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Journal of Photochemistry and Photobiology A: Chemistry 119 (1998) 93–99

Journal of
Photochemistry
and
Photobiology
A:Chemistry

Photosensitized cycloreversion of the dimer of methyl 2-naphthoate via reversible electron transfer and exciplex

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Received 13 March 1998; received in revised form 25 August 1998; accepted 2 September 1998

Abstract

Photosensitized cycloreversion of the photodimer of methyl 2-naphthoate (**1**) by using 1-cyanonaphthalene (CN), 9,10-dicyanoanthracene (DCA) and chloranil (CHL) as sensitizers has been examined. **1** can efficiently isomerize to its monomer, methyl 2-naphthoate (**2**), by a reversible electron transfer or exciplex mechanism. In the case of using singlet sensitizers (CN and DCA), the cycloreversion of **1** to **2** proceeded via an efficient cation-radical chain process in acetonitrile, while in dichloromethane and benzene **1** isomerized to **2** through an exciplex or partial charge transfer. For triplet sensitizer CHL, in all solvents examined the reaction occurred through a cation-radical chain process, and the efficiencies were higher compared with those for the singlet sensitizers. This cycloreversion likely involves two [2+2] processes. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photo sensitized cycloreversion; Photodimer; Methyl 2-naphthoate

1. Introduction

Cycloreversion of strained compounds possessing cyclobutyl frameworks has been the subject of intense experimental and theoretical investigation in view of their significance in solar energy storage and mechanistic interests [1–24]. Among them, the isomerizations of quadricyclane to norbornadiene [12–24], hexamethyl (Dewar benzene) to hexamethylbenzene [25] and cubane-like compounds to cyclic dienes [26,27] are well-investigated examples. Due to the unusual electron donor properties of the strained compounds, the cycloreversion reactions can be photoinduced by using electron acceptors as sensitizers to promote electron transfer. It is thought that electron transfer or even partial charge transfer from the strained compounds to the sensitizers may weaken the strained carbon–carbon bonds, thus to lower activation energies for isomerization. Apparently, the strain release is one of the driving forces for such bond-cleavage reactions [28,29]. In many cases, the quantum yields for the bond-cleavage in polar solvents were greater than 1.0, indicating that the reactions proceed via cation-radical chain processes [25–27]. On the other hand, in non-polar solvents the evidences for bond-cleavage through exciplex have been reported [25–27].

Up to now, reports of cycloreversion proceeding by photoinduced electron transfer mechanism are restricted in [2+2] ([12–27]) or [4+4] ([30]) processes. We present here an example of cycloreversion photosensitized via reversible electron transfer which involves two [2+2] processes (Scheme 1).

$$\mathbf{1}^{\bullet +} \xrightarrow{\text{rev.}[2+2]} \mathbf{4}^{\bullet +} \xrightarrow{\text{rev.}[2+2]} \mathbf{2}^{\bullet +}$$

In a separate paper [31,32] we reported that photoirradiation of alkyl 2-naphthoate (**2**) results in a cubane-like photodimer (**1**) as the unique product, and the photodimerization is a two-photon process (Scheme 1). We proposed that the first photon gives a [4+4] product (**3**) followed by Cope rearrangement to give **4**. Absorption of the second photon by either **3** or **4** leads to a [2+2] cycloaddition resulting in **1**. Now we report that **1** undergoes efficient photoinduced cycloreversion to give **2** in the presence of electron-deficient sensitizers such as 1-cyanonaphthalene (CN), 9,10-dicyanoanthracene (DCA) and chloranil (CHL). We will demonstrate that in polar solvents this cycloreversion proceeds via a cation radical chain process, while in non-polar solvents the reaction is through an exciplex or partial charge transfer.

