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Pressure control of enantiodifferentiating polar addition of 1,1-diphenylpropene sensitized by chiral naphthalenecarboxylates

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Received 23rd January 2004, Accepted 10th March 2004
First published as an Advance Article on the web 8th April 2004

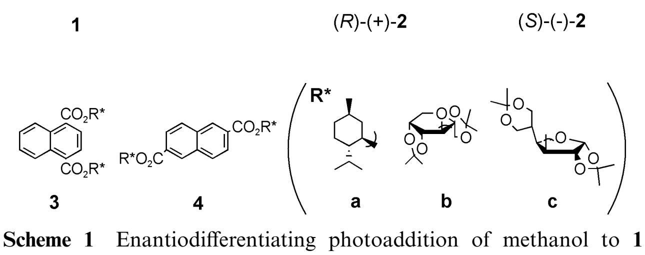
Effects of pressure on the enantiodifferentiating methanol addition to 1,1-diphenylpropene (**1**) sensitized by chiral naphthalenedicarboxylates (**3** and **4**) were investigated over 0.1–400 MPa. The logarithm of enantiomeric excess (ee) of photoadduct, *i.e.* 1,1-diphenyl-2-methoxypropane (**2**), was a linear function of both pressure (P) and temperature (T); further, the product chirality was switched by P in some cases. From the slope of $P - \ln(k_R/k_S)$ plot, the differential activation volume ($\Delta\Delta V^\ddagger$) was determined for the first time for bimolecular asymmetric photoreactions. The $\Delta\Delta V^\ddagger$ values obtained are mostly larger than those obtained for relevant unimolecular photoreactions, and are a critical function of the nature of the chiral auxiliary and solvent, indicating conformation changes of the intervening diastereomeric exciplex or transition state in different solvents. Indeed, fluorescence spectral examinations of the sensitizer and exciplex under high pressure revealed the existence of exciplexes of variable energy and structure, which may rationalize the different $\Delta\Delta V^\ddagger$ and product ee obtained. A three-dimensional diagram, correlating the ee with P and T, was constructed from the pressure dependence data at different T, from which we may propose an idea of the multidimensional control of asymmetric reaction by the combined use of the entropy-related enviromental factors.

Introduction

Asymmetric photochemistry, as a novel access to optically active compounds and an alternative to the conventional catalytic or enzymatic asymmetric syntheses, attracts much attention and interest from both mechanistic and synthetic points of view.[1] In particular, entropy-related factors, such as temperature and solvation, have been shown to critically influence the stereochemical outcome of enantiodifferentiating photosensitized reactions, leading to a dynamic dependence of the optical yield and even to a dramatic switching of the product chirality by these environmental variables.[1c,d,2]

In contrast, the effects of pressure have rarely been explored in asymmetric (photo)chemistry,[3] although hydrostatic pressure is expected to function as an entropy-related factor for controlling the stereochemical consequence through a difference in activation and/or reaction volumes. Recently, we have investigated the effects of pressure upon the enantiodifferentiating geometrical photoisomerizations of (Z)-cyclooctene and (Z,Z)-cycloocta-1,5-diene sensitized by optically active (poly)alkyl benzene(poly)carboxylates.[4,5] It was shown that the enantiomeric excesses (ee's) of chiral photoproducts, *i.e.* (E)-cyclooctene and (E,Z)-cycloocta-1,5-diene, are critically affected by pressure (P) and a switching of product chirality is induced by changing P in an extreme case. The logarithm of relative enantiodifferentiating rate constants was a linear function of P at least in an applied pressure range of 0.1–200 MPa (occasionally, up to 400 MPa) to give moderate to large differential activation volumes (of up to 5.6 $\mathrm{cm^3\ mol^{-1}}$) particularly upon sensitization with *ortho*-benzene(poly)carboxylates.[4] Further attempts to examine the effect of P up to 750 MPa revealed a pressure-induced alternation of the mechanism, leading to a discontinuous pressure dependence of ee. This unexpected behavior was accounted for in terms of the conformational changes of mutually interacting *ortho*-ester moieties in chiral sensitizers, which occur at common pressures of 200 and 400 MPa. Experimentally this hypothesis is supported by discontinuous circular dichroism (CD) spectral changes occurring at the same P's.[5]

However, the pressure dependence study is limited to unimolecular enantiodifferentiation photoisomerizations so far, and no such examination has been done with bimolecular photoreactions, where more complicated excited-state termolecular interactions among chiral sensitizer, substrate and reagent are involved and could be highly susceptible to the environmental factors, such as temperature, solvent, and presumably pressure. To examine the pressure effects on such termolecular chiral interactions in the excited state, we chose the enantiodifferentiating polar photoaddition of methanol to 1,1-diphenylpropene (**1**),[6] which affords chiral anti-Markovnikov adduct (**2**) (Scheme 1). This polar photoaddition is efficiently sensitized by 1,4- and 2,6-naphthalenedicarboxylates (**3** and **4**) carrying optically active alkyl and saccharide auxiliaries, such as **a**–**c** (Scheme 1), to give optically active **2** in moderate to good ee's. The product ee is highly sensitive to the chiral auxiliary, temperature and solvent polarity, reaching the best value of 35% ee upon sensitization with **4c** in diethyl ether at 0 °C.[6b] In the present study, to examine the pressure dependence of the



Scheme 1 Enantiodifferentiating photoaddition of methanol to **1** sensitized by **3a**–**c** and **4a**,**b**.

DOI: 10.1039/b401108b

enantiodifferentiating polar photoaddition, we employed naphthalenedicarboxylates **3** and **4** as sensitizers and terpenoid (**a**), furanose (**b**) and pyranose (**c**) ester groups as chiral alkyl and saccharide auxiliaries, and the factors and mechanisms controlling the pressure dependence of product ee were elucidated from the kinetic and spectroscopic studies at $P = 0.1$–400 MPa.

Results and discussion

Pressure effects on conversion and chemical yield

Photosensitized enantiodifferentiating addition of methanol to **1** (20 mM) was performed at 25 °C in a pressure vessel fitted with sapphire windows for external irradiation at $P = 0.1$–400 MPa in pentane, methylcyclohexane (MCH), toluene and diethyl ether, containing 0.5 M methanol. Irradiation periods of 15–60 min, which are much shorter than the previous ones (4–48 h),[6] were employed in order to keep the conversion low to moderate, which enabled us to more precisely examine the pressure effect on photosensitization efficiency. As shown in Table 1, photosensitization with menthyl ester **3a**, particularly in pentane solution, led to a rapid consumption of **1** and low yields of adduct **2** (<10%), for which photo-induced polymerization and/or oxidation would be responsible, as revealed in the previous studies.[6] However, this is rather an exceptional case, as the conversion-based yields are much better (20–45%) in the other cases, including the photosensitization with **3a** in toluene and ether. Nevertheless, the chemical yield of **2** is a critical function of sensitizer, chiral auxiliary and solvent employed. Thus, 1,4-naphthalenedicarboxylates with saccharide auxiliaries (**3b**,**c**) afford **2** in yields much higher than the corresponding menthyl ester (**3a**) does. This is due to the electron-transfer nature of this photosensitization, which is enhanced by the use of a polar saccharide auxiliary or solvent, although highly polar solvents accelerate the dissociation of photochemically generated radical ion pairs to spoil the chirality transfer from sensitizer to substrate. Hence, a trade-off phenomenon is often observed between chemical and optical yield, which is however overcome in this electron-transfer photosensitization by using a saccharide sensitizer in less-polar solvent. The saccharide moiety enhances the local polarity around the sensitizer to facilitate the electron transfer, while the low bulk polarity prevents the dissociation of radical ion pair, guaranteeing a close mutual contact for efficient chiral transfer.

