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In-Cage Formation of Carbanions in Photoinduced Electron-Transfer Reaction of Carboxylate Ions

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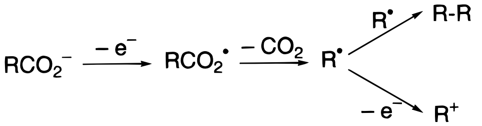
Abstract: To develop a novel method for the photochemical generation of carbanions, the photoinduced electron-transfer reaction of carboxylate salts was investigated. The photolysis of tetra-*n*-butylammonium or metal ion/crown ether salts of diphenylacetate ($Ph_2CHCO_2^-$) sensitized with 1-cyanonaphthalene or 1,4-dicyanonaphthalene in THF or benzene yielded Ph_2CH_2 as the protonated product of the corresponding carbanion (Ph_2CH^-). This reaction was not affected by the presence of oxygen, and nanosecond transient absorption spectroscopy allowed the observation of Ph_2CH^- immediately after the laser pulse. The suggested reaction mechanism involves (1) photoexcitation of the sensitizer, (2) the one-electron oxidation of the carboxylate ion, (3) the decarboxylation of the resulting carboxyl radical generating $Ph_2CH^\bullet$, and (4) the back electron-transfer from the sensitizer radical anion to the radical to yield the carbanion, which occurs smoothly within cage of the geminate radical ion pair. When the sensitizer employed was 9,10-dicyanoanthracene, which has a less negative reduction potential, $Ph_2CH^\bullet$ was observed by laser flash photolysis. The free energy change ($-\Delta G$) on the electron transfer is the crucial factor determining the radical/anion selectivity.

Introduction

The photochemical generation of closed-shell ions is a topic of current interest in organic photochemistry.[1] For example, photogenerated cations may act as an initiator of cation polymerizations,[2] and much attention has recently been focused on "caged compounds" which lead to the photorelease of biologically active ionic compounds.[3] Another advantage of photogeneration is that very fast reactions can be followed by laser flash photolysis techniques. Carbanions are one of the most common reactive intermediates in organic syntheses,[4] and hence the photogeneration of such ionic species may contribute to progress in mechanistic organic chemistry. Only a few examples are known for the photochemical formations of carbanions,[5] most of which are based on the photodissociation of carboxylic acids.

A related reaction is the anodic oxidation of carboxylate ions (RCO_2^-), i.e., the Kolbe reaction (eq 1),[6] in which carbon-centered radicals ($R^\bullet$) are formed via decarboxylation of carboxyl radicals ($RCO_2^\bullet$). These carbon radicals undergo dimerization



(1)

or further oxidation, yielding R−R or R^+, respectively. It is known that the photoinduced electron-transfer (PET) reaction of carboxylic acids also gives carbon-centered radicals via decarboxylation.[7] In this reaction, carbon radicals are formed together with sensitizer radical anion ($Sens^{-\bullet}$), and hence the formation of carbanion might be expected if an effective electron transfer between them takes place. However, the reported PET reactions yielded a mixture of radical−sensitizer adducts and other radical coupling products.[8,9] While several synthetically useful reactions have been explored by the photosensitized

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Scheme 1

$$\text{Sens} \xrightarrow{h\nu} \text{Sens}^{*} \qquad \text{(i)}$$

$$\text{Sens}^{*} + \text{RCO}_2^{-} \xrightarrow{(-\Delta G_q)} \text{Sens}^{-\bullet} + \text{RCO}_2^{\bullet} \qquad \text{(ii)}$$

$$\text{Sens}^{-\bullet} + \text{RCO}_2^{\bullet} \xrightarrow{-\text{CO}_2} \text{Sens}^{-\bullet} + \text{R}^{\bullet} \qquad \text{(iii)}$$

$$\text{Sens}^{-\bullet} + \text{R}^{\bullet} \xrightarrow{(-\Delta G)} \text{Sens} + \text{R}^{-} \qquad \text{(iv)}$$

decarboxylations[10] in the presence of hydrogen donors, carbanion formation has never been intended in these studies.