2. Experimental

2.1. Instrumentation and materials

UV spectra were recorded on a Hitachi 340 spectrometer. Fluorescence spectra were measured on a Hitachi MPF-4

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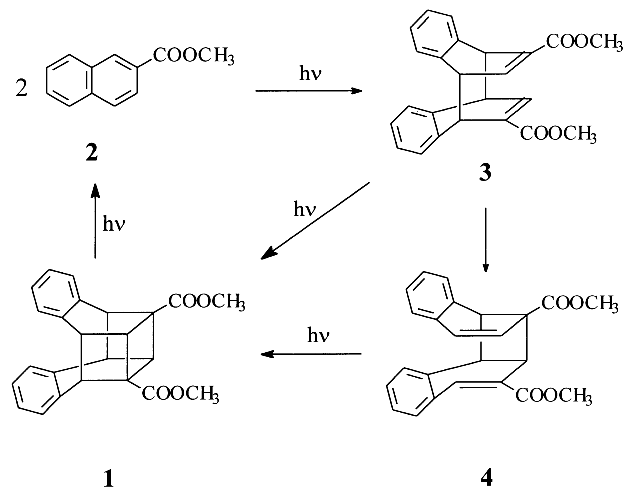
PII: S1010-6030(98)00388-8



Scheme 1.

spectrophotometer. The ^{1}HNMR spectra were recorded at 300 MHz with a Varian XL-300 spectrometer. Redox potential were determined by cyclic voltammetry vs. SCE in acetonitrile using tetrabutylammonium perchlorate as the supporting electrolyte.

Cage compound **1** was prepared [31,32] and purified by recrystallization from acetone. 1-cyanonaphthalene (CN) was from Aldrich and was distilled before use. 9,10-Dicyanoanthracene (DCA) and chloranil (CHL) were purchased from Aldrich and purified by recrystallization from benzene three times. 1,4-Dimethoxybenzene was from Fluka and recrystallized twice from methanol. Acetonitrile was distilled over phosphorus pentoxide and then calcium hydride. Benzene was treated sequentially with concentrated sulfuric acid, 5% aqueous sodium hydroxide, and calcium chloride and then distilled over calcium hydride. Dichloromethane was spectroscopic grade and were used without further purification.

2.2. Fluorescence quenching

Fluorescence quenching experiments of the sensitizers by **1** were conducted by using degassed solutions at room temperature. Slopes ($k_q\tau$) of Stern–Volmer plots were determined by a least-squares treatments, and quenching rate constants (k_q) were calculated from the known singlet lifetimes (τ) of the sensitizers.

2.3. Photosensitized cycloreversion and quantum yield measurements

Photoirradiation was carried out with 450 W Hanovia medium pressure Hg arc lamp under cooling with water in a 'merry-go-round' turntable. A combination of corning 0–52 and 7–60 glass filter was used to isolate the 366 nm light, whereas the 313 nm light was obtained by the passage through a solution (10 mm path length) of $K_2Cr_2O_4$ (0.27 g/l) and Na_2CO_3 (1 g/l) in water [44]. Solutions of **1** (10–12 mM) containing sensitizer (0.37–0.53 mM for DCA and 4.3–4.9 mM for CHL) with or without 1,4-dimethoxybenzene (43–57 mM) in Pyrex reactors were irradiated after purging with nitrogen. The reaction was followed by UV, and the product was isolated by chromatography on silica and identified by ^{1}H NMR. In quantum yield measurements, a benzophenone–benzohydrol actinometer [46] and a 2-hexanone actinometer [46] were used for the determination at 366 nm for the DCA and CHL-photosensitized reactions and at 313 nm for the CN runs, respectively.

3. Results and discussion

3.1. Fluorescence quenching

The fluorescences of DCA both in polar and non-polar solvents were quenched by **1** following the linear Stern–Volmer relationships. Table 1 gives the Stern–Volmer constants ($k_q\tau$) and the fluorescence quenching rate constants (k_q) calculated from $k_q\tau$ and the fluorescence lifetimes (τ) in the absence of quencher. In acetonitrile and dichloromethane, the k_q values are close to the diffusion-controlled rate constants, while in benzene the k_q value is one order in magnitude smaller than those in polar solvents. Similarly, the fluorescence of CN in acetonitrile was also efficiently quenched by **1**, and the quenching parameters were listed in Table 1. However, in dichloromethane and benzene the fluorescence of CN was hardly quenched. Significantly, the quenching of DCA or CN fluorescence by **1** is accompanied by the appearance of weak exciplex emission even in polar solvents. Fig. 1 shows the fluorescence spectra of DCA in acetonitrile and benzene in the presence of **1**. Both spectra exhibit exciplex emission at longer wavelength with isoemissive points at ca. 516 and 514 nm, respectively. The exciplex emission in benzene is relatively stronger than in acetonitrile.

