Mechanistic Study on the Enantiodifferentiating Anti-Markovnikov Photoaddition of Alcohols to 1,1-Diphenyl-1-alkenes in Near-Critical and Supercritical Carbon Dioxide

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Enantiodifferentiating anti-Markovnikov photoaddition of alcohol (methanol, ethanol, 2-propanol, and *tert*-butanol) to aromatic alkene (1,1-diphenylpropene and 1,1-diphenyl-1-butene), sensitized by optically active alkyl and saccharide naphthalene(di)carboxylates, was investigated in supercritical carbon dioxide at varying pressures to elucidate the effects of clustering on photosensitization and enantiodifferentiation behavior, in particular on the product's enantiomeric excess (ee). For all the alkene/alcohol/chiral sensitizer combinations examined, a sudden change in the product's ee was consistently observed near the critical density, which is attributable to the critical pressure dependence of clustering around the intervening exciplex intermediate.

Introduction

Photochirogenesis, or chiral photochemistry, provides us with a new photochemical route to asymmetric synthesis and attracts much attention of a broad spectrum of chemists from both mechanistic and synthetic viewpoints. Of several strategies to achieve photochirogenesis, enantiodifferentiating photosensitization is of mechanistic interest and synthetic importance as a method alternative to conventional catalytic and enzymatic asymmetric syntheses, enabling us to transfer and multiply molecular chirality through the excited state.[1−5] Since the first report on the asymmetric photosensitization by Cole and Hammond,[6] a significant amount of effort has been devoted to the control of photochirogenic processes by internal and external factors.[1−5] We demonstrated that the enantiodifferentiating photoisomerization of (*Z*)-cyclooctene, sensitized by chiral polyalkyl benzenepolycarboxylates, gives optically active (*E*)-cyclooctene in good enantiomeric excesses (ee) of up to 73% at −110 °C,[7] whereas the enantiodifferentiating polar photoaddition of methanol to 1,1-diphenyl-1-butene, sensitized by chiral naphthalenedicarboxylates, affords optically active 1,1-diphenyl-2-alkoxy-butane in moderate ee's of up to 36% at 0 °C.[8,9] Interestingly, it turned out that the ee value is a critical function of temperature, pressure, and solvent polarity, and even the chiral sense of photoproduct is switched by these environmental variants.[7,12,13] Through the analyses of activation parameters, we revealed that such unprecedented behavior originates from the vital contribution of the entropy term in the enantiodifferentiation process occurring in the exciplex intermediate.[7−13]

In this relation, supercritical fluid (SCF) is of our particular interest as a reaction medium, not only from the viewpoint of "green" chemistry, but also from the entropic control of photochirogenesis. The use of SCF provides us with a rare opportunity to investigate the effects of clustering on (photo)chemical reaction and also to develop methods for controlling the reaction rate and selectivity[14,15] through the dramatic changes in medium properties, such as viscosity, density, and dielectric constant, in a very narrow range of pressure and temperature.[16−18] In the photochirogenesis context, it is intriguing to elucidate the stereochemical consequences of such a dynamic fluctuation of medium structure and useful to exploit it as an extra entropy-related factor for controlling a photochirogenic process. Nevertheless, the first photosensitized enantiodifferentiating isomerization of (*Z*)-cyclooctene in supercritical carbon dioxide ($scCO_2$) was reported only recently, which revealed a unique discontinuous change of the product's ee just above the pressure that gives the critical density.[19] More recently, we have reported that a more clear jump of the product's ee occurs near the critical density in the photosensitized enantiodifferentiating polar addition of alcohol to 1,1-diphenylpropene performed in $scCO_2$ (Scheme 1, $R^1 = Me$), which was tentatively attributed to different degrees of clustering to the exciplex intermediate above and below the apparent critical density,[20] since the preferential solubilization of substrate or sensitizer may result in some changes in conversion and yield but never lead to an error in the product's ee simply because the identical solubilities for the enantiomeric isomers.

In this mechanistic study to elucidate the origin of such discontinuous ee changes and the role of clustering effect in photochirogenesis, we performed the enantiodifferentiating photoaddition reaction of primary to tertiary alcohols (**3a**−**d**) to 1,1-diphenylpropene (**1**) and 1,1-diphenyl-1-butene (**2**) sensitized by chiral naphthalenedicarboxylates with saccharide (**6a**) and alkyl ester moieties (**6b**) under a variety of conditions and examined the photophysical behavior of chiral naphthalenedicarboxylate sensitizers and the exciplex intermediates derived therefrom. This photochirogenic system is suitable for both spectral examinations and further mechanistic investigations, since the sensitizers and the exciplex intermediates are fluorescent and the product's ee is moderate to good even at ambient or higher temperatures and critically responds to the environmental factors, in particular, to the solvent polarity.[8,9]

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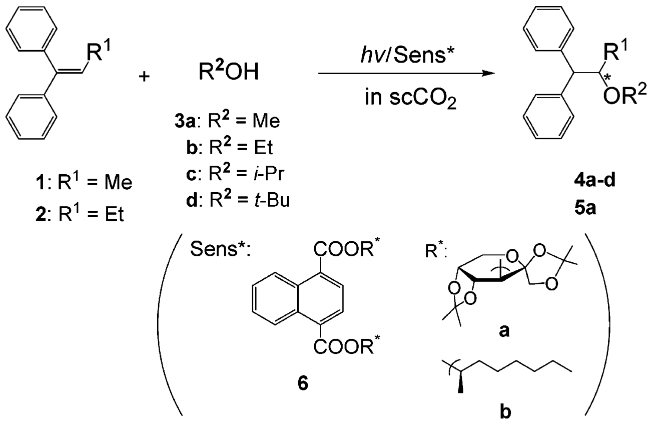
SCHEME 1: Enantiodifferentiating Photosensitized Polar Addition of a Series of Alcohols 3 to 1,1-Diphenyl-1-alkenes 1 and 2 in $scCO_2$ at 45 °C



Taking these advantages, we elucidate the vital roles of clustering in the photochirogenesis in SCF.

Results and Discussion

Effects of Alcohol's Bulk. It has been amply demonstrated that many photochirogenic reactions are critically affected by temperature and higher ee's are often obtained at lower temperatures.[1−5] In this context, SCF as a reaction medium appears to have an inherent limitation in available temperature range, which is higher than the critical point ($T_c = 31$ °C at $P_c = 7.38$ MPa for CO_2). Hence, we should use such a chiral photoreaction system that affords reasonably high ee's at ambient and higher temperatures in order to seriously examine the effects of clustering on the photochirogenic process in SCF media. Fortunately, it is known that the product's ee increases with increasing temperature in the polar photoaddition of alcohol to 1,1-diphenylpropene (**1**) sensitized by saccharide 1,4-naphthalenedicarboxylate.[8,9] By utilizing this relatively rare case, we can closely investigate the effects of clustering and other entropy-related factors on the photophysical and photochemical behavior of excited sensitizer and exciplex intermediate in $scCO_2$.