Obviously, the conversion of **1** gradually decreases with increasing *P*, which may be attributed to a slower attack of substrate to an excited sensitizer due to the increased solvent viscosity at higher *P*'s. This will be examined later by the fluorescence quenching experiment at high *P*. On the other hand, the conversion-based yield appears to be less sensitive to *P*, showing only low to modest dependence on pressure, except for **3a** in MCH. The slow decreases observed for some sensitizers and solvents may be related at least in part to the reaction of radical cationic **1** with remaining oxygen in an argon-purged solution particularly at high *P*, since the oxidation products, *i.e.* benzophenone **5** and racemic epoxide **6**, were detected indeed by GC-MS analysis of the photolyzate obtained at high *P*. Eriksen and Foote reported the formation of analogous products in the photoelectron transfer oxidation of 1,1-diphenylethylene.[7] In the present case, although sample solutions were purged with argon at 0 °C for 3 min, oxygen in the solution and in the dead space of a cell may not completely be eliminated by this treatment, and the increased solubility of oxygen at elevated *P* may facilitate the trapping of radical cationic species. Hence, we performed photosensitization of **1** with **3b** in ether with and without prior argon purge (Table 1). Under identical irradiation conditions, an air-saturated sample afforded slightly lower conversion (49.5%) and yield (13.2%) than those (53.9% conversion and 14.5% yield) obtained with an argon-saturated sample, probably due to the quenching by oxygen. Similarly, an ee of −20.6% was obtained in the presence of air, while a slightly higher ee of −22.0% was obtained under Ar. Another possibility would be photocycloaddition of **1** to naphthalenecarboxylate **3** or **4**, which is known to occur with 1,1-diphenylethylene but not with **1**.[8]

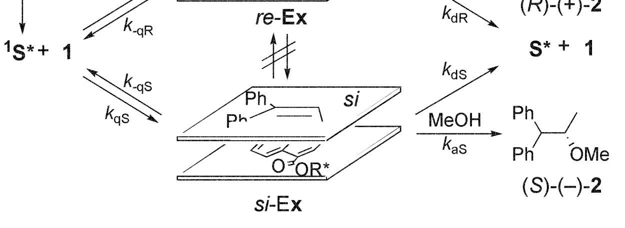
Pressure effect on enantiodifferentiation

As shown in Table 1 (where the sign of ee indicates that of optical rotation of obtained **2**), the menthyl esters **3a** and **4a** afford adduct **2** in low ee's of <4% at ambient *P*, irrespective of the solvent used, and the ee is moderately improved from −3.7% to −7.1% for **3a** and from −1.2% to −5.3% for **4a** by increasing *P* from 0.1 to 400 MPa, while the irradiation in toluene or ether gave almost racemic **2** at all *P*'s examined. In contrast, the sensitizations with saccharide derivatives (**3b**,**c** and **4b**) gave higher ee's (of up to 28%) in most solvents, and interestingly, the switching of product chirality is seen upon sensitization by **3b** in nonpolar pentane and MCH solutions, yielding the antipodes of **2** at the both ends of the examined *P* range; *i.e.* −8.5% ee (0.1 MPa) *versus* +3.1% ee (400 MPa) in pentane and −5.0% ee (0.1 MPa) *versus* +3.5% ee (300 MPa) in MCH. Although the absolute ee values are not particularly high, this is the first example of a pressure inversion of product chirality observed for photosensitized *bimolecular* reactions.

In toluene and ether, the product ee obtained upon photosensitization with **3b**,**c** and **4b** monotonically decreased with increasing *P*, extension of which may also lead to an inversion of product chirality at much higher *P*. Such a gradual decrease in ee would be attributable to the increased methanol concentration by pressure-induced volume contraction, as the product ee is known to decrease at higher methanol concentrations.[7] This interpretation is not compatible with the opposite behavior of ee observed for **3a** and **4a** in MCH and the product chirality switching observed for **3a** in pentane and MCH.

Mechanism

In the previous study,[6] we elucidated the reaction mechanism of this enantiodifferentiating polar photoaddition, which involves the initial formation of an equilibriating diastereomeric exciplex (Ex) pair and the subsequent nucleophilic attack of methanol from the open face. Scheme 2 illustrates the mechanism, where S* denotes chiral sensitizer and k_q and k_{-q} represent the rate constants for the association and dissociation of Ex, k_d the nonradiative decay from Ex, and k_a the addition of alcohol to Ex (the subscripts *S* and *R* refer to the absolute configuration of **2**). Detailed kinetic analyses revealed that the rate-determining methanol attack is less selective but the ratio of the diastereomeric Ex pair is a crucial factor determining the ee of **2**.[6] It is inferred that this fundamental mechanism is not significantly altered even under high pressures of up to 400 MPa, as judged from the smooth pressure-induced changes in photophysical and photochemical behavior, including the absorption



Scheme 2 Mechanism of the enantiodifferentiating photoaddition of methanol to **1** sensitized by chiral naphthalenedicarboxylates (**S***).

Table 1 Enantiodifferentiating photoaddition of methanol to **1** sensitized by chiral naphthalenedicarboxylates (Sens*) at various pressures (*P*) at 25 °C[a]