3.2. Photosensitized cycloreversion

Photoirradiation with 366 nm light of a degassed mixture solution of **1** (1.1×10^{-2} M) and DCA (3.7×10^{-4} M) in acetonitrile at room temperature results in cycloreversion of **1** to **2**. The yield of **2** is 100% on the basis of the consump-

Table 1
Parameters of fluorescene quenching of DCA and CN by **1**

Sensitizer	Solvent	τ (ns)	$k_q\tau$ (M^{-1})	$k_q \times 10^{-9}$ (M/s)
DCA	MeCN	13.4[a]	61.39	4.58
	CH_2Cl_2	11.7[b]	18.87	1.61
	C_6H_6	12.4[c]	3.44	0.28
CN	MeCN	12.3[d]	23.09	2.2

[a] From reference [33].
[b] From reference [30].
[c] From reference [34].
[d] From reference [35].

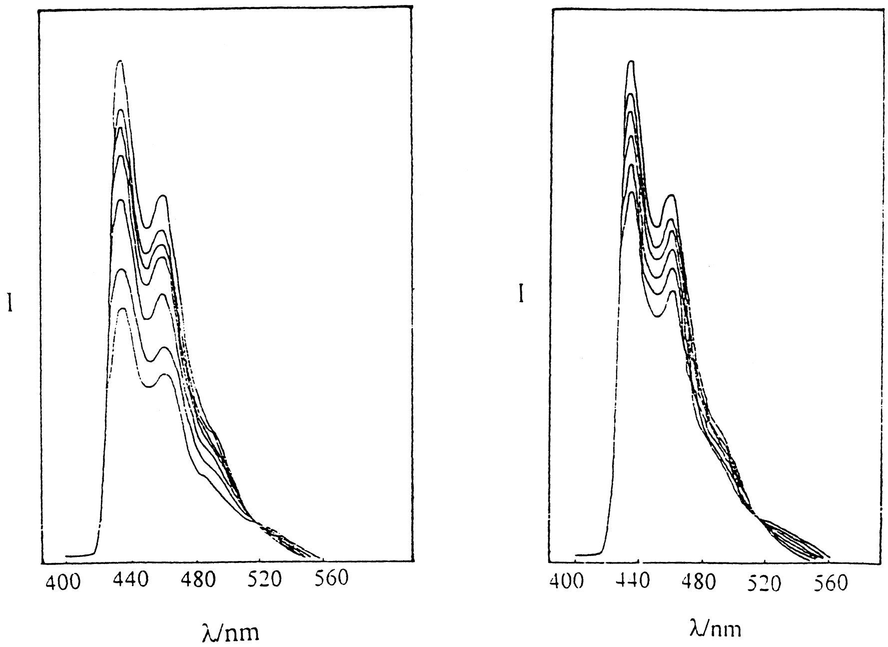


Fig. 1. DCA fluorescence quenching by **1** in acetonitrile (left; [DCA] = 2.0 × 10^{-5} M; [**1**] = 0, 4.2, 5.3, 6.7, 7.9, 10.5, 21.0 × 10^{-3} M) and in benzene (right; [DCA] = 2.0 × 10^{-5} M; [**1**] = 0, 20.0, 31.3, 50.6, 72.4, 100.3 × 10^{3} M).

tion of the starting material. Under the irradiation condition only DCA absorbs the light. Thus, the cycloreversion of **1** must be attributed to the sensitization by DCA. Since the fluorescence of DCA is efficiently quenched by **1**, we infer that the sensitization is mainly originated from the singlet excited state of DCA. This conclusion is supported by the observation that the double-reciprocal plot of quantum yield of product formation vs. concentration of **1** is linear as reported in the next section. Similarly, CN may also efficiently sensitize the cycloreversion of **1** to **2** in acetonitrile via singlet excited state.

The energy of the singlet excited state of **1** is 105 kcal/mol as determined by UV absorption spectrum, which is much higher than that of DCA (66.0 kcal/mol [36]) and CN (89.5 kcal/mol [36]). Thus the possibility of singlet energy transfer responsible for the fluorescence quenching and sensitized cycloreversion is excluded. Therefore we examined the reality of electron transfer from **1** to the aromatic nitrile singlet excited states as the cause of the fluorescence quenching and the sensitized cycloreversion. The free energy change (ΔG) involved in a photostimulated electron transfer process can be estimated by Eq. (1) ([37–42])