We first examined the bulkiness effect of alcohol **3** on the reactivity and the ee of adduct **4** produced upon photosensitization with diacetonefructosyl (DAF) 1,4-naphthalenedicarboxylate (**6a**, R* = 1,2:4,5-di-*O*-isopropylidene-α-D-fructopyranosyl) in $scCO_2$; the results obtained are summarized in Table 1.

As can be seen from Table 1, longer periods of irradiation are needed for bulkier alcohols to obtain comparable conversions under the identical irradiation conditions, yet the less bulky alcohols **3a**−**c** afforded the corresponding photoadducts **4a**−**c** in moderate to good yields in $scCO_2$. These results prompted us to re-examine the photoaddition of the most bulky *tert*-butanol **3d** to **1** in $scCO_2$, despite the negative results obtained for the same reaction in conventional organic solvents.[9] In $scCO_2$ of low density and polarity, alcohols are expected to more intimately interact, forming clusters, with an exciplex intermediate of charge-transfer nature. However, the repeated experiments with prolonged irradiations of up to 24 h in near-critical and supercritical CO_2 merely led to the formation of some amounts of side products such as benzophenone, without affording the *tert*-butanol adduct. This indicates that *tert*-butanol is too bulky to approach the radical cationic substrate even in near-critical and supercritical CO_2 media and that the clustering effect is not sufficient to overcome the steric hindrance of *tert*-butyl.

TABLE 1: Enantiodifferentiating Photoaddition of Various Alcohols to 1,1-Diphehylpropene (1) Sensitized by Diacetone-Fructose (DAF) 1,4-Naphthalenedicarboxylate (6a) in Supercritical Carbon Dioxide ($scCO_2$) at 45 °C[a]

R^2OH	pressure /MPa	irradiation time/h	conversion /%	yield/%[b]	ee/%[c]
MeOH (**3a**)	7.7	1	51	79	−6.5
	8.0	1	25	20	−6.8
	8.3	1	44	21	−7.2
	9.0	1	80	50	−8.0
	9.4	1	55	49	−9.7
	10.0	1	34	89	−17.5
	12.0	1	29	84	−18.5
	18.0	1	41	32	−20.7
EtOH (**3b**)	7.8	2	34	15	−18.3
	8.4	2	53	40	−15.2
	9.0	2	59	50	−16.6
	9.5	2	52	47	−20.7
	10.0	2	46	44	−21.8
	10.6	2	43	43	−23.9
	11.6	2	43	40	−22.5
	18.0	2	31	38	−27.6
i-PrOH (**3c**)	8.0	4	28	26	+21.2
	8.5	4	52	71	+22.4
	8.8	4	70	22	+23.9
	9.0	4	58	10	+24.9
	9.5	4	31	63	+33.6
	10.0	4	40	29	+39.3
	12.4	4	33	20	+39.6
	18.0	4	36	17	+42.3
t-BuOH (**3d**)	8.5	12	*d*		
		24	*d*		
	9.0	3	*d*		
		6	*d*		
	18.0	3	*d*		

[a] [**1**] = 2 mM; [**6a**] = 0.3 mM; [**3a**−**d**] = 0.5 M. [b] Chemical yield based on the consumption of the starting material. [c] Enantiomeric excess determined by chiral GC; error <0.3% ee. Except for the **4a** case, the sign of ee does not mean the sign of optical rotation or absolute configuration but is tentatively assigned according to the elution order on ASTEC B-PH and B-DM column for **4b** and **4c**, respectively; the first eluted enantiomer is given a positive sign. [d] Practically no reaction.

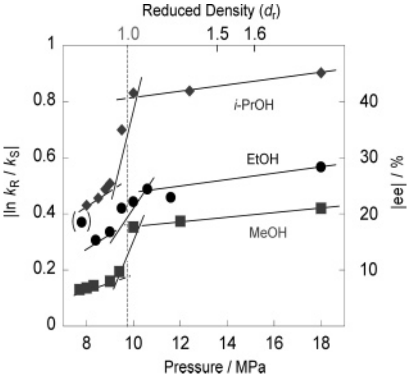


Figure 1. Pressure dependence of the relative rate constants ($|\ln(k_R/k_S)|$) and the absolute ee values of **4a**−**c** obtained in the enantiodifferentiating photoaddition of alcohols to **1** sensitized by **6a** in near-critical and supercritical CO_2 at 45 °C.

The pressure-dependence profiles of the absolute ee values of **4a**−**c** obtained are illustrated in Figure 1, where the natural logarithm of relative rate constant for the formation of (*R*)- and (*S*)-**4**, i.e., $|\ln(k_R/k_S)| = \ln[(100 + |\%\ ee|)/(100 - |\%\ ee|)]$, is plotted against the CO_2 pressure (note that the signs of ee for **4b** and **4c** indicate only the elution order on a specific chiral GC column (see the Experimental Section), as the absolute configurations of **4b** and **4c** are not known).

TABLE 2: Differential Activation Volumes ($\Delta\Delta V^{\ddagger}_{R-S}$) for the Enantiodifferentiating Photoaddition of Various Alcohols to 1 Sensitized by 6a in Carbon Dioxide Media in the Near-Critical (<9 MPa), Transition (9−10 MPa), and Supercritical (>10 MPa) Regions

	$\lvert\Delta\Delta V^{\ddagger}_{R-S}\rvert$/cm^3 mol^{-1}		
R^2OH	7.7−9 MPa	9−10 MPa	10−18 MPa
MeOH (**3a**)	60	(530)	22
EtOH (**3b**)	130	(290)	26
i-PrOH (**3c**)	210	(850)	25

As can be seen from Figure 1, the ee values obtained for all the adducts derived from reactive alcohols (**3a**−**c**) increase in general with increasing pressure, but the pressure-dependence profiles are obviously discontinuous, showing an abrupt jump near the critical density ($d_c = 0.468$ g cm^{-3} at 9.9 MPa and 45 °C).[21] Similar behavior has been observed in the enantiodifferentiating photoisomerization of (*Z*)-cyclooctene in $scCO_2$,[19] where the ee profile showed a kink just above the critical density, but the ee behavior at pressures lower than 8 MPa (in the near-critical region) could not be examined due to the low solubility of the benzenepolycarboxylate sensitizers employed. In contrast, the present system allowed us to observe the ee profile over the whole pressure range starting from the near-critical region, since both the sensitizer and substrate are sufficiently soluble even in near-critical CO_2 that contains 0.5 M methanol, which probably functions as a cosolvent (or so-called “entrainer”) to enhance the solubility.

