

Formation and Decay of an Aromatic Vinyl Cation in Supercritical CF₃H

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The effect of local density enhancement on the diffusion-controlled reactions in supercritical (SC) fluids has been clearly detected in the recombination reaction of a vinyl cation, 1-(4-methoxyphenyl)-2,2-diphenyl cation, with Br[−] in SC CF₃H. With increasing density of SC CF₃H, the observed recombination rate as a whole decreased rapidly in proportion to $1/\eta\epsilon$, where η and ϵ are the bulk viscosity and dielectric constant of the medium, respectively. Near the critical density, the rate constant was found to be much smaller than the predicted value from the $1/\eta\epsilon$ relation based on the Smolchowski-Debye scheme. This deviation indicates that the local density enhancement retards the recombination rate mainly due to the enhancement of dielectric constant.

Introduction

Solvation in supercritical fluids and liquid solvents plays a critical role in determining the rates and the branching ratios of chemical reactions. In supercritical fluids, solvation holds a particularly important position because the density fluctuation near the critical point causes a large density difference between the bulk fluid and the local area around the solute molecule. Such density enhancement just around the reactant (solute) molecule is often called “local density enhancement” or “clustering”.¹ Detailed studies of solvatochromic shifts of solute molecules in supercritical fluids have clarified the relation between the density enhancement and the solute–solvent interaction.² Ordinary, this density enhancement becomes significant near the critical density and produces much larger solvent effects on the reaction rate than that predicted from the bulk supercritical fluid density.³ That is, the density enhancement amplifies the acceleration or deceleration of reaction rates to be caused by SC fluids of a given bulk density. Therefore, the quantitative study of the effect of density enhancement on reaction rates is essential for controlling the rate of reactions in actual industrial applications.⁴

In diffusion-controlled reactions, the reduction of rate constants is often observed in liquid solvents as compared with the gas phase because of the high viscosity of liquid.⁵ On the other hand, the viscosity of SC fluids is quite low even at the density comparable to the liquid phase and greatly favors the reactant encounter in diffusion-controlled reactions. Such character makes the SC fluid solvent quite attractive as a medium for diffusion-controlled reactions. For this reason, several studies on the recombination reactions have been conducted in SC fluid of various densities. Troe and co-workers⁶ are the first to notice the importance of SC fluid for studying recombination reactions as a function of fluid density. They showed that the rate of iodine recombination increased with density in the gaslike region because of the increasing deactivating collision of fluid molecules with the hot collision complex I₂^{*} whereas in the liquidlike region the rate decreased due to the large viscosity.

The maximum rate was obtained around the critical density. They also pointed out the presence of a van der Waals complex I₂–M_n in the medium-density region below ρ_c from the observed s-shape features of the rate constant in the density plot. Such effects by a van der Waals complex were also suggested from the rapidly decreasing quantum yield of the photodissociation of I₂ around the critical density. However, the recent reexamination of the quantum yield revealed that the clustering gave no effect on the quantum yield of free iodine atoms. The difference between these two research groups could originate from the difference in the wavelength of the photolysis laser.^{7,8}—the former excited I₂ molecules to the A' state where a potential well exists on the way to dissociation whereas the latter excited I₂ to the repulsive ¹Π_u state. For large organic molecules, Robert et al.⁹ examined the recombination of benzyl radicals in SC CO₂, C₂H₆, and CF₃H, and concluded that in all the fluids the clustering neither enhanced nor slowed the reaction rate. Recently, Tanko and Pacut¹⁰ showed that the ratio between the intra-cage reaction and the escape of radicals from the cage after the photolysis increased with increasing SC CO₂ density, though they did not examine the clustering effects. More recently, Ohmori et al.¹¹ reported that the diffusion of benzyl radicals in medium-density methanol could be retarded due to the clustering. Thus, the presence of the clustering effect on diffusion-controlled reactions is still a controversial issue.