$$\Delta G = E_{\mathrm{ox}}(\mathrm{D}) - E_{\mathrm{red}}(\mathrm{A}) - \Delta E_{00} - e^2/\varepsilon R_{\mathrm{cc}} - e^2/2(1/r_+ + 1/r_-)(1/37 - 1/\varepsilon) \qquad (1)$$

where ΔE_{00} is the excited state energy and in this case represents the singlet excited state energy of DCA or CN. $E_{\mathrm{ox}}(\mathrm{D})$ and $E_{\mathrm{red}}(\mathrm{A})$ are the oxidation potential of the donor and the reduction potential of the acceptor respectively determined in acetonitrile solution. $e^2/\varepsilon R_{\mathrm{cc}}$ is the Columbic interaction in the ion pair state whose magnitude depends on the distance between the donor and acceptor (R_{cc}) and on the dielectric constant (ε) of the medium separating the charges. The last term in Eq. (1) is the Born Correction to the solvation energy which depends on the radii of the donor cation (r_+) and the acceptor anion (r_-). The oxidation potential of **1** was determined by cyclic voltammetry in acetonitrile to be 1.89 V vs. SCE[1] and the reduction potentials of DCA and CN were obtained from the literatures [36] to be −0.89 and −1.98 V vs. SCE, respectively. In DCA sensitized system, we set r_+ and r_- to equal to 5.6 and 4.8 Å, respectively by assuming that both donor and acceptor are spherical[2]. Thus R_{cc} equals to 10.4 Å for the contact ion pair. For the CN sensitization system, we set r_+ and r_- are 5.6 and 3.6 Å, respectively, and $R_{\mathrm{cc}} = 9.2$ Å. Calculation according to Eq. (1) reveals that electron transfer from **1** to DCA and CN singlet excited state in acetonitrile is exothermic by 2.8 and 1.3 kcal/mol, respectively. Thus we attributed the fluorescence quenching and sensitization reaction in acetonitrile to electron transfer. On the other hand, in dichloromethane and benzene the free energy change (ΔG) for the electron transfer from **1** to singlet excited DCA is 0 and 10.6 kcal/mol, respectively. We suggest that exciplex or partial charge

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[1] The oxidation potential of **1** was determined by cyclic voltammetry vs. saturated calomel reference electrode (SCE) in acetonitrile using tetraethylammonium perchlorate as the supporting electrolyte. The cyclic viltammogram observed for this oxidation is irreversible. The peak potential, occuring at 1.89 V at a sweep rate of 200 mV/s, has been taken as the oxidation potential

[2] The ion radii were taken the same values as those of the donor and the acceptors, which were calculated roughly with Alchemy II program produced by Tripos Associates, The calculated radii of the donor and acceptors by assuming they are spherical are: 1, 5.6 Å, DCA, 4.8 Å, CN, 3.6 Å, CHL, 3.2 Å. R_{cc} is calculated by r_+ plus r_-.

transfer is responsible for the fluorescence quenching and sensitized cycloreversion for DCA–**1** system in moderate and non-polar solvents.

Similarly, CHL may also sensitize the cycloreversion of **1** to **2**. Since the intersystem crossing of the singlet excited state to triplet excited state for CHL is extremely efficient [43] (the rate $>10^{10}\ \mathrm{s}^{-1}$), the sensitization is obviously originated from the triplet state of CHL. However, triplet energy transfer from CHL to **1** is unlikely to occur, since no isomerization of **1** was detected at all in the photosensitization by benzophenone which has a higher triplet energy (69.2 kcal/mol [44]) than CHL (62.3 kcal/mol [45]). On the other hand, electron transfer from **1** to triplet CHL (the reduction potential of CHL is 0.02 V vs. SCE [36]) can be responsible to the photosensitization as revealed by calculation according to Eq. (1). The free energy changes for such electron transfer in acetonitrile and dichloromethane are -20.2 and -16.6 kcal/mol, respectively.

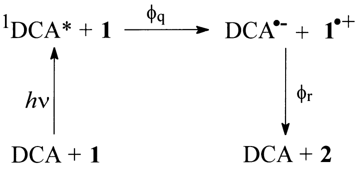
The quantum yield for the photosensitized cycloreversion of **1** shows solvent dependence. Table 2 gives the relative quantum yields of the cycloreversion sensitized by DCA and CHL in different solvents under identical irradiation condition. Obviously, in polar solvents such as acetonitrile, the quantum yields of the cycloreversion both for DCA and CHL sensitization are higher than those in moderate polar solvents (dichloromethane). In non-polar solvents such as benzene, the quantum yield of the cycloreversion is very low.