Obviously, the abrupt ee leap observed in the transition region (from the near-critical to the supercritical region) indicates a sudden change in the surroundings of the sensitizer and/or the exciplex intermediate, probably the structure and properties of cluster around the exciplex that determines the stereochemical outcome of the alcohol attack. The scattered ee plot in the near-critical region may be related not to the partial deposition of substrate or sensitizer but rather to the fluctuation of alcohol clustering since the product’s ee is not appreciably affected by the concentration of substrate or sensitizer.[8,9] To more quantitatively analyze this unique pressure-dependence behavior of ee, we calculated the differential activation volume ($\lvert\Delta\Delta V^{\ddagger}_{R-S}\rvert = \lvert\Delta V^{\ddagger}_{R} - \Delta V^{\ddagger}_{S}\rvert$) at $T = 318$ K (or 45 °C) for each of the near-critical, transition, and supercritical regions by using eq 1:[22]

$$\ln(k_R/k_S) = -(\Delta\Delta V^{\ddagger}_{R-S}/RT)P + C \qquad (1)$$

where R stands for the gas constant and C for the intrinsic enantiodifferentiation at zero pressure, i.e., the $\ln(k_R/k_S)$ value at $P = 0$. The $\lvert\Delta\Delta V^{\ddagger}_{R-S}\rvert$ values calculated from the data obtained in the near-critical (7.7−9 MPa), transition (9−10 MPa), and supercritical (10−18 MPa) regions are shown in Table 2. It is noted that, apart from the extraordinarily large values (290−850 cm^3 mol^{-1}) tentatively assigned for the transition region, the $\lvert\Delta\Delta V^{\ddagger}_{R-S}\rvert$ values for the supercritical region (22−26 cm^3 mol^{-1}) and for the near-critical region (60−210 cm^3/mol) are 1−2 orders of magnitude larger than those (1−2 cm^3 mol^{-1}) obtained for the same photoreaction performed in conventional organic solvents under pressure.[22] These results indicate that the difference in volume between the diastereomeric transition states, leading to (*R*)- and (*S*)-**4**, are much larger in the supercritical region and specifically in the near-critical region than in organic solvents, which is probably one of the unique features of near-critical and supercritical media originating from the clustering effect. This means that the product’s ee is more efficiently controlled by pressure in the following order: near-critical > supercritical ≫ conventional organic media. In this connection, Kim and Johnston have reported that the activation volume and the ratio of the local versus bulk density are correlated to the compressibility of SCFs,[23] and Ikushima et al. have also observed similar behavior near the critical density in the Diels−Alder reaction of isoprene with methyl acrylate.[24] Such unique behavior has been attributed to the density fluctuation of SCF.[25]

Supercritical CO_2 versus Conventional Solvents. It is interesting to further examine the medium effects on the present photochirogenesis by comparing the results obtained in $scCO_2$ with those in conventional organic solvents. The chemical and optical yields of alcohol adducts **4a**−**c** obtained upon photosensitizations with DAF 1,4-naphthalenedicarboxylate (**6a**) in $scCO_2$ at 18 MPa and in conventional solvents are listed in Table 3. As reported previously,[8,9] the product’s ee increases with increasing solvent polarity from methylcyclohexane to toluene and then to ether. It should be noted, however, that the use of more polar solvents, such as methanol and acetonitrile, leads to a dramatic decrease of ee as a result of dissociation of the intervening exciplex to a solvent-separated radical ion pair. Hence, the precise manipulation of solvent polarity is extremely crucial to overcome the tradeoff relationship between the chemical and optical yields.

The steric bulk of attacking alcohol plays another important role in determining the product’s ee. Thus, in methylcyclohexane (MCH) and toluene solutions, the product’s ee consistently increases with increasing bulkiness of alcohol to reach the highest values of 25% (MCH) and 32% (toluene) for **4c** upon irradiation with 2-propanol (Table 3). In ether solutions, the ee was similarly enhanced from 27% (**4a**) to 34% (**4b**) by increasing the alcohol’s bulk from methanol to ethanol. However, the use of bulkier 2-propanol did not further improve the ee but simply afforded comparable 35% ee for **4c**, as if there is an apparent ceiling value of ee in organic solvents. In this context, it is interesting that the ee obtained in $scCO_2$ (18 MPa) smoothly increases with increasing bulkiness of alcohol from 21% (**4a**) to 28% (**4b**) and then to the highest value of 42% for **4c**, without encountering such a ceiling phenomenon (Table 3). As demonstrated for alcohols used as an entrainer in $scCO_2$ extraction,[26] tight clustering and appreciably increased nucleophilicity of alcohol to the exciplex intermediate in $scCO_2$ would be responsible for the continued enhancement of ee throughout the alcohol series up to 2-propanol.

It is to note that, while serving as an environmentally benign reaction medium, $scCO_2$ enables us to overcome the apparent limitation of conventional organic solvents in enhancing the product’s ee. To explore the general validity of such unique pressure dependence and also to obtain a better ee, we employed a higher homologue, 1,1-diphenyl-1-butene (**2**), as a new substrate in the following experiments.

Effects of Vinylic Substituent’s Bulk. In the previous studies,[8,9] we demonstrated that 1,1-diphenyl-1-butene **2**, possessing a larger ethyl substituent at the vinylic C-3, consistently affords higher ee’s than 1,1-diphenylpropene **1** under the comparable conditions. This prompted us to examine the effects of the substituent’s bulk on the enantiodifferentiating photoaddition in $scCO_2$ at varying pressure by using **2** as a bulkier substrate and saccharide and 1-methylheptyl naphthalenedicarboxylates **6a** and **6b** as chiral sensitizers. The chemical and optical yields of photoproduct **5a**, determined by chiral GC, are summarized in Table 4, along with the conversion.

The optical yields of methanol adduct **5a** (34% ee) obtained from **2** upon photosensitization with **6a** in $scCO_2$ (18 MPa) are

TABLE 3: Enantiodifferentiating Photoaddition of Various Alcohols to 1,1-Diphehylpropene 1 Sensitized by DAF 1,4-Naphthalenedicarboxylate 6a in $scCO_2$[a] and Organic Media[b]

R^2OH	medium	pressure MPa	temp /°C	irradiation time/h	conversion /%	yield/%[c]	ee/%[d]
MeOH (**3a**)	methylcyclohexane (MCH)	0.1	25	24	82	54	−4.7
	toluene	0.1	25	24	75	47	−15.7
	ether	0.1	25	24	82	32	−27.0
	$scCO_2$	18.0	45	1	41	32	−20.7
EtOH (**3b**)	MCH	0.1	25	24	84	52	−9.5
	ether	0.1	25	24	80	23	−34.0
	$scCO_2$	18.0	45	2	31	38	−27.6
i-PrOH (**3c**)	MCH	0.1	25	24	64	30	+24.9
	toluene	0.1	25	24	57	27	+31.6
	ether	0.1	25	24	65	43	+35.0
	$scCO_2$	18.0	45	4	36	17	+42.3

[a] [**1**] = 2 mM; [**6a**] = 0.3 mM; [**3a**−**c**] = 0.5 M. [b] [**1**] = 20 mM; [**6a**] = 3 mM; [**3a**−**c**] = 0.5 M. [c] Chemical yield based on the consumption of the starting material. [d] Enantiomeric excess determined by chiral GC; error <0.3% ee.