Regarding the ionic species, pulse radiolysis has been considered the only method to produce reactive ionic species sufficient for detection in supercritical fluids with low dielectric constants. Using pulse radiolysis technique, Zhang et al.¹² examined the bimolecular reaction of arylmethyl cations with neutral nucleophiles in SC C₂H₆ and CF₃H. The increase of the rate constant with increasing density was interpreted from the correlation with the increasing bulk solvent dielectric constant. They also analyzed the pressure dependence of the bimolecular reaction rate in terms of TST theory, and demonstrated that the combination of the Drude-Nernst equation with Penn-Robinson equation of state could explain the observed trends.

In the present study, the recombination of ionic species has been examined in supercritical CF₃H. Laser flash photolysis has

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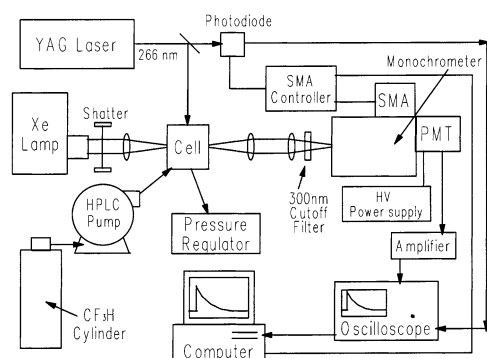
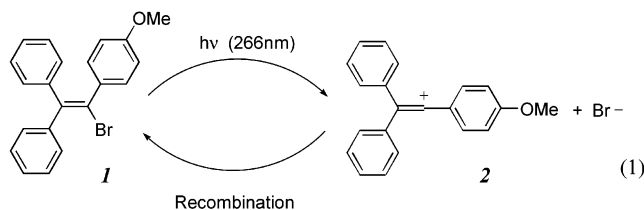


Figure 1. Laser flash photolysis system.

an advantage over pulse radiolysis in selectively producing ionic species without any contaminating species because of the selective excitation at low energy. Ionic species are suitable for detecting the effect of density enhancement since they are sensitive to dielectric stabilization by the medium. In the recombination reaction, the Coulomb attraction between the ions of opposite charge is significantly reduced with increasing dielectric constant and hence the local density enhancement should considerably decrease the recombination rate. In this experiment, a vinyl cation was produced from corresponding vinyl bromide, 1-bromo-1-(4-methoxyphenyl)-2,2-diphenylethylene, by the photolysis at 266 nm as in eq 1. CF₃H was utilized as SC fluid because of its large density dependence of dielectric constant.



Experimental Section

Materials. 1-Bromo-1-(4-methoxyphenyl)-2,2-diphenylethylene (**1**) was synthesized from 1-(4-methoxyphenyl)-2,2-diphenylethanol according to the reported method.¹³ Commercially available CF₃H (Daikin Industries Ltd., 99.95% purity) and O₂ (Teisan Co., >99.995% purity) were used without further purification. The critical temperature and pressure of CF₃H are 25.9 °C and 4.858 MPa, respectively. All liquid solvents purchased (Nakarai Tesque and Kanto Chemical Co.) were of spectrum grade and used as received.

Method. The schematic diagram of the laser flash photolysis (LFP) system is shown in Figure 1. The 266 nm light (~20 mJ/pulse, pulse width ~10 ns) from the fourth harmonic generator of a pulsed Nd:YAG laser (Spectra Physics DCR11) was used for the photolysis whereas a 150 W CW Xe lamp (Hamamatsu L2274) was utilized as a monitoring light source. The laser beam was focused when required. The light emitted from the 150 W Xe lamp was passed through a sample cell and collimated onto the slit of the monochromator. The absorption spectrum was recorded with an SMA system composed of a 15 cm monochromator (Thermo Vision Colorado Monospec 18) and an intensified diode array detector. The signals were accumulated with the SMA controller for 100 laser shots and averaged in a personal computer. For the time-dependent measurement of the absorption signal, a photomultiplier (Hamamatsu R928) was used instead of the diode array. Each decay curve at a fixed wavelength was digitized with the oscilloscope (Phillips

PM3320A) and more than 100 decay curves were accumulated and averaged in the personal computer. The time-resolution of the detecting system was ~5 ns. The detecting wavelength was selected at 360 nm where the absorption band of the precursor vinyl bromide was negligible, though the wavelength did not correspond to the absorption maximum of the cation. A 300 nm cutoff filter was inserted in front of the monochromator to eliminate the scattered laser light. Due to the weak absorption by the transient species, the resulting rate constants contained the statistical error of about 10% as recognized from the scattered plot in Figure 5.