To support the occurrence of electron transfer from **1** to the excited state of DCA and CHL, quenching experiments were performed using 1,4-dimethoxybenzene (DMB). DMB has lower oxidation potential (1.35 V vs. SCE [46]) than **1**. Electron transfer from DMB to the exited state of DCA or CHL should be more favorable than that from **1**. Thus, one might expect that DMB may intercept the cycloreversion of **1** sensitized by DCA or CHL. Experiments revealed that this is indeed the case. Addition of DMB into the mixed solution of **1** and the sensitizer in acetonitrile efficiently quenched the cycloreversion reaction. However, the degree of reaction quenching in dichloromethane was comparably low (Table 2).

Table 2
Conversion of **1** to **2** sensitized by DCA and CHL under identical irradiation condition[a,b]

Sensitizer	Solvent	[DMB][b] (mM)	Irradiation time (min)	conversion (%)
DCA[c]	MeCN	0	10	80
	MeCN	56.2	10	3
	CH_2Cl_2	0	60	35
	CH_2Cl_2	56.6	60	5
	C_6H_6	0	60	3
CHL[d]	MeCN	0	10	100
	MeCN	43.7	10	5
	CH_2Cl_2	0	60	100
	CH_2Cl_2	44.6	60	25

[a] Irradiated with 366 nm light.
[b] $[\mathbf{1}] = 11$ mM.
[c] $[\mathrm{DCA}] = 0.37$ mM.
[d] $[\mathrm{CHL}] = 4.4$ mM.



Scheme 2.

3.3. *Quantum yields*

Limiting quantum yields for the disappearance of **1** were determined by usual double-reciprocal plots of quantum yield vs. concentration of **1**. In the case of DCA or CN as the sensitizer, assuming that only the singlet excited state of the sensitizer is responsible for the sensitization, the photosensitized cycloreversion can be expressed by Scheme 2. The quantum yield of the cycloreversion (Φ_r) should be the product of the quenching efficiency (ϕ_q) and the efficiency for chemical reaction to **2** from the quenched species (ϕ_r). Obviously, the ϕ_r value is dependent on the concentration of **1** in radical chain processes. However, when the concentration of **1** increases, ϕ_r approaches a constant quantum yield at infinite concentration (limiting quantum yield). Thus, ϕ_r is the efficiency for chemical reaction to **2** from the quenched species at relatively high concentration region of **1**.

$$\phi_q = \frac{k_q[\mathbf{1}]}{1/\tau + k_q[\mathbf{1}]} \tag{2}$$

$$\Phi_r = \phi_r\phi_q = \phi_r\frac{k_q[\mathbf{1}]}{1/\tau + k_q[\mathbf{1}]} \tag{3}$$

Thus,

$$\frac{1}{\Phi_r} = \frac{1}{\phi_r}\left(1 + \frac{1}{k_q\tau[\mathbf{1}]}\right) \tag{4}$$

Obviously, the double-reciprocal plot of quantum yield of disappearance of **1** vs. concentration of **1** should give the intercept (I) and slope (S) as follows:

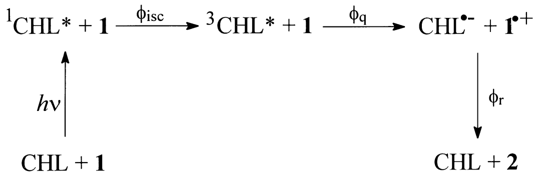
$$I = \frac{1}{\phi_r} \tag{5}$$

$$S = \frac{1}{\phi_r k_q \tau} \tag{6}$$

thus,

$$I/S = k_q\tau \tag{7}$$

In the case of CHL as the sensitizer, the photosensitized cycloreversion can be represented by Scheme 3. The quantum yield of the cycloreversion (Φ_r) should be the product of



Scheme 3.

the efficiency of intersystem crossing of the singlet to triplet excited state of CHL (ϕ_{isc}), the quenching efficiency for the triplet CHL (ϕ_q)and the efficiency for chemical reaction to **2** from the quenched species (ϕ_r). It has been established that the efficiency of intersystem crossing of CHL (ϕ_{isc}) is 100% [43]. Thus, Φ_r can also be represented by Eq. (3), where k_q and τ represent the triplet quenching constant of CHL by **1** and the triplet excited state lifetime of CHL in the absence of **1**.