TABLE 4: Enantiodifferentiating Photoaddition of Methanol 3a to 1,1-Diphenyl-1-butene 2 Sensitized by Chiral Naphthalenedicarboxylates 6a and 6b in $scCO_2$ at 45 °C[a]

sensitizer	pressure/MPa	conversion/%	yield/%[b]	ee/%[c]
1,4-Np(DAF)$_2$ (**6a**)	8.0	59	*d*	−10.3
	8.6	35	17	−13.3
	9.2	44	36	−19.2
	9.7	33	35	−24.7
	10.2	32	28	−31.8
	12.0	17	25	−32.5
	18.3	5	77	−33.5
1,4-Np(Oct)$_2$ (**6b**)	8.1	31	51	+0.5
	8.5	43	33	+1.5
	9.1	30	28	+0.6
	9.6	15	34	+2.5
	10.0	12	28	+3.7
	10.2	10	34	+3.8
	12.0	2	35	+5.1
	18.0	3	10	+8.0

[a] [**2**] = 2 mM; [Sens*] = 0.3 mM; [MeOH] = 0.5 M; irradiated for 2 h. [b] Chemical yield based on the consumption of the starting material. [c] Enantiomeric excess determined by chiral GC; error <0.3% ee. [d] Not determined.

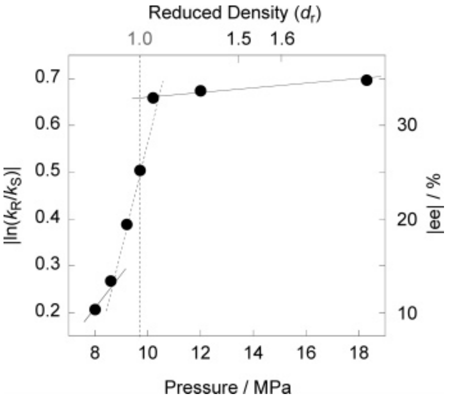


Figure 2. Pressure dependence of the relative rate constant (k_R/k_S), or the product's ee, in the enantiodifferentiating photoaddition of **3a** to **2** sensitized by **6a** in $scCO_2$ at 45 °C.

significantly larger than those of methanol adduct **4a** (5−27% ee) obtained from **1** in both $scCO_2$ (18 MPa) and conventional organic solvents (Table 3). The ee values of **5a** obtained by using **6a** and **6b** are plotted as a function of pressure in Figures 2 and 3. Again, abrupt changes are clearly seen near the critical density, indicating that this phenomenon is a rather general feature of the photochirogenesis in near-critical and supercritical media. However, the original ability of chiral sensitizers does not appear to be significantly changed by the medium employed, and hence the saccharide sensitizer **6a** consistently affords better ee's than the chiral alkyl sensitizer **6b**.

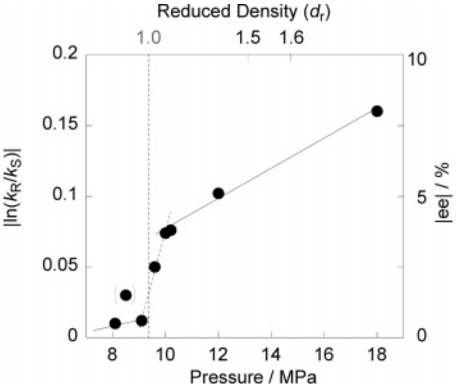


Figure 3. Pressure dependence of the relative rate constant (k_R/k_S), or the product's ee, in the enantiodifferentiating photoaddition of **3a** to **2** sensitized by **6b** in $scCO_2$ at 45 °C.

TABLE 5: Differential Activation Volumes ($|\Delta\Delta V^{\ddagger}_{R-S}|$/$cm^3$ mol^{-1}) Calculated for the Enantiodifferentiating Photoaddition of Methanol 3a to 1,1-Diphenyl-1-butene 2 Sensitized by 6a and 6b in Near-Critical, Transition, and Supercritical Pressure Regions of CO_2

	$|\Delta\Delta V^{\ddagger}_{R-S}|$/$cm^3$ mol^{-1}		
sensitizer	8−9 MPa	9−10 MPa	10−18 MPa
6a	*a*	(610)[b]	10
6b	*a*	(150)[b]	28

[a] Not calculated due to the limited number of available data points. [b] Tentative values due to the transition nature of this pressure region between the near-critical and supercritical states.

To more quantitatively analyze the pressure-dependence behavior, the differential activation volumes ($|\Delta\Delta V^{\ddagger}_{R-S}|$) were calculated from the slope of the plots in Figures 2 and 3, by using the equation derived in the previous studies.[20,21] Due to the discontinuous nature of the plots, we determined the $|\Delta\Delta V^{\ddagger}_{R-S}|$ values for the near-critical and supercritical regions but only as tentative values for the transition area. The $|\Delta\Delta V^{\ddagger}_{R-S}|$ values in $scCO_2$, shown in Table 5, are comparable to those obtained with substrate **1** (Table 2) but much (at least 1 order of magnitude) larger than those reported for organic solvents. Although no $|\Delta\Delta V^{\ddagger}_{R-S}|$ value is calculated for the near-critical region due to the limited number of data points available, the tentative $|\Delta\Delta V^{\ddagger}_{R-S}|$ values calculated for the transition region are also extremely large. We may conclude therefore that the sudden jump of ee near the critical density is a fairly common phenomenon observed for uni- and bimolecular