The optical cell for the SC fluid experiments was made of stainless steel (SUS 304) with four quartz windows of 15 mm diameter for the purpose of photoexcitation and detection by light absorption. Supercritical CF₃H was fed to the cell with an HPLC pump (JASCO, SCF-Get). The pressure in the cell was monitored with a strain pressure gauge (Kyowa, PGM-200KH). The temperature of the cell was monitored with a K-type thermocouple and maintained at 40 ± 0.2 °C by circulating hot water from the thermostated water bath (Tokyo Rika Co, UA-100G) through the cell.

The reaction in SC CF₃H was examined along the 40 °C isotherm. The concentration of the cation precursor **1** was normally (2.0–2.7 ± 0.3) × 10⁻⁵ mol dm⁻³ because of the limited solubility of **1** in SC CF₃H. The concentration of **1** was estimated from the UV–Vis absorbance. The generated 1-(4-methoxyphenyl)-2,2-diphenylethenyl cation (**2**) was identified from its transient absorption spectrum.

The rate constants for the recombination of **2** with Br⁻ in the present density range were evaluated by assuming the second-order reaction. That is, the rate law of the recombination is written as

$$\frac{d[A^+]}{dt} = -k_{bi}[A^+][B^-] \quad (2)$$

Since the initial concentration of A⁺ and B⁻ is equal

$$[A^+]_0 = [B^-]_0 \quad (3)$$

eq 2 can be rewritten as

$$k_{bi}t = \frac{1}{[A^+]} - \frac{1}{[A^+]_0} \quad (4)$$

Equation 4 was used to derive *k_{bi}* from the observed decay of A⁺.

To obtain the absolute value of the bimolecular rate constant, the extinction coefficient *ε* of the vinyl cation is required. However, the extinction coefficient of the transient vinyl cation was unknown at present. Therefore, we express the rate constant as *k_{obs}* in unit of Abs⁻¹ s⁻¹ and discuss only the density dependence of this relative rate constant. The absolute rate constant *k_{bi}* is related to *k_{obs}* as

$$k_{bi} = k_{obs} \times \epsilon l \quad (5)$$

where *ε* is the extinction coefficient of the vinyl cation at the observed wavelength and *l* is the effective excitation path length.

When we examine the density dependence of the bimolecular reaction rate, we should be careful about the density dependence of the extinction coefficient. In the case of neutral aromatic compounds, the extinction coefficient was found to increase with increasing fluid density.¹⁴ Thus, the bimolecular rate constant without correction tends to decrease with increasing density more significantly than the actual tendency. For the transient