Sens*	Solvent	*P*/MPa	Irrad. time/min	Conv.[b]/%	Yield[c]/%	Ee[d]/%
3a	MCH[e]	0.1	15	42.7	2.6 (6.1)	−3.7
		100	15	40.2	1.6 (4.0)	−5.0
		200	15	38.2	0.9 (2.3)	−7.4
		300	15	37.4	0.6 (1.7)	−7.1
	Toluene	0.1	15	16.9	4.6 (27.2)	−0.7
		100	15	15.6	4.6 (29.5)	−0.8
		200	15	11.5	3.2 (27.8)	0.2
		300	15	12.6	2.8 (22.2)	−0.6
		400	15	10.9	[f]	0.3
	Diethyl ether	0.1	15	14.7	2.4 (16.3)	1.2
		100	15	13.0	2.1 (16.2)	2.3
		200	15	11.8	1.8 (15.3)	1.7
		300	15	12.2	1.6 (13.1)	1.4
		400	15	9.3	1.7 (18.3)	2.0
3b	Pentane	0.1	30	60.4	9.5 (15.7)	−8.5
		100	30	43.1	8.8 (20.4)	−5.1
		300	30	27.3	6.8 (24.9)	0.6
		400	30	21.7	2.9 (13.4)	3.1
	MCH[e]	0.1	15	7.0	2.2 (31.4)	−5.0
		100	15	5.4	2.2 (40.7)	−0.1
		200	15	6.1	1.6 (26.2)	2.7
		300	15	5.9	1.8 (30.5)	3.5
		400	15	7.4	1.5 (20.3)	2.5
	Toluene	0.1	15	22.5	8.3 (36.9)	−14.7
		100	15	23.5	8.8 (37.4)	−11.7
		200	15	19.4	7.1 (36.6)	−10.7
		300	15	16.6	5.1 (30.7)	−7.3
		400	15	15.0	4.0 (26.7)	−6.0
	Diethyl ether	0.1	15	19.5	7.1 (36.4)	−21.3
			30	19.3	8.5 (44.0)	−18.6
			60	21.3	9.7 (45.5)	−19.1
			60[g]	53.9	14.5 (26.9)	−22.0
			60[h]	49.5	13.2 (26.7)	−20.6
		100	15	14.4	4.9 (34.0)	−15.6
		200	15	15.9	4.9 (30.8)	−13.4
		300	15	16.2	3.7 (22.8)	−3.3
		400	15	13.4	3.1 (23.1)	−7.4
3c	Toluene	0.1	15	30.1	11.7 (38.9)	−9.3
		100	15	27.0	11.4 (42.2)	−6.0
		200	15	23.4	8.5 (36.3)	−4.9
		300	15	19.9	5.5 (27.6)	−2.8
		400	15	17.5	5.1 (29.1)	−1.7
	Diethyl ether	0.1	15	25.4	4.7 (12.7)	−10.5
		100	15	21.8	5.1 (23.4)	−7.5
		200	15	22.1	4.9 (22.2)	−5.9
		300	15	18.3	3.8 (20.8)	−4.4
		400	15	12.4	3.6 (29.0)	−2.1
4a	MCH[e]	0.1	180	17.2	6.6 (38.4)	−1.2
		200	180	14.8	3.5 (23.6)	−7.9
		400	180	6.3	2.4 (38.1)	−5.3
	Diethyl ether	0.1	180	23.0	1.4 (6.1)	0.7
		200	180	16.1	1.4 (8.7)	0.5
		400	180	13.2	1.3 (9.8)	−0.8
4b	Diethyl ether	0.1	60	15.0	1.4 (9.3)	−27.8
		200	60	13.8	1.2 (8.7)	−16.0
		400	60	18.5	[f]	−10.5

[a] [**1**] = 20 mM; [Sens*] = 3 mM; [MeOH] = 0.5 M; unless stated otherwise, irradiation was performed under Ar in a high-pressure vessel with a 250 W ultra-high pressure mercury lamp (Wacom) fitted with a UV-33 glass filter. [b] Loss of **1** determined by GC. [c] Chemical yield determined by GC on the basis of the initial concentration of **1** and the consumed **1** (in parentheses). [d] Enantiomeric excess of **2** determined by chiral GC; error <±0.5%. [e] Methylcyclohexane. [f] Not determined. [g] Irradiation performed in a Pyrex tube with a 300 W high-pressure mercury lamp (reference 7) under Ar. [h] Irradiated as stated in footnote g, but without prior Ar purge.

and fluorescence spectra (both in the presence and absence of methanol) and the product ee.

Activation volume

The above results clearly demonstrate that the critical control by pressure is possible not only for unimolecular[4,5] but also for bimolecular enantiodifferentiating photosensitizations. In the latter process, the intervening Ex and the transition state (TS) are considered to be bulkier in volume and more complicated in structure, involving termolecular sensitizer–substrate–reagent interactions. It is intriguing therefore to quantitatively examine the pressure effect on ee and then to compare the results with those reported for unimolecular processes.[4,5]

The pressure dependence of product ee was quantitatively assessed by the differential volume of activation ($\Delta\Delta V^{\ddagger}_{R-S}$) for the formation of (*R*)- and (*S*)-enantiomers of **2**, which is determined from the slope of eqn. (1):[4,5]

$$\ln(k_{\mathrm{R}}/k_{\mathrm{S}})_T = -(\Delta\Delta V^{\ddagger}_{R-S}/RT)P + \ln(k_{\mathrm{R}}/k_{\mathrm{S}})_{P=0} \qquad (1)$$

Table 2 Differential activation volumes ($\Delta\Delta V^{\ddagger}_{R-S}$) for enantiodifferentiating photoaddition of methanol to **1** sensitized by chiral naphthalenedicarboxylates **3** and **4** at 25 °C

Sens*	Solvent	$\Delta\Delta V^{\ddagger}_{R-S}$/cm^3 mol^{-1}
3a	Methylcyclohexane	+0.6
	Toluene	−0.1
	Diethyl ether	0.0
3b	Pentane	−1.4
	Methylcyclohexane	−1.9
	Toluene	−1.0
	Diethyl ether	−1.7
3c	Toluene	−0.9
	Diethyl ether	−1.0
4a	Methylcyclohexane	+0.5
	Diethyl ether	−0.2
4b	Diethyl ether	−2.2

where k_R and k_S denote the rates of formation of (*R*)-(+)- and (*S*)-(−)-**2** and the relative rate constant (k_R/k_S) is experimentally equivalent to the (100 + %ee)/(100 − %ee) ratio.

As exemplified in Fig. 1, the ln(k_R/k_S) values were plotted against *P* to give a good straight line in each case, indicating that the pressure causes no alternations to the enantiodifferentiation mechanism or to the activation volumes at least in the employed pressure range (0.1–400 MPa). This is a logical consequence of eqn. (1), but is somewhat different from the pressure dependence behavior of the enantiodifferentiating photoisomerization of cyclooctene,[5b] where the *P* − ln(k_R/k_S) plot bends at 200 and 400 MPa only upon sensitization by *ortho*-benzenepolycarboxylates, for which discontinuous pressure-induced conformational changes of the adjacent *ortho*-ester moieties are thought to be responsible. Hence, the single straight lines obtained in the present study may be attributed to the lack of interacting *ortho*-ester moieties and the difference in chromophore (naphthalene *versus* benzene).

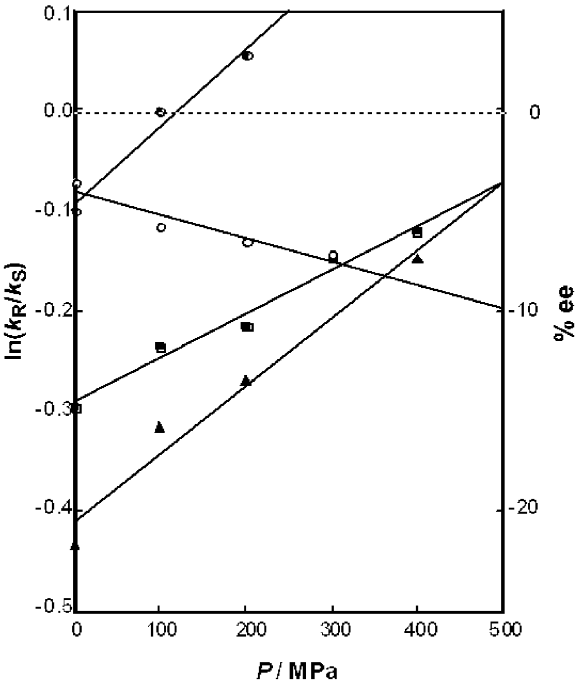


Fig. 1 Pressure dependence of the ee of **2** obtained in the enantiodifferentiating photoaddition of methanol to **1** sensitized by **3a** in methylcyclohexane (○) and by **3b** in methylcyclohexane (●), toluene (■) and diethyl ether (▲) at 25 °C.