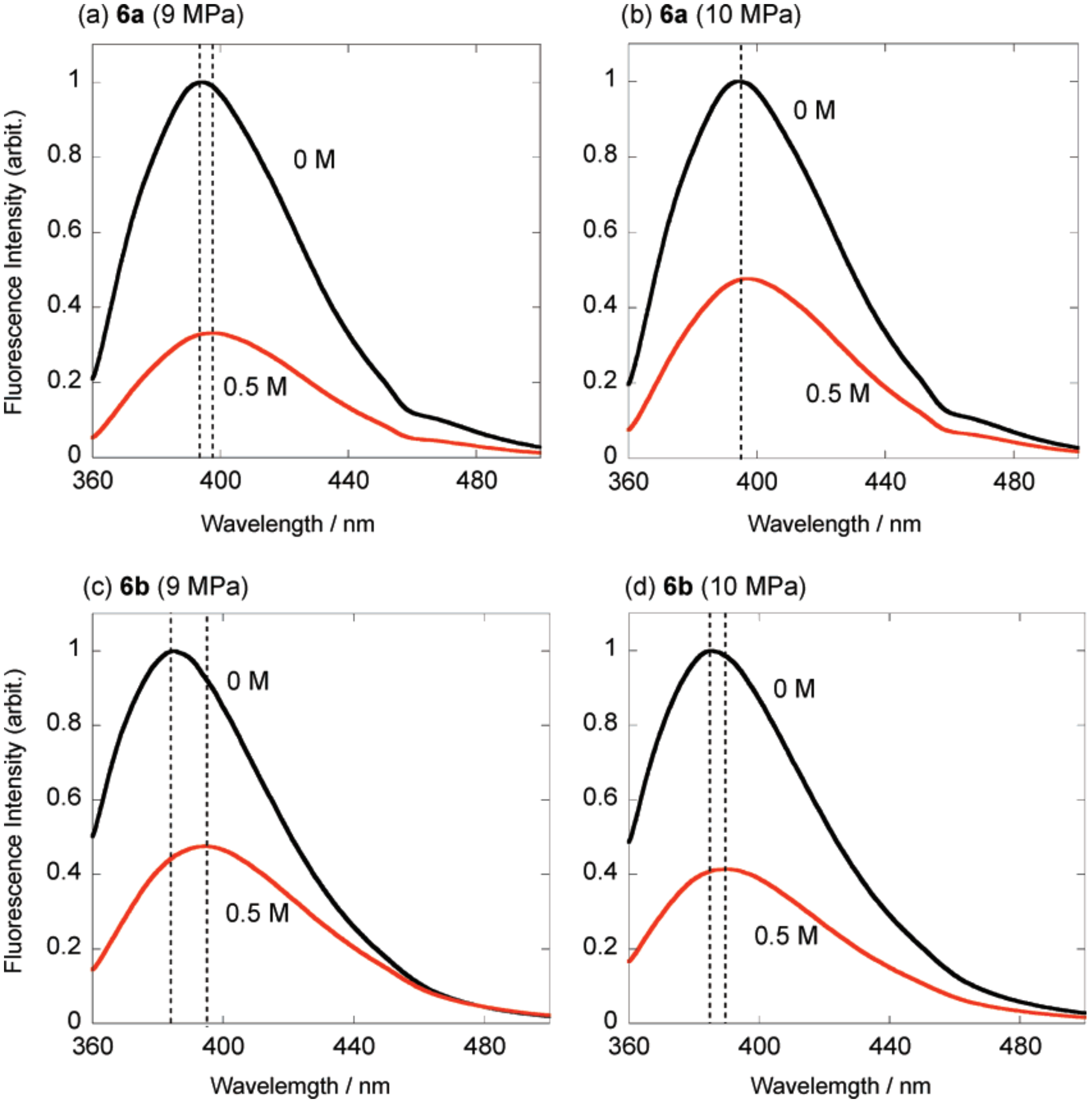


Figure 4. Fluorescence spectra of DAF and 1-methylheptyl 1,4-naphthalenedicarboxylates **6a** (0.01 mM) and **6b** (0.035 mM) excited at 340 nm in the presence and absence of methanol **3a** (0, 0.5 M) in (a and c) near-critical (9 MPa) and (b and d) supercritical (10 MPa) CO_2 media at 45 °C.

photochirogenic reactions and enables us to obtain the best ee in $scCO_2$ rather than conventional organic media.

Fluorescence Spectral Behavior of Chiral Sensitizers in $scCO_2$. As demonstrated in this and previous studies,[19,20] the abrupt change of the product's ee near the critical density is a feature common to both uni- and bimolecular enantiodifferentiating photoreactions performed in CO_2 media. Thus, the nature of intervening excited species and also the detailed enantiodifferentiation mechanism can be appreciably different in near-critical versus supercritical media. It is well-known that fluorescence spectrum is a good measure of the charge-transfer nature of relevant species,[27] and the local polarity around a solute molecule or complex can be deduced from the fluorescence measurement.[27−34] Hence, we investigated the fluorescence spectral behavior of saccharide and chiral alkyl ester sensitizers **6a** and **6b** in near-critical (9 MPa) and supercritical (10 MPa) CO_2 media at 45 °C in the presence and absence of methanol. The results are presented in Figure 4 and Table 6; note that a direct comparison of fluorescence intensity between the spectra taken in near-critical and supercritical CO_2 is not appropriate due to the difference in sample solubility (concentration) in near-critical and supercritical CO_2.

TABLE 6: Fluorescence Maxima (λ_{max}) and Full Width at Half-Maxima (fwhm) for DAF and 1-Methylheptyl 1,4-Naphthalenedicarboxylates (6a and 6b) Excited at 340 nm in Near-Critical (9 MPa) and Supercritical (10 MPa) CO_2 Media at 45 °C in the Presence and Absence of Methanol

		near-critical CO_2 (9 MPa)		supercritical CO_2 (10 MPa)	
sensitizer	[MeOH]/M	λ_{max}/nm	fwhm/nm	λ_{max}/nm	fwhm/nm
6a	0	394	60	394	61
	0.5	398 (+4)[a]	65 (+5)[a]	396 (+2)[a]	61 (±0)[a]
6b	0	385	61	385	63
	0.5	395 (+10)[a]	67 (+6)[a]	391 (+6)[a]	66 (+3)[a]

[a] Changes in λ_{max} and fwhm induced by the addition of 0.5 M methanol.

Upon addition of 0.5 M methanol, the fluorescence peak position (λ_{max}) and width (full width at half-maximum, fwhm) showed only negligible changes (0−2 nm) in supercritical CO_2 but exhibited a larger peak shift (by 4 nm) and broadening (by 5 nm) in near-critical CO_2, as shown in Figure 4 and Table 6. These results reveal that the clustering of polar methanol around excited **6a** is relatively weak in supercritical CO_2 and only slightly influences the fluorescence behavior. In contrast, the methanol clustering is rather strong in more gaseous near-critical CO_2, enough to induce the appreciable shift and broadening of the fluorescence peak. Such distinction in sensitizer photophysics