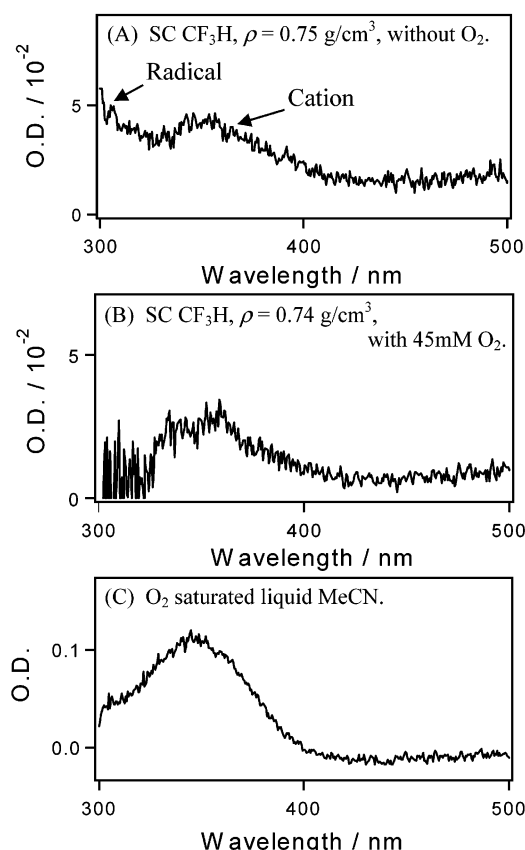


Figure 2. Transient absorption spectra of vinyl cation **2** at 300–500 ns after the laser pulse. (A) In SC CF₃H at the density of 0.75 g/cm³ without O₂ (<1.0 mM). The concentration of cation precursor **1** was 2.7×10^{-5} mol dm⁻³. (B) In SC CF₃H at the density of 0.74 g/cm³ with 45 mM O₂. The concentration of cation precursor **1** was 2.7×10^{-5} mol dm⁻³. (C) In O₂-saturated CH₃CN, at the temperature of 25 °C. The concentration of cation precursor **1** was 4.7×10^{-5} mol dm⁻³. In the SC CF₃H, the transient spectrum showed red shift from that in MeCN. Addition of O₂ gave negligible effect on the intensity of the spectrum.

aromatic ion used in the present experiment, the density dependence of the extinction coefficient has not been reported so far probably because the quantitative generation of the ion is quite difficult. There are two major sources of the density dependence of ϵ . One is the variation of the refractive index which varies the velocity of light and hence changes the flux of light, enhancing ϵ with increasing density. The other is the electrostatic perturbation by solvent molecules to facilitate the participation of the excited states with high oscillator strength in the photoabsorption process. Since the first excitation band of aromatic ions is a strong allowed transition, solvent perturbation cannot enhance the transition moment any more and in some cases may decrease the extinction coefficient with increasing fluid density. The relative importance of these two contributions is not clear at present. Therefore, we did not try to make corrections to the density dependence of the extinction coefficient and rather focused our attention on the tendency of the uncorrected rate constant around the critical density.

Results and Discussion

1. Formation and Detection of 1-(4-Methoxyphenyl)-2,2-diphenylethynyl Cation. Figure 2A shows the transient absorption spectrum recorded immediately after the photolysis of the precursor vinyl bromide **1** at 266 nm in supercritical CF₃H at the density of 0.75 g/cm³. The transient absorption spectrum of

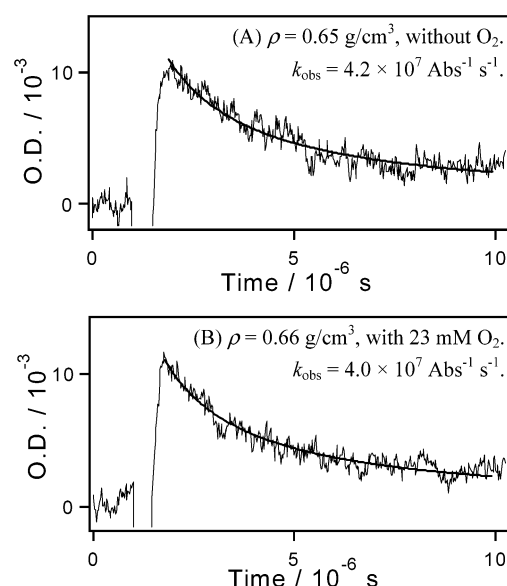


Figure 3. Time-dependent absorption spectra of the vinyl cation **2** in SC CF₃H, (A) at the density of 0.65 g/cm³ without O₂ (<1.0 mM). The concentration of cation precursor **1** was 5.4×10^{-5} mol dm⁻³. (B) In SC CF₃H at the density of 0.66 g/cm³ with 23 mM O₂. The concentration of cation precursor **1** was 5.4×10^{-5} mol dm⁻³. The recombination rate constants were not affected by the O₂ addition. The decay of the absorption well fits to the line predicted from the bimolecular rate law as in eq 4 (see text).

the vinyl cation **2** has already been reported and confirmed in the liquid-phase experiments.¹⁵ According to Kobayashi et al. who generated the vinyl cation from the precursor vinyl bromide by laser flash photolysis in CH₃CN, the peak position of its spectrum was about 345 nm, which is quite close to our spectrum shown in Figure 2. Since the solvent polarity of SC CF₃H ($\epsilon = 3$ –5.5)¹⁶ is much less than that of CH₃CN ($\epsilon = 36$), the red shift of the peak position from the spectrum by Kobayashi et al. is quite reasonable. Ordinarily, the excited state of the ionic species is less polar than its ground state and hence the polar solvent stabilizes the ground state more than the excited state, resulting in the blue shift in the more polar solvent.¹⁷