Somewhat unexpectedly, the obtained $\Delta\Delta V^{\ddagger}_{R-S}$ values (Table 2), varying from −2.2 to +0.6 cm^3 mol^{-1}, are apparently smaller than those (−4.2 to +5.4 cm^3 mol^{-1}) reported for the unimolecular photoisomerization.[5b] However, this is not a fair comparison, as the latter data contain the values obtained with *ortho*-benzenepolycarboxylate sensitizers; indeed, the $\Delta\Delta V^{\ddagger}_{R-S}$ values for non-*ortho* benzene(di)carboxylates fall in a much narrower range of −0.12 to +0.36 cm^3 mol^{-1}.[4] Hence, we may conclude with some reservations (due to the limited amount of the $\Delta\Delta V^{\ddagger}_{R-S}$ data available for the bimolecular photoreactions) that bimolecular, rather than unimolecular, photoreactions are more sensitive to pressure change. Comparable $|\Delta\Delta V^{\ddagger}|$ values were reported for the diastereoselective [2 + 2] photocycloaddition ($|\Delta\Delta V^{\ddagger}|$ = 2.0 cm^3 mol^{-1})[9] and for the enantioselective thermal cycloaddition catalyzed by chiral Lewis acid ($|\Delta\Delta V^{\ddagger}|$ = 1.7 cm^3 mol^{-1}).[3e]

Closer inspections of the obtained $\Delta\Delta V^{\ddagger}_{R-S}$ values shed more light on the difference in volume (and structure) of the Ex or TS. Sensitization with menthyl esters afford moderate, positive $\Delta\Delta V^{\ddagger}_{R-S}$ values in nonpolar MCH (+0.6 and +0.5 cm^3 mol^{-1} for **3a** and **4a**, respectively), indicating that the diastereomeric Ex or TS leading to (*S*)-**2** is more compact and hence favored at higher *P*'s. The small negative $\Delta\Delta V^{\ddagger}_{R-S}$ values in toluene (–0.1 cm^3 mol^{-1} for **3a**) and in ether (0.0 and −0.2 cm^3 mol^{-1} for **3a** and **4a**, respectively) indicate that the precursor Ex/TS to (*R*)-**2** is slightly smaller in volume than the antipodal one in the polar solvents. In contrast, sensitization with the saccharide esters affords relatively large negative $\Delta\Delta V^{\ddagger}_{R-S}$ values of −1.0 to −2.2 cm^3 mol^{-1}, regardless of the solvent polarity. It is noted that (*S*)-**2** is consistently favored at 0.1 MPa in all cases examined, except for the sensitization with **3a** in ether. This means that the *si*-Ex/TS, to which methanol attacks from the *si* face to give (*S*)-**2**, is energetically more stable/favored than the antipodal *re*-Ex/TS at 0.1 MPa. This stabilization originates probably from a closer contact between excited sensitizer and substrate, which makes the resulting *si*-Ex/TS more compact and favored at higher *P*'s. The saccharide sensitizers also give small to moderate negative ee's of up to 27.8% at 0.1 MPa but, in sharp contrast to the menthyl esters, afford negative $\Delta\Delta V^{\ddagger}_{R-S}$ values of up to −2.2 cm^3 mol^{-1} in all solvents used. These results indicate that the *si*-Ex/TS is energetically favored at ambient pressure but the antipodal *re*-Ex/TS is more compact and hence favored at high *P*'s. The origin of the compact structure of *re*-Ex/TS is not very clear at present, but the highly solvated/stabilized saccharide auxiliaries[6] around the naphthalene chromophore may render the *re*- and *si*-Ex/TS geometries very different in volume from those of the menthyl sensitizers. This interpretation is compatible with the fact that the menthyl esters **3a** and **4a** afford the oppositely signed $\Delta\Delta V^{\ddagger}_{R-S}$ values in MCH *versus* toluene and/or ether, since the latter solvents are considered to promote solvation to more stabilized/polarized *si*-Ex/TS, making it bulkier and less favored at higher *P*'s.

Sensitizer and exciplex fluorescence under pressure

We first examined the effect of added methanol on the absorption spectra of chiral sensitizers to check the association (specific solvation) of methanol to a sensitizer molecule in the ground state. However, no appreciable difference was observed in the presence of methanol at both 0.1 and 400 MPa; for example, the absorption maximum of DAF 1,4-naphthalenedicarboxylate (**3b**) in ether showed practically the same spectral shifts from 317 nm at 0.1 MPa to 324 nm at 400 MPa in the absence of methanol and from 316 nm at 0.1 MPa to 324 nm at 400 MPa in the presence of 0.5 M methanol. This clearly indicates that no appreciable methanol association takes place even at 400 MPa.

We further investigated the pressure effects on the energy and structure of excited sensitizer and Ex. The fluorescence spectral behavior of menthyl and DAF 1,4-naphthalenedicarboxylates (**3a** and **3b**) was comparatively examined at *P* = 0.1–400 MPa in the presence/absence of quencher **1** in various solvents. In the following fluorescence measurements at different *P*'s, we employed an approximate correction method; *i.e.*, the fluorescence intensity (F_P) obtained at each P was divided by the relative absorbance ($A_P/A_{0.1}$) at the excitation wavelength (340 nm) to compensate for the volume contraction under P, as reported previously.[5b] This correction is justified, as we used a small cuvette of 2 mm light path and the sample A was kept low (<0.1) at the excitation wavelength.[10]

Fig. 2 illustrates the pressure dependence of the fluorescence spectra of **3b** in ether at 25 °C in the absence (a) and presence (b) of 0.5 M methanol. In the absence of methanol, F_P increases with increasing P to show a 16% enhancement at 400 MPa, which is likely to be caused by the increased viscosities at high P's as the fluorescence efficiency is enhanced in viscous solvent,[11] while the small bathochromic peak shifts of ≤5 nm may be attributed to the slightly enhanced dielectric constant of solvent at high P.[12] However, in the presence of methanol, F_P decreases by 6% at 400 MPa with less pronounced bathochromic shifts. Such a seemingly conflicting phenomenon may be rationalized by the increased concentration of methanol or solvent polarity at elevated P.