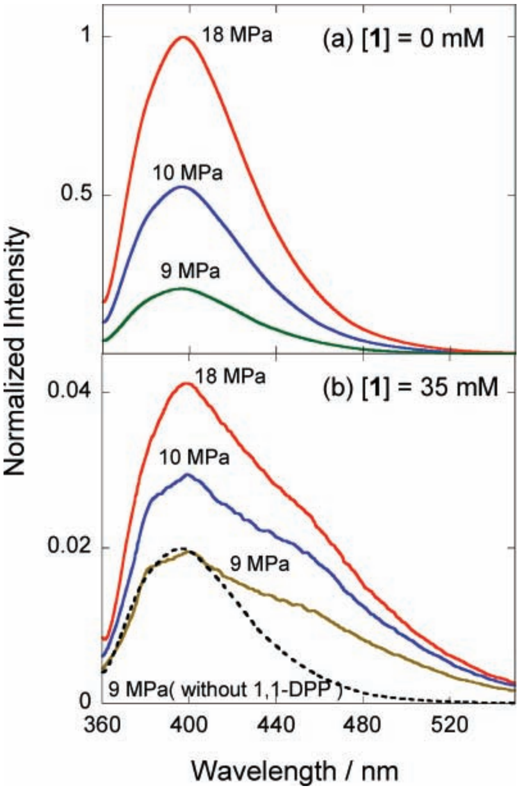


Figure 5. Fluorescence spectra of DAF 1,4-naphthalenedicarboxylate **6a** (0.065 mM) excited at 340 nm (a) in the absence and (b) in the presence of 1,1-diphenylpropene **1** (35 mM) in near-critical (9 MPa) and supercritical (10 and 18 MPa) CO$_2$ at 45 °C; the dotted line in the bottom of panel b indicates the normalized spectrum of **6a** in the absence of **1** at 9 MPa.

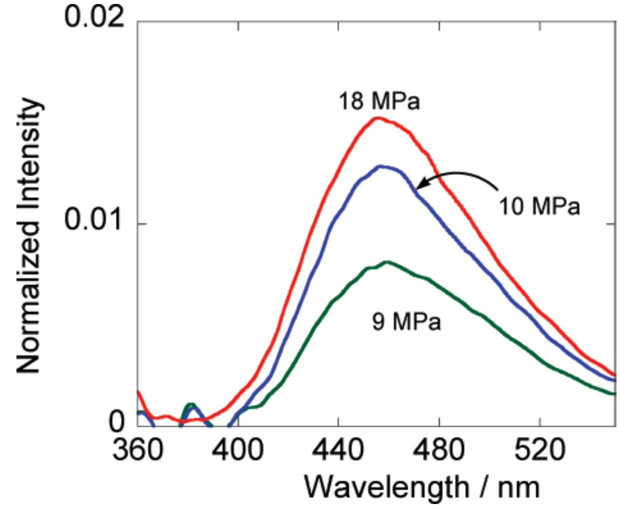


Figure 6. Exciplex fluorescence spectra obtained by subtraction of the spectra of **6a** in the presence (Figure 5b) and absence (Figure 5a) of substrate **1** at the same pressure.

is probably related to the completely different photochirogenic behavior observed in near-critical versus supercritical CO$_2$, and therefore we further investigated the fluorescence spectral behavior of the exciplex intermediate in the presence and absence of added methanol to obtain more direct evidence for the active role of methanol clustering particularly in near-critical CO$_2$.

The fluorescence spectral behavior of alkyl naphthalenedicarboxylate **6b** is more interesting, displaying larger changes in λ_{max} and fwhm upon addition of methanol. Thus, the original fluorescence of **6b** appears at 385 nm in both near-critical and supercritical CO$_2$, which is shorter in wavelength by 7 nm than that of **6a** (392 nm). Addition of 0.5 M methanol caused bathochromic shifts of 10 and 6 nm with accompanying band broadening of 6 and 3 nm in near-critical and supercritical CO$_2$, respectively. The induced peak shift and broadening are appreciably larger for alkyl ester **6b** than for saccharide ester **6a**, indicating that the saccharides in **6a**, working as built-in dipoles, enhance the microenvironmental polarity around the naphthalene fluorophore to induce the bathochromic shift even in the absence of methanol. However, the fluorescence maxima of **6a** and **6b** become closer in position upon addition of 0.5 M methanol; i.e., λ_{max} = 395−398 nm in near-critical CO$_2$ and 391−396 nm in supercritical CO$_2$. Irrespective of the ester moiety attached, the bathochromic shifts caused by the addition of the same concentration of methanol are consistently larger by 4 nm (or 0.7 kcal mol^{-1} in energy) in near-critical CO$_2$ than in supercritical CO$_2$, which may be rationalized by stronger clustering of methanol in near-critical CO$_2$.

TABLE 7: Fluorescence Maxima (λ_{max}) of Sensitizer 6a and Its Exciplex with Substrate 1 upon Excitation at 340 nm, as Well as the Peak Shift ($\Delta\lambda_{max}$) and Energy Difference (ΔE) Caused by Exciplex Formation, in Near-Critical (9 MPa) and Supercritical (10 and 18 MPa) CO$_2$ at 45 °C and in Conventional Solvents at 25 °C

media	temp /°C	pressure /MPa	λ_{max}/nm		$\Delta\lambda_{max}$/nm (ΔE/kcal mol^{-1})^b	ref
			sensitizer	exciplex^a		
near-critical CO$_2$	45	9	394	459	65 (10.4)	*c*
supercritical CO$_2$	45	10	394	457	63 (10.1)	*c*
		18	396	456	60 (9.6)	*c*
methylcyclohexane	25	0.1	396	459	63 (10.0)	*d*
diethyl ether	25	0.1	405	463	58 (9.0)	*e*
acetonitrile	25	0.1	418	*f*	*f*	*e*
toluene	25	0.1	420	462	42 (6.2)	*d*

[a] Exciplex fluorescence obtained by spectrum subtraction; error <2 nm. [b] $\Delta\lambda_{max} = \lambda_{max}(\text{exciplex}) - \lambda_{max}(\text{sensitizer})$; $\Delta E = \Delta E(\text{sensitizer}) - \Delta E(\text{exciplex})$. [c] This work. [d] Ref 8. [e] Ref 9. [f] Exciplex emission not observed.

Fluorescence Spectral Behavior of Exciplex in scCO$_2$. The fluorescence behavior of an exciplex has rarely been investigated in SCF. Inomata et al. reported that the fluorescence intensity of a pyrene−*N*,*N*-dimethylaniline exciplex decreases with increasing pressure in near-critical and supercritical CO$_2$.[30] A few photophysical studies on other systems have also been done more recently.[33,35] In our photochirogenic system, the exciplex intermediate, rather than the excited sensitizer, plays the key role in determining the reactivity and selectivity of the enantiodifferentiating photoaddition.[8,9] Hence, we tried to elucidate the nature of exciplex species by examining and comparing the fluorescence spectral behavior in near-critical and supercritical CO$_2$ media.