Fig. 2 shows the double-reciprocal plots of quantum yield of disappearance of **1** vs. concentration of **1** for the sensitization by DCA, CN and CHL. All the plots are linear, suggesting that the sensitization cycloreversion by DCA or CN is only originated from the singlet excited state of the sensitizer, while in the case of CHL as the sensitizer the reaction is totally from the triplet sensitization. The limiting quantum yields together with the intercept–slope ratios (*I*/*S*) of the plots in Fig. 2 are given in Table 3. The order of *I*/*S* values for DCA and CN sensitization roughly agreed with that of $k_q\tau$ values obtained from fluorescence quenching (Table 1), again, indicating that the cycloreversion proceeds via typical singlet-sensitization mechanism. The difference between the *I*/*S* and $k_q\tau$ values may be in part due to the concentration difference of **1** to determine these values.

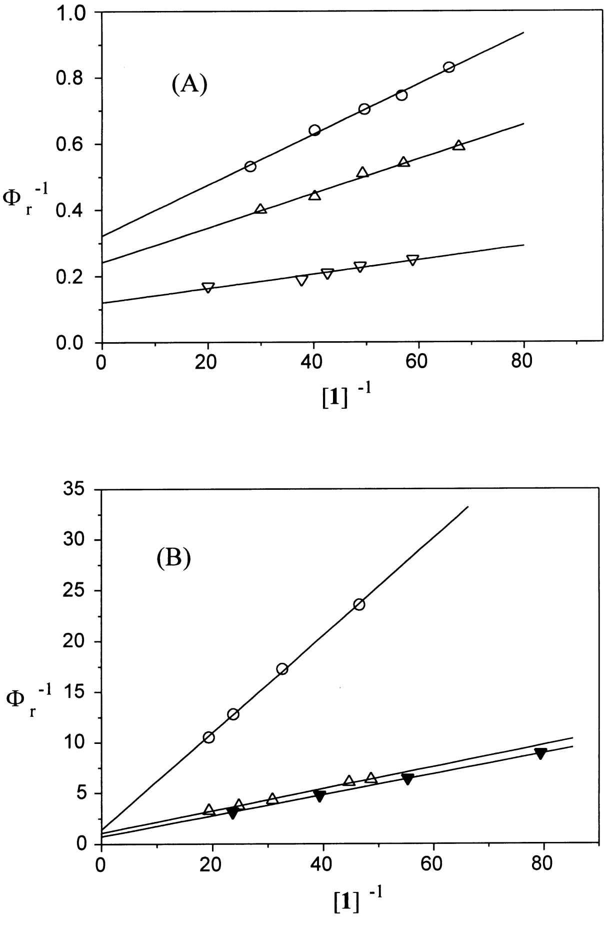


Fig. 2. Double-reciprocal plots of quantum yield for cycloreversion vs. concentration of 1: (A) CHL in CH_2Cl_2 (○), DCA in MeCN (△), CHL in MeCN (▽); (B) DCA in benzene (○), DCA in CH_2Cl_2 (△), CN in MeCN (▼).

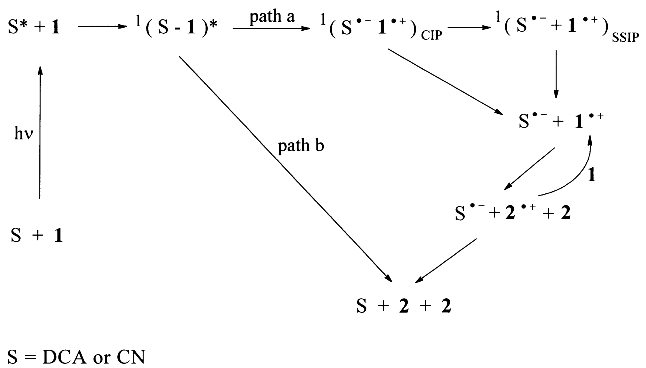
Table 3
Limiting quantum yields for the sensitization cycloreversion of **1** to **2**

Sensitizer	Solvent	ΔG	ϕ_r	*I*/*S*
DCA	MeCN	−2.8	4.43	40.12
DCA	CH_2Cl_2	0	0.99	9.60
DCA	C_6H_6	10.6	0.7	2.98
CHL	MeCN	−20.2	8.23	56.81
CHL	CH_2Cl_2	−16.6	3.02	44.49
CN	MeCN	−1.3	1.32	7.37