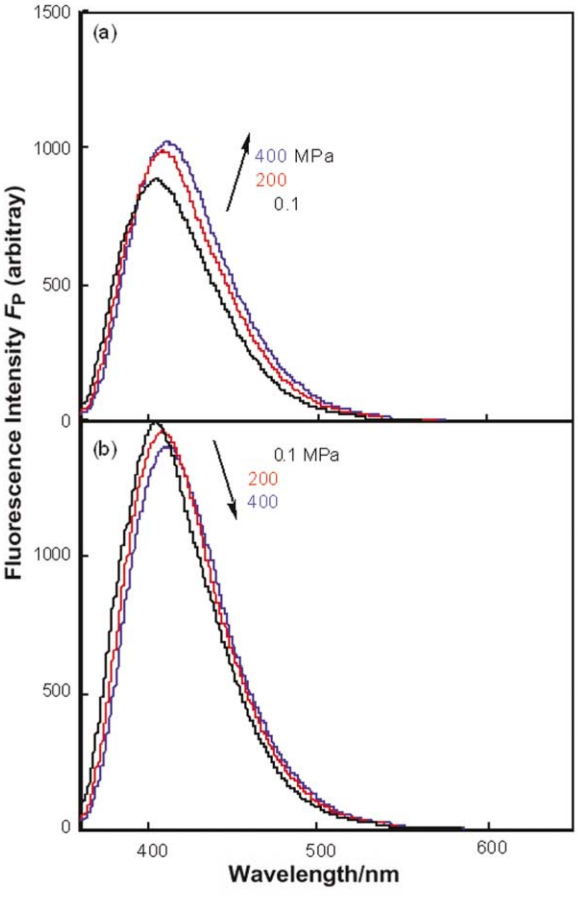


Fig. 2 Fluorescence spectra of **3b** (5×10^{-5} M) excited at 340 nm at 0.1, 200 and 400 MPa in diethyl ether at 25 °C in the absence (a) and presence (b) of methanol (0.5 M), corrected for the concentration changes caused by the pressure-induced contraction of solution.

As shown in Figs. 3a and 4a, the sensitizer fluorescence is very efficiently quenched by **1** in ether at P = 0.1 MPa. Thus, the fluorescence at *ca*. 400 nm is rapidly decreased by adding **1** of up to 150 mM and a new emission attributable to an Ex emerges at longer wavelengths with an isoemissive point. The Ex fluorescence peak is clearly seen in the differential spectra obtained by spectrum subtraction (Figs. 3 and 4, inset).[7] Interestingly, at P = 400 MPa, the sensitizer fluorescence is much less efficiently quenched by **1** with a slower development of the Ex fluorescence at appreciably different positions in the presence and absence of methanol. The relevant results are summarized in Table 3.

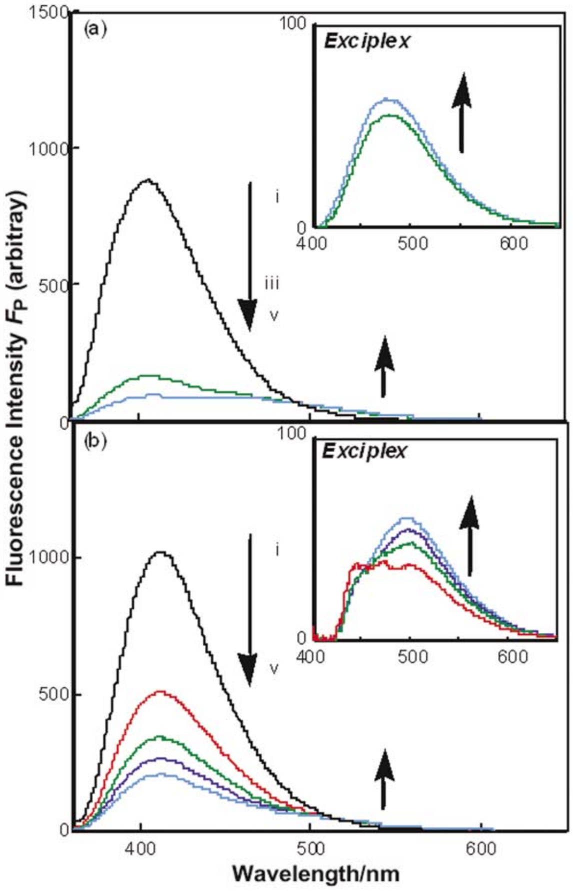


Fig. 3 Fluorescence quenching in diethyl ether (containing no methanol) at (a) 0.1 and (b) 400 MPa; excitation: 340 nm; [**3b**]: 0.050mM; [**1**]: (i) 0, (ii) 39, (iii) 77, (iv) 113, (v) 151 mM. Inset shows the exciplex fluorescence spectra obtained by spectral subtraction.

In the absence of methanol, the fluorescence maximum ($\lambda^F{}_{max}$) of **3a** shows a slight bathochromic shift from 389 nm in MCH to 395 nm in diethyl ester at 0.1 MPa by changing solvent polarity. A change in chiral auxiliary from menthyl to saccharide further drives the $\lambda^F{}_{max}$ to 405 nm. The Ex fluorescence is a more critical function of solvent and auxiliary polarity, affording the $\lambda^F{}_{max}$ for **3a** at 432 nm in MCH and at 450 nm in ether and the $\lambda^F{}_{max}$ for **3b** at 476 nm in ether. The greater bathochromic shift observed for saccharide ester **3b** is attributable to the enhanced microenvironmental polarity around the naphthalene chromophore by the saccharide auxiliaries.[6]

Addition of 0.5 M methanol to the solution did not induce further significant changes in fluorescence behavior of **3a** and **3b**. However, the Ex fluorescence suffers a significant bathochromic shift upon addition of methanol; the stabilization of Ex in energy amounts to 4.0 and 0.9 kcal mol^{-1} for **3a** in MCH and in ether, respectively, and 0.8 kcal mol^{-1} for **3b** in ether. This is reasonable because the Ex is more polarized and sensitive to the change in environmental polarity than the excited sensitizer itself. Intriguingly, the effect of added methanol on the fluorescence of Ex derived from **3a** is more pronounced in nonpolar MCH (E_T = 31.5 kcal mol^{-1})[13] than in ether (E_T = 34.6),[13] due to the remarkably high E_T value of a 0.5 M methanol–MCH mixture ($E_T{}^{MeOH}$ = 49.4),[6] compared to that of a 0.5 M methanol–ether mixture ($E_T{}^{MeOH}$ = 41.0).[6] Mechanistically, such a specific shift in MCH is believed to originate from the selective solvation of methanol to Ex in the nonpolar solvent.[6] This extraordinarily high $E_T{}^{MeOH}$ of MCH containing 0.5 M methanol also rationalizes the greater bathochromic shift of Ex (460 nm) in 0.5 M methanol–MCH than that (456 nm) in 0.5 M methanol–ether. Nevertheless, it is concluded that the stabilization energy (ΔE), associated with the Ex formation, is