First, we measured the fluorescence spectra of sensitizer **6a** in the presence and absence of substrate **1** in near-critical (9 MPa) and supercritical (10 and 18 MPa) CO$_2$ at 45 °C without adding methanol. As shown in Figure 5a, the fluorescence intensity of **6a** was increased with increasing pressure, probably reflecting the solubility enhancement. The addition of substrate **1** (35 mM) to the same solution dramatically quenched the fluorescence of **6a** at all pressures examined with accompanying development of a new peak (shoulder) at longer wavelengths, which is assignable to the exciplex fluorescence, as illustrated in Figure 5b. Subtraction of the normalized fluorescence spectrum of **6a** (Figure 5a) from the obtained spectrum (Figure 5b) affords the exciplex fluorescence spectrum at each pressure. The results are shown in Figure 6 andsummarized in Table 7, along with the relevant data in conventional solvents.[9]

As can be seen from Table 7, the sensitizer fluorescence is insensitive to pressure, but the exciplex fluorescence is more or less affected by the pressure in CO_2 media. Thus, appreciably better stabilization of up to 0.8 kcal mol^{-1} (or 1.4 kcal mol^{-1} if ether is taken as a reference solvent) is achieved upon exciplex formation in near-critical CO_2 than in supercritical CO_2 or conventional organic solvents (although the direct comparison of the spectral data in organic solvents at a different temperature would be risky). However, the observed effect is rather small in the absence of methanol that is expected to cluster more strongly. Hence, we further attempted to measure the exciplex fluorescence in the presence of added methanol but, unfortunately, failed to detect any meaningful signal beyond the noise level. The complete loss of fluorescence in the presence of methanol would be attributable to the very strong methanol clustering in near-critical and supercritical CO_2 of low polarity. We have previously demonstrated that the fine-tuning of solvent polarity is essential in optimizing the product's ee in this photochirogenic reaction and the best ee's are obtained in moderately polar solvents such as dialkyl ether,[8,9] where the substrate moiety of the exciplex is sufficiently electron-deficient to accept the nucleophilic attack of the alcohol but the charge-transfer character of the exciplex is not enough to give a solvent-separated (or free) radical ion pair which is totally useless in view of chirality induction. Similarly, we speculate that the strong clustering of methanol particularly in near-critical CO_2 (as demonstrated in the fluorescence spectral examinations mentioned above) ruptures the exciplex at least in part to give generally lower ee's.

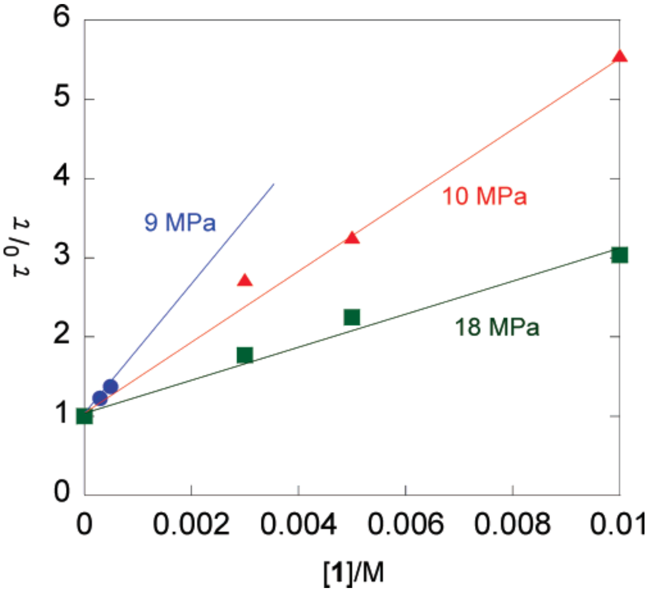


Figure 7. Stern−Volmer plots obtained for the fluorescence quenching of DAF 1,4-naphthalenedicarboxylate **6a** (0.01 mM) with 1,1-diphenylpropene **1** (0−10 mM) in near-critical (9 MPa) and supercritical (10 and 18 MPa) CO_2 media.

TABLE 8: Fluorescence Lifetime (τ) of 6a (0.05 mM) with 1 (0−10 mM) in Near-Critical (9 MPa) and Supercritical (10 and 18 MPa) CO_2 Media at 45 °C

media	pressure /MPa	[**1**]/mM	τ/ns[a]
near-critical CO_2	9	0	6.7
		0.3	5.5
		0.5	4.9
supercritical CO_2	10	0	6.9
		3	2.5
		5	2.1
		10	1.2
supercritical CO_2	18	0	6.6
		3	3.7
		5	2.7
		10	2.3

[a] Error <0.5 ns.

Stern−Volmer Study: Fluorescence Quenching of 6a by 1 in CO_2 Media. It is of particular interest to examine the fluorescence quenching in such highly diffusive low-density media as near-critical and supercritical CO_2. Since the fluorescence intensity is not very reliable or reproducible in SCF experiments performed in high-pressure vessels, the fluorescence lifetime is used for the Stern−Volmer quenching experiment.[36−41] Hence, we also measured the fluorescence lifetime in a high-pressure vessel (with three quartz windows) precisely mounted in the sample chamber of a fluorimeter. The quantitative fluorescence quenching experiments were done by the following procedures: first, an ether solution of **6a** (0.01 mM) and **1** (0−10 mM) was placed in the vessel, the solvent was evaporated under a reduced pressure, the void space of the vessel was purged three times with CO_2 gas, and finally the vessel was charged with $scCO_2$ at a given temperature and pressure. Each sample, containing a fixed amount of **6a** and a varying amount of quencher **1** (0−10 mM) was measured at three different pressures (9, 10, and 18 MPa) to give the results shown in Table 8.

At all pressures examined, the fluorescence of **6a** was efficiently quenched by **1**, and the results were analyzed by using the Stern−Volmer equation (eq 2)[42] to give the plots shown in Figure 7.

TABLE 9: Stern−Volmer Constant ($k_Q\tau$), Fluorescence Lifetime (τ), and Quenching Rate Constant (k_Q) Obtained by Fluorescence Quenching of 6a (0.05 mM) with 1 (0−10 mM) in Near-Critical (9 MPa) and Supercritical (10 and 18 MPa) CO_2 Media at 45 °C and in Conventional Solvents at 25 °C

media	temp /°C	pressure /MPa	k_{diff} /10^{10} M^{-1} s^{-1} [a]	$k_Q\tau$ /M^{-1} [b]	τ /ns[c]	k_Q /10^{10} M^{-1} s^{-1}	ref
near-critical CO_2	45	9	26	730	6.7	11	*d*
supercritical CO_2	45	10	19	450	6.9	6.5	*d*
		18	9.7	200	6.6	3.0	*d*
methylcyclohexane	25	0.1	0.99	31	5.8	0.54	*e*
diethyl ether	25	0.1	3.0	75	8.6	0.88	*f*
acetonitrile	25	0.1	1.8	89	10.5	0.85	*f*
toluene	25	0.1	1.2	11	11.6	0.094	*e*
methanol	25	0.1	1.2	40	5.8	0.69	*d*

[a] Diffusion rate constant in CO_2 media at 45 °C (ref 22) and in organic solvents at 25 °C (ref 43). [b] Stern−Volmer constant obtained by analyzing the data in Figure 7 with eq 2. [c] Fluorescence lifetime of **6a** (0.05 mM) determined independently in the absence of **1** by single-photon-counting technique; error <0.5 ns. [d] This work. [e] Ref 8. [f] Ref 9.

$$\tau^0/\tau = 1 + k_Q\tau^0[\mathbf{1}] \qquad (2)$$

where τ and τ^0 refer to the fluorescence lifetimes in the presence and absence of quencher **1** and k_Q is the quenching rate constant.