Direct photolysis of carboxylate anions produces carbanions,[8c,11] but their spectroscopic observation has been achieved only for carbanions stabilized by electron-withdrawing substituents (e.g., *p*-nitrobenzyl anion)[12] or by resonance with a carbonyl group.[13]

During our study on the redox reactions of neutral radicals,[14] it has been elucidated that the reduction of benzylic radicals by cyanoaromatic radical anions proceeds quite efficiently under appropriate conditions. Thus, we tried to generate carbanions via photosensitized decarboxylations. The strategy is to use carboxylate salts ($RCO_2^-M^+$) in aprotic solvents in order to produce basic carbanions (R^-). Fast and efficient carbanion formation would be expected under appropriate conditions in the photochemical redox reaction, as shown in Scheme 1. Four elementary steps are involved here: (i) the excitation of an electron-accepting sensitizer, (ii) the one-electron oxidation of carboxylate ion, (iii) the decarboxylation of the carboxyl radical, and (iv) the electron transfer from sensitizer radical anion to the resulting carbon-centered radical.

We report here that the predicted reaction sequence of Scheme 1 is operative and carbanions are observable spectroscopically. It is shown that the electron transfer from $Sens^{-\bullet}$ to $R^\bullet$ occurs efficiently within the geminate radical ion pair (in-cage).

Results and Discussion

Conditions for the Sensitized Photooxidations of Carboxylate Ions. We examined the photosensitized one-electron oxidation of carboxylate ions (RCO_2^-) in aprotic solvents in order to develop a novel method of carbanion formation. Solvents used were tetrahydrofuran (THF) and benzene; acetonitrile (MeCN) could not be employed since it forms complexes with crown ethers[15] and has acidic methyl protons.[16] Sensitizers employed are listed in Table 1, together with their singlet excitation energies (E_s) and reduction potentials ($E_{1/2}^{red}$) in MeCN.[14,17] Efficiencies of electron-transfer quenching of excited sensitizers by carboxylate anions ($E_{1/2}^{ox} = +1.7-1.8$ V vs NHE in MeCN for R = alkyl)[18] could be evaluated from the Rehm−Weller relationship[19] to be high for all sensitizers (i.e., $-\Delta G_q \geq 0$, as listed in the last column in Table 1). Here, solvent effects were neglected since the potential shifts in the sensitizers may be mostly canceled by the ones in RCO_2^-.

Table 1. Electrochemical and Photophysical Data of Sensitizers and Radicals

	$E_{1/2}^{red}$ (V vs SCE)[a]	E_s (eV)	$-\Delta G_q$ (eV)[b]
Sensitizers			
1,2,4,5-tetracyanobenzene (TCB)	−0.65[c]	3.80[c]	1.7
1,4-dicyanobenzene (DCB)	−1.60[d]	4.27[d]	0.7
1,4-dicyano-2,5-dimethylbenzene (DMDCB)	−1.75[e]	3.89[f]	0.6
1,4-dicyano-2,3,5,6-tetramethylbenzene (TMDCB)	−1.90[e]	3.74[f]	0.3
1-cyanonaphthalene (CN)	−1.98[d]	3.88[d]	0.4
1,4-dicyanonaphthalene (DCN)	−1.28[d]	3.45[d]	0.7
9-cyanoanthracene (CA)	−1.58[g]	3.04[g]	0.0
9,10-dicyanoanthracene (DCA)	−0.89[d]	2.86[d]	0.5
Radicals			
p-chlorobenzyl	−1.40[h]		
p-methoxybenzyl	−1.82[h]		
diphenylmethyl	−1.14[i]		
α-naphthylmethyl	−1.27[j]		

[a] Redox potentials obtained at room temperature in CH_3CN. [b] Estimated from Rehm−Weller relationship[19] based on the assumption that $E_{1/2}^{ox}(RCO_2^-)$ is 1.5 V vs SCE.[18] [c] From ref 17b. [d] From ref 17c. [e] From ref 14. [f] From ref 17d. [g] From ref 17a. [h] From ref 23b. [i] From ref 23a. [j] From ref 23c.