3.4. Mechanism, free cation-radical vs. exciplex or partial charge transfer

The limiting quantum yields for cycloreversion of **1** sensitized by DCA or CN in acetonitrile are greater than 1.0 (Table 3), which implies that **1** isomerized to **2** via an efficient cation-radical chain process (Scheme 4, path a). On the other hand, in dichloromethane and benzene the limiting quantum yields are less than 1.0, which is consistent with the fact that the isomerization proceeds via an exciplex or partial charge transfer (Scheme 4, path b).

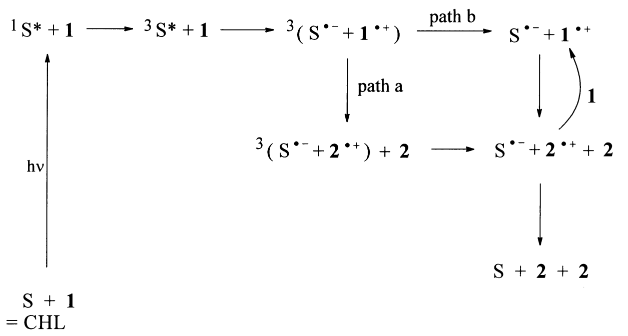
Since we observed the exciplex fluorescence between **1** and DCA (or CN) in acetonitrile, we believed in polar solvent that the ion-radical pair $^1(S^{\bullet-}\mathbf{1}^{\bullet+})$ is formed via the exciplex. After the exciplex is formed, the subsequent electron transfer gives a contact ion pair (CIP) $^1(S^{\bullet-}\mathbf{1}^{\bullet+})_{CIP}$ (Scheme 4, path a). The contact ion pair may directly form free ion radicals or first give a solvent separated ion pair (SSIP) $(S^{\bullet-}+\mathbf{1}^{\bullet+})_{SSIP}$, then generates the free ion radicals



Scheme 4.

$S^{\bullet-}$ and $\mathbf{1}^{\bullet+}$. The formed $\mathbf{1}^{\bullet+}$ then isomerized to $\mathbf{2}^{\bullet+} + \mathbf{2}$. The cation radical $\mathbf{2}^{\bullet+}$ may suffer electron transfer with **1** to generate **2** and $\mathbf{1}^{\bullet+}$. Thus, $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+} + \mathbf{2}$ and $\mathbf{2}^{\bullet+} + \mathbf{1} \rightarrow \mathbf{2} + \mathbf{1}^{\bullet+}$ comprise the propagation steps of the chain reaction. The termination step involves a quenching reaction of the cation-radical $\mathbf{1}^{\bullet+}$ or $\mathbf{2}^{\bullet+}$ with the anion radical $S^{\bullet-}$. The cation radical $\mathbf{1}^{\bullet+}$ can be expected to dissociate easily into $\mathbf{2} + \mathbf{2}^{\bullet+}$ due to its strain release. This is supported by cyclic voltammograph experiment. The electrochemical formation of $\mathbf{1}^{\bullet+}$ is found to be irreversible, suggesting that secondary reaction is significant on the time scale of the electrochemical experiment. The electron transfer from **1** to $\mathbf{2}^{\bullet+}$ demands that **2** has a higher oxidation potential than **1**. The oxidation potential of **2** has been determined to be 1.94 V vs. SCE, which is indeed higher than that of **1** (1.89 V vs. SCE). Thus, it is thermodynamically possible for $\mathbf{2}^{\bullet+}$ to oxidize **1**. To summarize, in polar solvents the sensitized cycloreversion occurs through the cation-radical chain process (Scheme 4, path a), thus the limiting quantum yields are over 1.0. On the other hand, in non-polar solvents, such as dichloromethane and benzene, although the exciplex is formed, the electron transfer is thermodynamically unfavorable. By preference to precedent works of sensitized cycloreversion of strained compounds, [25–27] we proposed that the cycloreversion of **1** sensitized by DCA or CN in non-polar solvents proceeds via an exciplex or partial charge transfer mechanism.