The Stern−Volmer plot gave a good straight line at each pressure (Figure 7), from the slope of which we obtained the Stern−Volmer constant ($k_Q\tau$) in near-critical and supercritical CO_2, as listed in Table 9. Interestingly, the Stern−Volmer constants obtained in near-critical and supercritical CO_2 are 1 order of magnitude larger than those obtained in conventional organic solvents. In order to determine the quenching rate constant k_Q, we measured the fluorescence lifetime of **6a** (τ^0) in the absence of quencher by using the single-photon-counting technique. As listed in Table 9, the lifetimes obtained in diverse media did not greatly differ, ranging from 5.8 to 11.6 ns. Although the lifetime becomes longer in polar aprotic or aromatic solvents, no clear gap exists in the lifetime either between the organic and CO_2 media or between the near-critical and supercritical CO_2. From the fact that the fluorescence lifetime of sensitizer is insensitive to the CO_2 pressure and is practically the same in all CO_2 media examined, we may further suggest that the exciplex intermediate with a charge-transfer character plays the major roles in determining the photochirogenic behavior in near-critical and supercritical CO_2 in view of the much larger pressure dependence observed in the product's ee and in the exciplex fluorescence behavior.

It is also interesting that the unusually large Stern−Volmer constants of up to several hundreds are attributable solely to the very fast fluorescence quenching by substrate **1**, and the quenching rate constant (k_Q) amounts to 3.0×10^{10} M^{-1} s^{-1} in supercritical CO_2 and even to 1.1×10^{11} M^{-1} s^{-1} in near-critical CO_2. For fluorescence quenching of 9,10-dimethylanthracene and 9,10-dicyanoanthracene by oxygen, Okamoto et al. reported the rate constants of 4×10^{10} and 1×10^9 M^{-1} s^{-1} in supercritical CO_2 at 10 MPa and 35 °C, respectively.[38] Bunker et al. reported the fluorescence quenching rate constants for anthracene, perylene, 9-cyanoanthracene, and 9,10-diphenylanthracene upon addition of carbon tetrabromide to be $2-4 \times 10^{10}$, $2-5 \times 10^{10}$, $1-2 \times 10^{10}$, and $2-6 \times 10^{10}$ M^{-1} s^{-1} in near-critical and supercritical CO_2 at 35 °C.[41] These results are compatible with our present data, indicating that the fluorescence quenching is more or less faster in near-critical and supercritical CO_2 media than in organic solvents. In the present case, the quenching rate constants are obviously 1−2 orders of magnitude faster than those observed in conventional solvents but do not exceed the diffusion limit in CO_2 media[22] (Table 9). We may conclude therefore that the quenching is not a static but a diffusion-controlled dynamic process even in $scCO_2$.

Conclusions

Despite the unique features as highly fluctuating, clustering, and "green" media, SCFs have rarely been employed as reaction media particularly in photochirogenesis studies. In the present study to expand the scope of photochirogenesis in SCF, we have investigated the bimolecular enantiodifferentiating polar addition of alcohols to aromatic alkenes in $scCO_2$ to find several intriguing phenomena, which are summarized and rationalized as follows: (1) The product's ee displays a dramatic jump near the critical density. Such a sudden change in ee appears to be common to uni- and bimolecular photochirogeneses in SCF media and may be used as a convenient tool for controlling the product selectivity not only in photochirogenesis but also in a wide variety of (photo)reactions. (2) The photochirogenesis in $scCO_2$ gives comparable or even higher ee's than that in conventional solvents. This is an encouraging result to further promote the photochirogenesis studies. (3) The clustering of alcohol added as a reagent (and also as an entrainer) dominates both the photophysical properties and the photochemical (stereochemical) consequences of excited sensitizer and exciplex intermediate, and hence the choice of alcohol and its concentration are critical factors for controlling the photochirogenesis. (4) The clustering of polar entrainer becomes stronger in the near-critical region, which is the major cause of the lowered ee's in the present case. (5) The fluorescence quenching is dynamic and extremely fast in supercritical CO_2 and even faster in near-critical CO_2, although the rate constant never exceeds the diffusion limit.

Experimental Section

Materials. Carbon dioxide of 99.99% purity was purchased from Neriki Gas Co. and used without further purification. Spectral grade solvents were used throughout the work. 1,1-Diphenyl-1-alkenes **1** and **2** and chiral sensitizers **6a** and **6b** were synthesized and characterized, as described previously.[8,9]

Instruments. Fluorescence lifetimes of the sensitizers were determined by the time-correlated single-photon-counting technique, using a Hamamatsu Photonics FL920S instrument equipped with a pulsed H_2 light source. The emission from the sample solution (0.01 mM) was detected through a UV-37 (Toshiba) glass filter. A high-pressure vessel (SUS-316) equipped with three sapphire windows (manufactured by Teramex Co., Kyoto) was used for spectroscopy and photoreaction. Enantiomeric excesses of **4a**−**c** and **5a** were determined by chiral gas chromatography on a 30 m ASTEC B-PH column for **4a** (operated at 140 °C; retention times 49−50 min), **4b** (operated at 140 °C; retention times 53−54 min), and **5a** (operated at 145 °C; retention times 55−56 min) or a 30 m ASTEC B-DM column for **4c** (operated at 115 °C; retention times 113−114 min). Under these GC conditions, racemic samples prepared separately by using achiral dimethyl 1,4-naphthalenedicarboxylate as sensitizer gave ee's smaller than 0.3% ee upon repeated analyses.

Photolysis. Samples were charged in the high-pressure vessel as follows. First, an ether solution containing given amounts of substrate **1** and sensitizer **2** was placed in the vessel and the solvent was evaporated under vacuum to leave a residue, to which a given amount of alcohol was added. Then the vessel was closed, and carbon dioxide was introduced to the vessel until the desired pressure (7.7−18.3 MPa) was reached at the fixed temperature (45.0 ± 0.1 °C). Unfiltered light from a 500 W ultrahigh-pressure mercury lamp was collimated, passed through a water layer and a UV-32 or UV-31 filter, and then focused in front of the sapphire window with a quartz lens. The phase homogeneity inside the vessel was visually checked through the window. After irradiation for a given period of time at 45.0 °C, the vessel was cooled down to 0 °C and the pressure was released at that temperature. The effluent from the vessel outlet was gently bubbled into ice-cooled hexane or diethyl ether to collect any volatile materials. The residue in the vessel was also extracted with hexane or diethyl ether. Both were combined and subjected to the chiral GC analysis.

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