The homolytic dissociation of precursor vinyl bromide by photoirradiation could form radical species which show an absorption band in shorter wavelength region around 300 nm. According to Verbeek et al.,¹⁸ the absorption band of the vinyl radical which was generated by laser flash photolysis of 1-(4-methoxyphenyl)-2-(2,2'-biphenyldiyl)vinyl bromide in CH₃CN appeared near 300 nm. These absorption bands of the vinyl radicals were quenched efficiently by 8.2 mM of O₂. To distinguish the radicals and triplets from the singlet ionic species, the effect of O₂ on the absorption band was examined. As is shown in Figure 2B and 2C for SC CF₃H and CH₃CN solution, respectively, the transient absorption band at 360 nm did not suffer from O₂ addition in contrast to the complete quenching of the 300 nm band of radical species. Furthermore, no acceleration was observed in the decay of the 360 nm absorption band as in Figure 3B. These observations confirmed that the vinyl cation is responsible for the 360 nm band. The slight deduction of the absorption at 360 nm by O₂ addition may suggest that a part of the vinyl cation was generated via the triplet state of parent vinyl bromide **1**. Kobayashi et al.^{15a} also noticed in CH₃CN solution that the observed spectrum was not quenched by the addition of O₂.

For the additional confirmation of the vinyl cation formation on the photolysis, the reactivity to the nucleophile was examined in the liquid methanol/CH₂Cl₂ solution. CH₂Cl₂ was selected

as a solvent because it has a relatively small dielectric constant close to that of SC CF₃H and has no absorption band around 266 nm. The pseudo-first-order rate constant for the reaction of the vinyl cation **2** with methanol increased linearly with increasing methanol concentration as in Figure 4A. The bimolecular rate constant for the reaction with methanol in CH₂-Cl₂ was calculated from the slope of Figure 4A to be $8.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, which was larger than the value reported for the CH₃-CN solution, $4.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.¹⁹ This result is quite reasonable, because the stability of the vinyl cation **2** was expected to be smaller in CH₂Cl₂ than in CH₃CN. Furthermore, the yield of photogenerated vinyl cation **2** increased with increasing methanol concentration. Figure 4B implies the dielectric constant of the solvent strongly affects the stability of the vinyl cation **2**. From these experiments, we concluded that the observed absorption band is attributable to the vinyl cation **2**.

2. The Recombination Rate of the Vinyl Cation as a Function of Fluid Density. The vinyl cation **2** and Br⁻ that successfully escape from the cage then slowly recombine to form the initial compound **1**. This process occurs as a diffusion-controlled process and the disappearance of the cation **2** obeys the second-order rate law with respect to the ionic species as in Figure 3. The bimolecular recombination rates are governed by the following two factors. One is the solvent viscosity that controls the mobility of the solute ions, and the other is the solvent dielectric constant which affects the Coulomb interaction between the two ionic species. Both of these factors slow the recombination rates with increasing fluid density.

Under the context of Stokes-Einstein-Smoluchowski (SES) treatment, the rate of recombination reactions can be written as follows:

$$k_{\text{bi}} = 4\pi(D_A + D_B)\lambda \quad (6)$$

$$D_A + D_B = \frac{k_B T}{6\pi\eta} \left(\frac{1}{r_A} + \frac{1}{r_B} \right) \quad (7)$$

$$\lambda^{-1} = \int_{r_c}^{\infty} \frac{\exp\left\{\frac{V(r)}{k_B T}\right\}}{r^2} dr \quad (8)$$