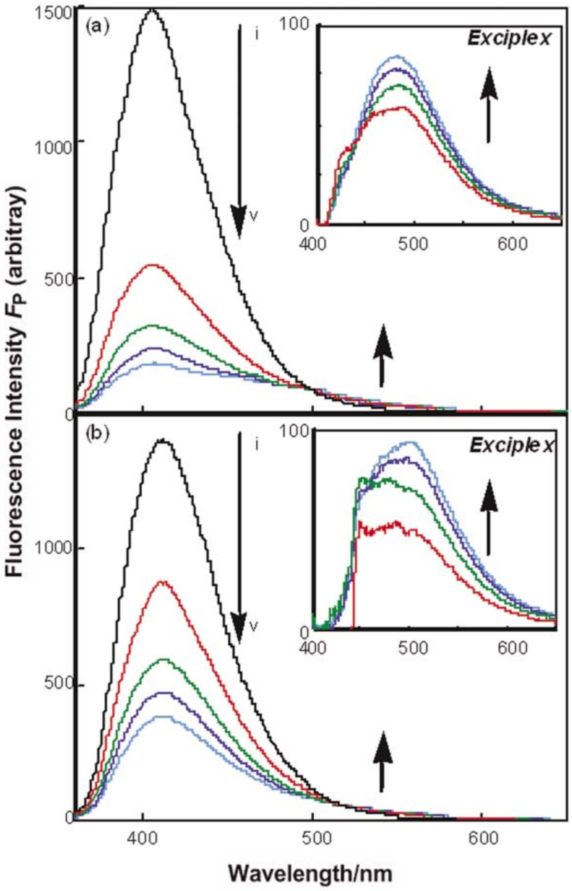


Fig. 4 Fluorescence quenching in diethyl ether (containing 0.5 M methanol) at (a) 0.1 and (b) 400 MPa; excitation: 340 nm; [**3b**]: 0.053mM; [**1**]: (i) 0, (ii) 38, (iii) 76, (iv) 113, (v) 151 mM. Inset shows the exciplex fluorescence spectra obtained by spectral subtraction.

definitely increased (by 0.5–3.3 kcal mol^{-1}) by adding 0.5 M methanol to the solution.

By applying pressure of up to 400 MPa, the $\lambda^F{}_{max}$'s of both sensitizer and Ex shift to longer wavelengths in all solvents examined by 2–8 nm (0.4–1.4 kcal mol^{-1}) for sensitizer and 6–20 nm (0.8–2.4 kcal mol^{-1}) for Ex. In the absence of methanol, the bathochromic shifts of sensitizer fluorescence at elevated *P*'s can be attributed to the enhanced dielectric constant of solvent.[12] However, the pressure effect upon Ex fluorescence is a more complicated issue, since applied pressure affects not only the solvent polarity but also the sensitizer–substrate distance, and the volume, of Ex. Hence, we calculated the stabilization energy (ΔE) associated with the Ex formation as listed in Table 3. By applying pressure, the ΔE of **3a** increases monotonically with a net increase of 1.1–1.6 kcal mol^{-1} at P = 400 MPa at least in ether (in the presence/absence of added methanol). In contrast, the ΔE of **3a** in MCH behaves quite differently, displaying a rapid increase (of 1.6 kcal mol^{-1}) until 200 MPa and a subsequent decrease (of 1.0 kcal mol^{-1}) in the absence of methanol, and a very flat profile with a much smaller initial increase of 0.4 kcal mol^{-1} at 100 MPa in the presence of methanol. The slow increase of ΔE in ether is probably due to the increased solvent polarity at elevated *P*[12] and the flat profile in methanol-containing MCH may be rationalized by the originally strongly solvation to Ex in MCH, which is less sensitive to the global polarity enhancement by *P*. However, we have no plausible rationale for the increase–decrease profile of ΔE observed for **3a** in MCH, although this phenomenon is certainly attributable to the unusual fluorescence behavior of Ex, accompanying the initial bathochromic shift up to P = 200 MPa and the subsequent hypochromic shift. Probably, some discontinuous changes in Ex structure would take place around 200 MPa only in the absence of methanol.

Stern–Volmer analysis under pressure

For more quantitative understanding of the excited-state interactions, a series of fluorescence quenching experiments were preformed under pressure with **3a** and **3b** in MCH and ether at 25 °C in the presence/absence of added methanol. Fluorescence intensities of an aerated MCH or ether solution of **3a** or **3b** (0.05 mM) in the presence (F_p) and absence ($F_p{}^\circ$) of **1** were measured at varying *P*'s. Under the identical optical conditions, similar measurements were repeated at different quencher concentrations. By using the fluorescence intensity F_p and quencher concentration $[Q]_p$ corrected for the volume contraction, the quenching behavior at each *P* was analyzed by the Stern–Volmer eqn. (2):[6,14]

$$F_p{}^\circ/F_p = 1 + k_Q\,\tau_p\,[Q]_p \qquad (2)$$

where k_Q represents the apparent quenching constant and τ_p the fluorescence lifetime of sensitizer at each *P*. As shown in Fig. 5, the Stern–Volmer plot gave a good straight line at each *P* both in the presence and absence of methanol to give the Stern–Volmer constant, $k_Q\tau_p$, listed in Table 3. Irrespective of the sensitizer, solvent or methanol content used, the $k_Q\tau_p$ value gradually decreases with increasing *P*, although the reduction ratio varies from 1/2 for **3a** in ether (with or without methanol) to 1/5 for **3a** in MCH containing methanol. Unfortunately, we could not measure the fluorescence lifetime of sensitizer or Ex

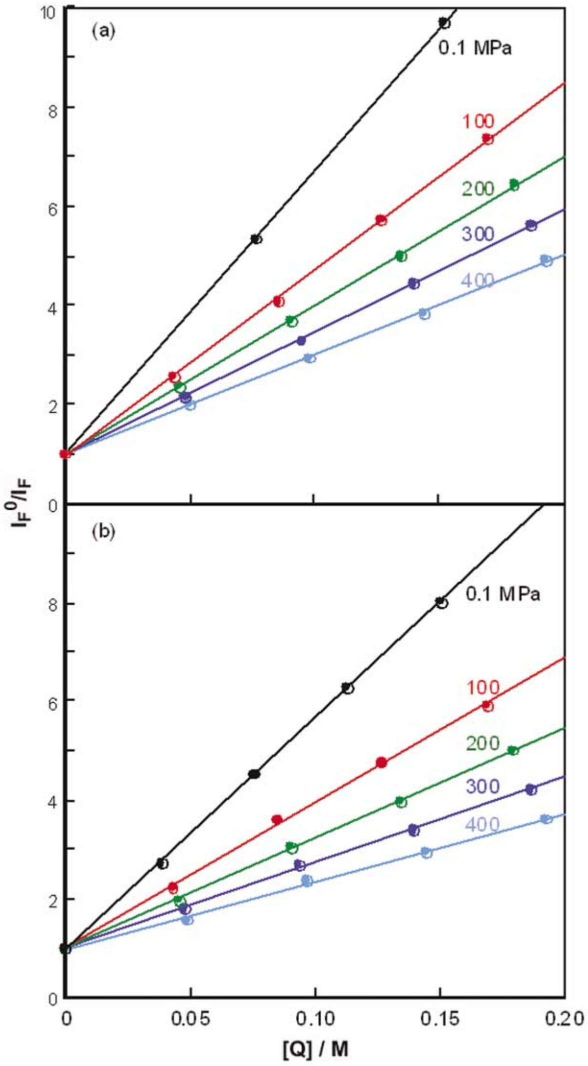


Fig. 5 Stern–Volmer plots for fluorescence quenching of **3b** by **1** in the absence (a) and presence (b) of 0.5 M methanol at varying pressure of 0.1 to 400 MPa in diethyl ether at 25 °C.

