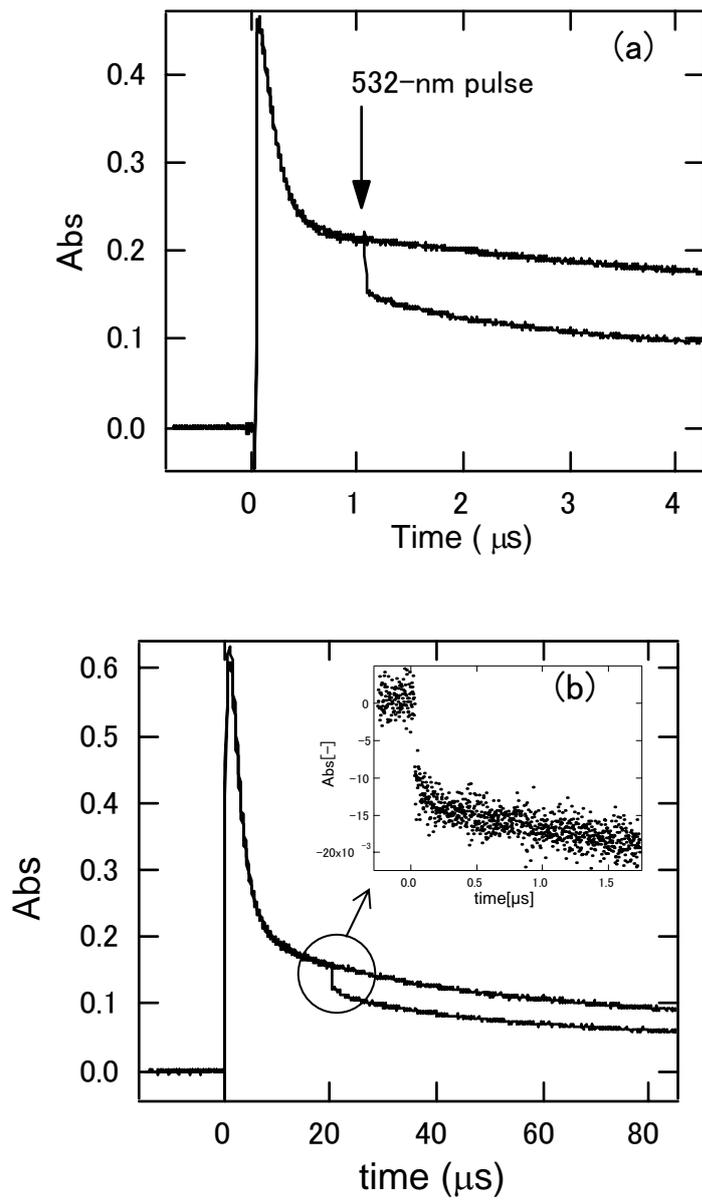


Fig. 5.

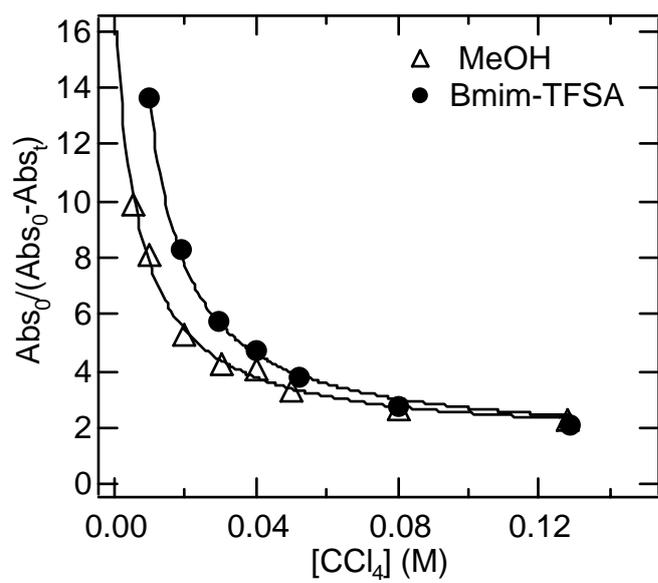
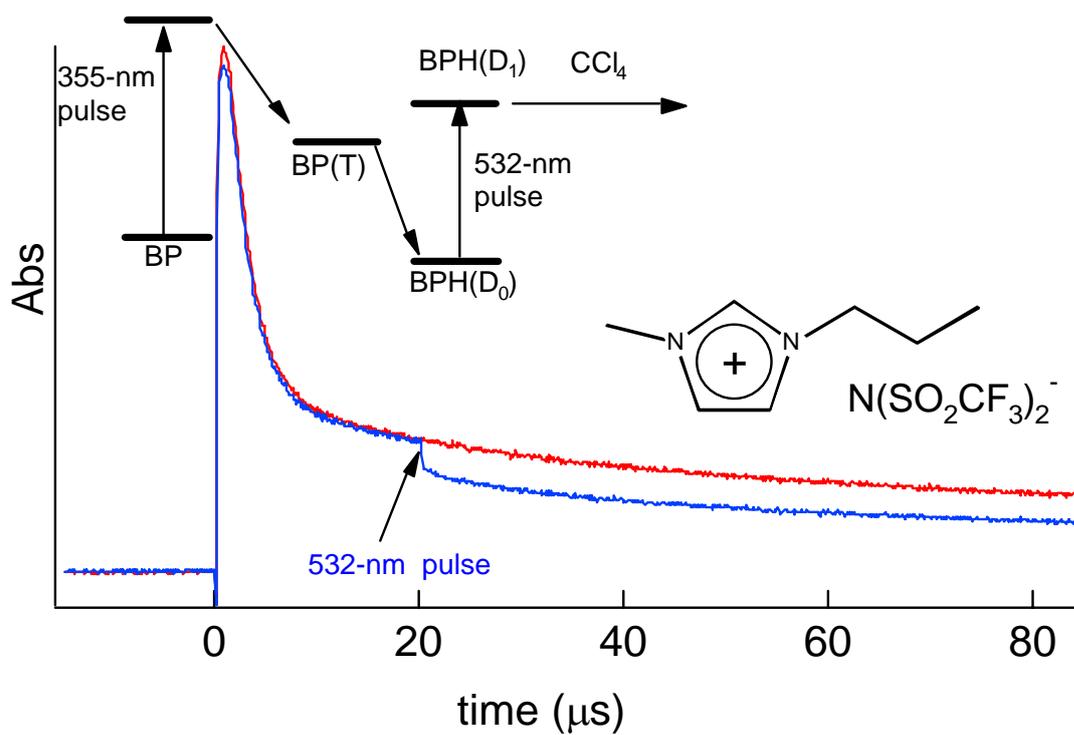


Fig. 6.

Graphical Abstract



Benzophenone ketyl radical, which is excited by 532-nm laser pulse, reacts with CCl₄ in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide.