$$V(r) = \frac{Z_A Z_B e^2}{4\pi\epsilon\epsilon_0} \frac{1}{r} \quad (9)$$

where D_A and D_B are the binary diffusion coefficients of the ions A⁺ and B⁻, respectively. k_B is the Boltzmann constant, η the solvent bulk viscosity, and T the absolute temperature. Z_A and Z_B are the numbers of charges on the ion A⁺ and B⁻, respectively. e is the charge of an electron, ϵ_0 the permittivity of vacuum, and ϵ the solvent bulk dielectric constant. $V(r)$ is the Coulomb potential between the ions, and r_A and r_B denote the radii of the ionic reactants, A⁺ and B⁻, respectively. This equation quantitatively represents the contributions of the above-mentioned two factors, the solvent viscosity and the solute-solvent Coulomb interaction. The viscosity factor appears in the η of the Stokes' approximation to the diffusion coefficients and the electrostatic interaction is included in the integral λ . The solute-solvent interaction also implicitly contributes to the Stokes radius r .

Let us first consider the density effect on the recombination rate of neutral species. For the recombination of iodine atoms, Troe and co-workers⁶ proposed a model for the density dependence of the recombination rate and derived the following

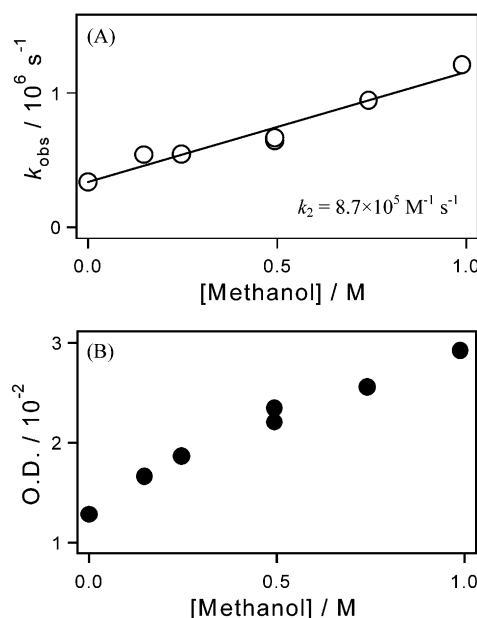


Figure 4. The methanol concentration dependence of (A) the bimolecular rate constant and (B) the yield of the vinyl cation **2**.

equation which covers the wide range of fluid density:

$$k_{\text{rec}} = 4\pi R D N_A \frac{k_{\text{rec}}^g}{k_{\text{rec}}^g + 4\pi R D N_A} \quad (10)$$

where D is the binary diffusion coefficient of iodine atom in solvent M, N_A is the Avogadro number, and R is the contact distance. k_{rec}^g denotes the hypothetical recombination rate constant at a given density "in the absence of diffusion control". The experimental results of Troe et al. showed good agreement with this equation in combination with the Stokes-Einstein-Smoluchowski (SES) equation.⁶ In the case of large organic radicals, such as benzyl radical,⁹ the density dependence of the observed bimolecular rate constant was also in accordance with the value estimated from the SES equation, though we have to set the radius of the moving radicals to be slightly larger than the van der Waals radius of the radical. This is due to the larger molecular interaction between the solvent molecule and the radical species as compared with the parent species. Actually, in liquid phase²⁰ and in SC fluid phase,²¹ radical species showed smaller diffusion coefficients than their parent neutral molecules.

In the case of SC fluids, the clustering around the radical can further increase the Stokes radius r_A . Since the cluster becomes much larger than that expected from the bulk density near the critical point, the recombination rate may deviate significantly downward from the $1/\eta$ curve because of the sudden increase in r_A around the critical density. In the actual experiments, however, such deviation has not been unambiguously detected so far. This means that the effect of clustering on the diffusion should be undetectably small for neutral species. In other words, the contribution of the clustering to the increase in the Stokes radius is considered to be quite small. Such insensitivity of Stokes radius to the clustering may be related to the time scale of the fluctuation in the cluster. According to the molecular dynamics calculations,²² the clustering molecules are quickly replaced by the molecules in the bulk region within a few picoseconds because the kinetic energy of the clustering molecules are comparable to the solute-solvent interaction energy. The time scale of diffusion, in contrast, is several orders of magnitude longer and hence not much affected by the quickly changing clustering molecules.