The above proposal was supported by the observation that the limiting quantum yields are dependent on the spin state of the ion-radical pair. As shown in Scheme 5, electron transfer from **1** to the triplet state of CHL should give triplet ion-radical pair ${}^{3}(S^{\bullet-} + \mathbf{1}^{\bullet+})$. This ion-radical pair may undergo isomerization to ${}^{3}(S^{\bullet-} + \mathbf{1}^{\bullet+}) + \mathbf{2}$. Recombination of the triplet ion-radical pair ${}^{3}(S^{\bullet-} + \mathbf{1}^{\bullet+})$ or ${}^{3}(S^{\bullet-} + \mathbf{2}^{\bullet+})$ would generate the triplet state of one of the substrates, and is thermodynamically impossible in this case. The triplet ion-radical pair must first undergo intersystem cross to the singlet state ${}^{1}(S^{\bullet-} + \mathbf{1}^{\bullet+})$ or ${}^{1}(S^{\bullet-} + \mathbf{2}^{\bullet+})$, then undergoes back electron transfer. Thus, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ in the triplet ion-pairs have enough time to escape from the solvent cage to form free radical, followed by chain reaction. Indeed, as shown in Table 3, the limiting quantum yields of the cycloreversion sensitized by CHL are over 1.0 both in acetonitrile and dichloromethane and greater than those by DCA.



Scheme 5.

3.5. Bond cleavage

Many examples for cycloreversion proceeding by photoinduced electron transfer mechanism, such as the isomerizations of quadricyclane to norbornadiene [12–24], cage compound to cyclic diene [26,27] and anthracene dimer to anthracene, [30] have been examined in detail. All of the examples involves either a [2+2] or a [4+4] process and formally cleavage two σ-bonds. In the present case, the cycloreversion of **1** to **2** would formally cleavage 4 σ-bonds, and might involve either two [2+2] processes (Scheme 1)

$$\mathbf{1}^{\bullet+} \xrightarrow{\text{rev.}[2+2]} \mathbf{4}^{\bullet+} \xrightarrow{\text{rev.}[2+2]} \mathbf{2}^{\bullet+}$$

or one [2+2] plus one [4+4] processes (Scheme 1)

$$\mathbf{1}^{\bullet+} \xrightarrow{\text{rev.}[2+2]} \mathbf{3}^{\bullet+} \xrightarrow{\text{rev.}[4+4]} \mathbf{2}^{\bullet+}$$

However, in the cation radical intermediate, the cation radical center will be mainly located on the benzene ring. The bond cleavage in $\mathbf{1}^{\bullet+}$ leading to $\mathbf{4}^{\bullet+}$, and that in $\mathbf{4}^{\bullet+}$ leading to $\mathbf{2}^{\bullet+}$ would be reasonable in energetic consideration, because such conversions involve the cleavage of benzylic bond. On the other hand, in the mechanism of one [2+2] plus one [4+4] processes, while the [4+4] process from $\mathbf{3}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$ is favorable, the conversion of $\mathbf{1}^{\bullet+}$ to $\mathbf{3}^{\bullet+}$ would be difficult since such process involves the bond cleavage of β-position of the phenyl ring. Thus, we prefer that the cycloreversion of **1** to **2** proceeds via two [2+2] processes rather than one [2+2] plus one [4+4] processes.

We have demonstrated that the photodimerization of **2** to **1** is a two-photo process [31,32]. For the photosensitized cycloreversion of **1** to **3** via electron transfer, we found that the plot of the yield of **2** at constant concentration of **1** vs. light intensity is linear, suggesting that the cycloreversion is one-photo process. Thus, the cation-radical $\mathbf{1}^{\bullet+}$ or exciplex, once formed, would induce cleavage of 4 σ-bonds resulting in **2**.

4. Conclusion

Compound **1** has been found to undergo sensitization cycloreversion via reversible electron transfer by using electron–acceptor sensitizers. The cycloreversion sensitized by aromatic nitriles, such as DCA and CN, proceeds via a cation-radical chain reaction and the limiting quantum yields are greater than 1.0 in polar solvents, while in non-polar solvents this reaction proceeds via an exciplex or partial charge transfer. On the other hand, in the case of using a triplet sensitizer such as CHL, the cycloreversion proceeds through a cation-radical chain reaction both in polar and moderate polar solvents. Since the formed triplet ion-radical pair easily undergoes escape to generate free ion-radicals, the efficiency of the cycloreversion is higher than those for singlet sensitizers. This reaction is the first example of cycloreversion involving two [2+2] processes.

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