Table 3 Fluorescence quenching of chiral sensitizers by **1** in the presence and absence of methanol at various pressures at 25 °C[a]

					λ_{max}/nm (kcal mol^{-1})		
Sens*	Solvent	[MeOH]/M	P/MPa	$k_Q\tau_p{}^\circ$/M^{-1}	Sensitizer	Exciplex[b]	ΔE^c/kcal mol^{-1}
3a	MCH	0	0.1	13	389 (73.5)	432 (66.2)	7.3
			100	10	391 (73.1)	444 (64.4)	8.7
			200	8.0	392 (73.0)	446 (64.1)	8.9
			300	5.7	392 (73.0)	442 (64.7)	8.3
			400	4.3	393 (72.8)	441 (64.9)	7.9
		0.5	0.1	12	393 (72.8)	460 (62.2)	10.6
			100	6.5	393 (72.8)	463 (61.8)	11.0
			200	4.3	395 (72.4)	464 (61.6)	10.8
			300	3.0	394 (72.6)	463 (61.8)	10.8
			400	2.3	395 (72.4)	466 (61.4)	11.0
	Diethyl ether	0	0.1	32	395 (72.4)	450 (63.6)	8.8
			100	28	400 (71.5)	457 (62.6)	8.9
			200	23	401 (71.3)	462 (61.9)	9.4
			300	20	402 (71.1)	468 (61.1)	10.0
			400	16	403 (71.0)	464 (61.6)	9.4
		0.5	0.1	27	397 (72.0)	456 (62.7)	9.3
			100	25	399 (71.7)	462 (61.9)	9.8
			200	21	401 (71.3)	461 (62.0)	9.3
			300	17	401 (71.3)	467 (61.2)	10.1
			400	14	402 (71.1)	471 (60.7)	10.4
3b	Diethyl ether	0	0.1	59	405 (70.6)	476 (60.1)	10.5
			100	38	406 (70.4)	487 (58.7)	11.7
			200	30	409 (69.9)	488 (58.6)	11.3
			300	25	409 (69.9)	494 (57.9)	12.0
			400	20	410 (69.8)	496 (57.7)	12.1
		0.5	0.1	47	405 (70.6)	482 (59.3)	11.3
			100	29	407 (70.3)	489 (58.5)	11.8
			200	23	409 (69.9)	490 (58.4)	11.5
			300	17	410 (69.8)	490 (58.4)	12.3
			400	14	410 (69.8)	502 (57.0)	12.8

[a] Measured with a 0.05 mM aerated solution of sensitizer at 25 °C. [b] Exciplex fluorescence obtained by spectrum subtraction. [c] Difference in energy of sensitizer and exciplex fluorescence.

under P, due to the technical reason that our high-pressure vessel is too large to be installed in the sample chamber of our single-photon-counting instrument. However, judging from the relatively small pressure dependence of F_p (6–16% deviation from the original value even at P = 400 MPa; see Fig. 2), the sensitizer τ_p does not appear to be significantly affected by applied P. If this is the case with all of the present systems, the 1/2 to 1/5 reductions in $k_Q\tau_p$ at 400 MPa are primarily ascribed to the pressure effect on the k_Q value, which most likely originates from the increased viscosity at high P. These decreased quenching constants may also account for the decreased chemical yields at higher P's.

Temperature effect on enantiodifferentiation under high pressure

The pressure effects on the enantiodifferentiating photoaddition was also examined at lower temperatures (0 and −20 °C). As shown in Table 4, the conversion, yield and ee decreased with lowering temperature at 0.1 and 200 MPa. The ee data obtained at three different temperatures were analyzed by the modified Eyring equation (3) to give the differential activation enthalpy ($\Delta\Delta H^{\ddagger}_{R-S}$) and entropy ($\Delta\Delta S^{\ddagger}_{R-S}$) at each pressure.[6]

$$\ln(k_R/k_S) = -\Delta\Delta H^{\ddagger}_{R-S}/RT + \Delta\Delta S^{\ddagger}_{R-S}/R \qquad (3)$$

Fig. 6 illustrates the plots of the $\ln(k_R/k_S)$ value against T^{-1}. From the slope and intercept, the differential activation parameters for sensitization with **3b** were calculated, as shown in Table 5. The $\Delta\Delta H^{\ddagger}_{R-S}$ and $\Delta\Delta S^{\ddagger}_{R-S}$ are appreciably reduced by increasing pressure from 0.1 to 200 MPa. This indicates that efficient enantiodifferentiation becomes more difficult to achieve at high P, for which the compact exciplex structure under pressure may be responsible in part in this photosensitized enantiodifferentiating polar addition.

Table 4 Temperature and pressure effects upon enantiodifferentiating photoaddition of methanol to **1** sensitized by **3b** in diethyl ether[a]

P/MPa	T/°C	% Conversion[b]	% Yield[c]	% Ee[d]
0.1	25	19.5	7.1	−21.3
	0	18.9	5.8	−19.2
	−20	13.4	4.6	−14.6
100	25	14.4	4.9	−15.6
	25	10.6	4.2	−14.3
	−20	6.3	4.2	[e]
200	25	15.9	4.9	−13.4
	0	17.8	3.4	−11.2
	−20	8.6	2.3	−9.5

[a] [**1**] = 20 mM; [Sens*] = 3 mM; [MeOH] = 0.5 M; irradiation time = 15 min (25 °C) or 120 min (0 and –20 °C). [b] Loss of **1** determined by GC. [c] Chemical yields determined by GC on the basis of the initial concentration of **1**. [d] Enantiomeric excess of **2** determined by chiral GC; error <±0.5%. [e] Not determined.