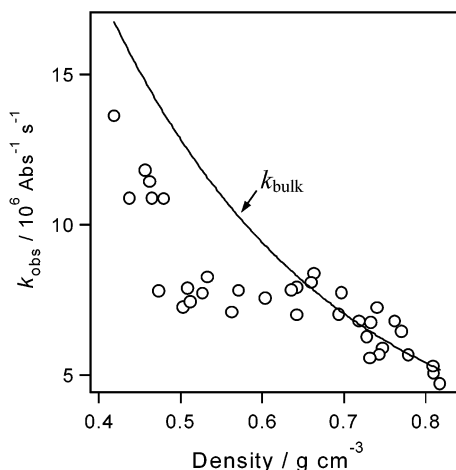


Figure 5. Density dependence of the observed rate constant (○) and the estimated tendency (—) from eq 12.

In the diffusion-controlled recombination of the ionic species such as the vinyl cation and Br^- , the second factor, Coulomb interaction, should be taken into account. For the conditions $T = 295 \text{ K}$, $r_c = 0.5 \text{ nm}$, and $\epsilon \leq 10$, eqs 6–9 can be simplified as

$$k_{bi} = \frac{-Z_A Z_B e^2}{6\pi\eta\epsilon\epsilon_0} \left(\frac{1}{r_A} + \frac{1}{r_B} \right) \quad (11)$$

This equation indicates that the recombination rate is proportional to the reciprocal of $(\eta\epsilon)$. Figure 5 shows the plot of the measured rate constant as a function of the bulk solvent density together with the plot according to the prediction by eq 11. The viscosity data was taken from the literature.²³ The recombination rate constant of the vinyl cation as a whole decreased with increasing solvent density. The most noticeable feature is the large downward deviation of the observed recombination rate from the predicted value near the critical density. Since neutral species did not show such s-shaped dependence, the density enhancement or clustering definitely affects the recombination rate of ionic species in contrast to the neutral species.

To interpret the remarkable difference in the clustering effect between the neutral species and ions, we have to consider how the above-mentioned two critical factors, viscosity and Coulomb interaction, are modified and work when the clustering becomes significant. For the contribution of the viscosity term in ionic species, the interaction between the ion and the clustering solvent molecules is probably strong enough to increase the Stokes radius and hence reduces the rate of the recombination reaction to some extent. The Coulomb interaction suffers the much more significant effect by the clustering. The enhancement of dielectric constant by the clustering causes considerable reduction of the attraction between the ionic species as apparent from eq 11. Note that such deduction in Coulomb attraction has nothing to do with the exchange of the clustering molecules because only the time-averaged number of clustering molecules is essential to determine the dielectric constant. Thus, local density enhancement always weakens the Coulomb attraction and slows down the rate of the recombination reaction between the ionic species of opposite charges.

It becomes apparent that the unambiguous observation of the clustering effects in diffusion-controlled recombination reaction can only be possible for ionic species because of the significant contribution of the enhanced dielectric constant to the Coulomb interaction. Less significant contribution to the diffusion may

arise from the viscosity term through the increase in the Stokes radius due to the strong ion–dipole interaction between the solute ion and solvent molecules.

Conclusion

The diffusion-controlled recombination rate of 1-(4-methoxyphenyl)-2,2-diphenyl cation with Br^- has been determined in SC CF_3H . Although the rate constant as a whole decreased with increasing density as a function of $1/(\eta\epsilon)$ according to the SES equation, a severe downward deviation of the rate constant from the $1/(\eta\epsilon)$ curve was observed near the critical density where the clustering is most significant. To our best knowledge, this is the first unambiguous observation of the clustering effect on the diffusion-controlled reaction in contrast to the ambiguous results for the recombination of neutral species. The reason for this successful observation in ion recombination lies in the participation of Coulomb attraction in determining the mutual diffusion of recombining partners. The Coulomb attraction is severely suppressed when the clustering solvent molecule enhance the dielectric constant around the ionic species. This study demonstrated that, between the factors for determining the diffusion-controlled reactions, the reactant diffusion against the solvent viscosity suffers no significant disadvantage by enhanced clustering near the critical density whereas the diffusion caused by the Coulomb attraction is considerably suppressed by the enhanced clustering.

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