Table 5 Differential activation parameters for enantiodifferentiating photoaddition of methanol to **1** sensitized by **3b** in diethyl ether

P/MPa	$\Delta\Delta H^{\ddagger}_{R-S}$/kcal mol^{-1}	$\Delta\Delta S^{\ddagger}_{R-S}$/cal mol^{-1} K^{-1}
0.1	−0.45	−2.4
200	−0.26	−1.4

In Fig. 7, the $\ln(k_R/k_S)$ values are plotted as a function P and T^{-1} to afford a (pseudo-flat) enantiodifferentiating plane in the three-dimensional ee *vs.* P–T^{-1} diagram, on which all of the available $\ln(k_R/k_S)$ data are accommodated. It is interesting to note that the enantiodifferentiating plane crosses the racemic plane to give the equipodal line and the product chirality is switched by passing through this critical line. This three-dimen-

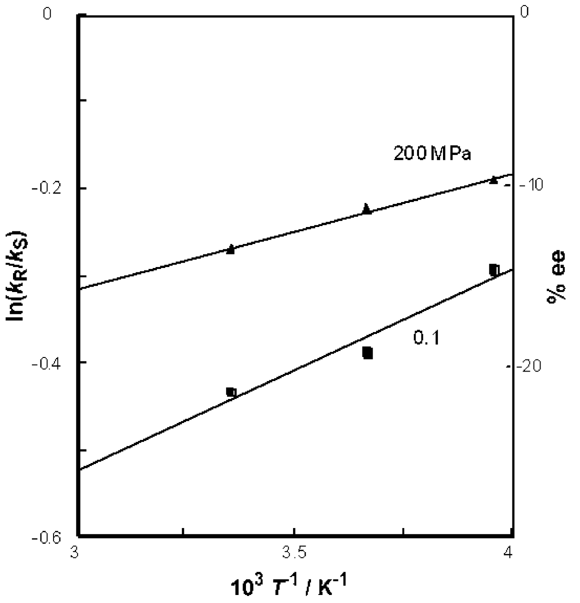


Fig. 6 Temperature dependence of the ee of **2** obtained in the enantiodifferentiating photoaddition of methanol to **1** sensitized by **3b** in diethyl ether at 0.1 (■) and 200 MPa (▲).

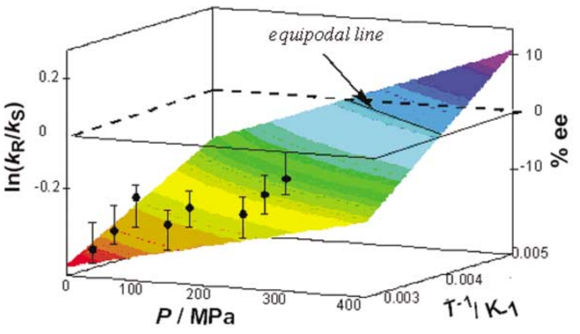


Fig. 7 The $\ln(k_S/k_R)$ *vs.* P-and-T^{-1} diagram: the pressure and temperature dependence of the enantiodifferentiating photoaddition of methanol to **1** sensitized by **3b** in diethyl ether.

sional diagram further indicates that the ee of (*R*)-**2** is enhanced up to +90% at $T = -159$ °C and $P = 1500$ MPa. This is an anomalous enhancement from the original value of −21% ee obtained under the ambient condition (25 °C and 0.1 MPa).

Conclusions

In this study to elucidate the pressure effect upon bimolecular asymmetric photoreactions, we have shown that the differential activation volume for enantiodifferentiation is appreciably larger for a bimolecular photoaddition than for a unimolecular photoisomerization, and also that the product chirality is switched by pressure as was the case with the enantiodifferentiating photoisomerization of cycloalkenes.[4,5] The observation may suggest that such a pressure switching of product chirality is a more general phenomenon which could be observed with not only photochemical but also thermal catalytic and enzymatic asymmetric reactions, provided that the sign of the differential activation/reaction volume of the relevant diastereomeric transition states or intermediates are the same as that of the product ee at $P = 0.1$ MPa (Fig. 1 and Table 2). The pressure dependence of ee observed in this study is not a very critical function of the position of substituents in photosensitizer, but is more significantly affected by the polarities of the chiral auxiliary and solvent employed, indicating the crucial role of solvation in the photoenantiodifferentiation process. Thus, the combined use of saccharide auxiliary and solvent polarity can be a versatile tool for critically controlling and enhancing product ee by pressure in both uni- and bimolecular asymmetric photoreactions. Furthermore, the three-dimensional ee *vs.* P–T^{-1} diagram drawn for the first time for a photosensitized enantiodifferentiating bimolecular reaction is useful for globally understanding the effects of entropy-related factors and also in predicting the condition that affords the optimized ee under a practically attainable condition. From the more global point of view, we may conclude that the entropy-related factors, such as temperature, pressure and solvation, should be jointly and more frequently exploited in the control of asymmetric processes occurring on the ground- and excited-state potential surfaces.

Experimental

Materials

Pentane and MCH used as solvents were stirred over concentrated sulfuric acid until the acid layer no longer turned yellow, washed with water, neutralized with aqueous sodium hydrogen carbonate, dried over sodium sulfate, and then distilled fractionally in the presence of sodium. Toluene and methanol were fractionally distilled in the presence of molten sodium and magnesium turnings, respectively. Ether was refluxed with potassium hydroxide and then fractionally distilled in the presence of sodium.

1,1-Diphenylpropene **1** was synthesized by dehydration of 1,1-diphenyl-1-propanol, which was prepared by the Grignard reaction of propiophenone with bromobenzene.[6] Optically pure 1,4- and 2,6-naphthalenedicarboxylates **3a**–**c** and **4a**,**b** were prepared from the corresponding alcohols and acid chlorides, and purified by the procedures reported previously.[6]

Spectroscopy

Electronic absorption and fluorescence spectra were recorded on a Shimadzu UV-3100PC spectrophotometer and a Hitachi F-4500 spectrofluorimeter, respectively.

All spectroscopic measurements under pressure were carried out by using a high-pressure vessel (designed and manufactured by Teramecs Co., Kyoto), which was equipped with three sapphire windows of a 7 mm aperture. A quartz inner cell (inside dimensions: 3 mm W × 2 mm D × 7 mm H) connected to a short flexible Teflon tube (for absorbing the volume change under *P*) was filled with a sample solution and the top end of the tube was stoppered, and the whole cell was placed inside the pressure vessel. The vessel was fixed in the sample chamber of the spectrometer and a given *P* of up to 400 MPa was applied.

Photolysis

Photosensitization experiments were conducted in the high-pressure vessel described above. A solution (150 µL), containing **1** (20 mM), methanol (0.5 M), optically active sensitizer **3a**–**c** or **4a**,**b** (5 mM) and cyclopentadecane (3 mM) added as an internal standard for GC analysis, was irradiated at λ >300 nm with a 250 W ultra-high pressure mercury lamp (Wacom) fitted with a UV-33 glass filter (Toshiba) and cylindrical quartz vessel filled with water (for eliminating the infrared radiation), keeping the vessel temperature at 25, 0, or −20 °C. The collimated radiation from the light source was focused with a quartz lens just before the front surface of the sapphire window, allowing efficient irradiation. The irradiated solution was retrieved from the vessel and subjected to the GC analysis on a 30 m chiral capillary column of Chiraldex B-PH (TCI/Astech) for determination of the conversion, yield and ee.

Although the solutions were purged with argon prior to irradiation, small amounts of benzophenone and racemic epoxide of substrate **1** were detected in the irradiated solutions upon GC analysis on a B-PH column. It turned out further that, under the previous GC conditions using a B-DA column, benzophenone elutes at a retention time very close to that of (*S*)-**2**, affording erroneous ee's in some cases in our previous paper.[6] The largest difference in ee was found for the photosensitization with **3b** in ether at 25 °C; the formerly reported ee was −27.0%, while the correct value was 21.3 ± 0.6%.

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