For the mechanistic analysis of the present study, four criteria should be satisfied: (i) the reduction potential of $R^\bullet$ should be known and should not be too negative, (ii) the resulting carbanion R^- should be observable in the visible range, (iii) the absorption spectrum of the carboxylate anion itself should not overlap with that of the sensitizer, and (iv) the decarboxylation of $RCO_2^\bullet$ should take place "instantaneously". While the decarboxylation is not so fast for primary alkyl, alkenyl, alkynyl, and aryl carboxyls,[20,21] those of benzylic carboxyls proceed very fast on the time scale of $10^{-12}-10^{-10}$ s.[22] The benzylic carboxylates employed here are listed in Chart 1, for which the reduction potentials of corresponding benzyl radicals are known (Table 1).[23] The one-electron reductions of $R^\bullet$ by sensitizer radical anions, the key step iv in Scheme 1, are expected to depend on the free energy changes ($-\Delta G$) for the electron transfer, which can be estimated from the difference in one-electron reductions between $R^\bullet$ and sensitizer (eq 2).

$$-\Delta G = -E_{1/2}^{red}(\text{sens}) + E_{1/2}^{red}(\text{R}^\bullet) \qquad (2)$$

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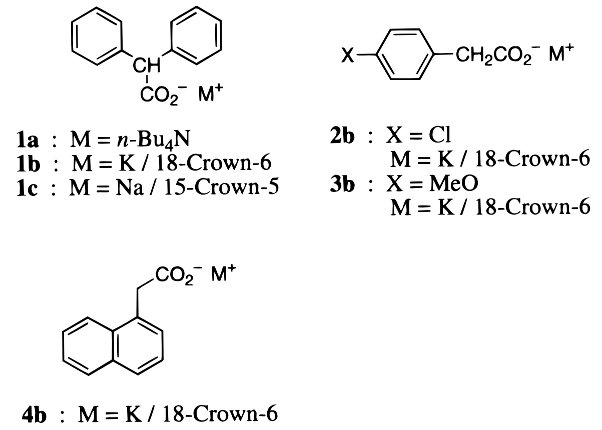
Chart 1



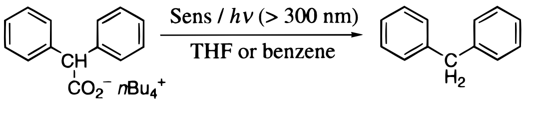
1a : M = *n*-Bu_4N
1b : M = K / 18-Crown-6
1c : M = Na / 15-Crown-5

2b : X = Cl
M = K / 18-Crown-6
3b : X = MeO
M = K / 18-Crown-6

4b : M = K / 18-Crown-6

Several carboxylate salts ($RCO_2^-M^+$) with various R's and M's were prepared from the corresponding carboxylic acids by adding equimolar bases or by cation exchange. The tetra-*n*-butylammonium salt (**1a**) was soluble in THF and benzene, and metal carboxylates (M = Li, Na, and K) could also be dissolved by stirring with an equimolar amount of 12-crown-4 (Li), 15-crown-5 (Na), or 18-crown-6 (K). Several carboxylate salts such as potassium 9-methyl-9-fluorenecarboxylate could not be employed since their spontaneous thermal decarboxylation proceeded rapidly at room temperature.[24]

Products of the Photooxidation of Carboxylates. (a) Diphenylacetates (1). The fluorescence of 1-cyanonaphthalene (CN) was found to be quenched efficiently by tetra-*n*-butylammonium diphenylacetate (**1a**) in THF, with a bimolecular rate constant of 9.0×10^9 M^{-1} s^{-1}. When an argon-saturated THF solution of 10 mM **1a** and 5 mM CN was irradiated (>300 nm) for 2 h, 58% of **1a** was converted to diphenylmethane (**5**) in 100% selectivity (run 1 in Table 2).



1a **5** (3)

Similar photoreactions of **1** were carried out with various sensitizers, solvents, and counterions, the results being summarized in runs 1−9 of Table 2. The use of naphthalene, instead of cyanoaromatic sensitizers, where the one-electron oxidation of carboxylate **1a** is slightly endothermic ($-\Delta G_q < 0$), resulted in practically no reaction. Thus, it is apparent that the decarboxylation is initiated by photoinduced one-electron oxidation of **1**, not by energy transfer. The CN-sensitized photooxidation of K/18-crown-6 (**1b**) and Na/15-crown-5 salts (**1c**) in THF proceeded similarly (runs 7 and 9), but the reaction was significantly decelerated by the addition of 10% H_2O. In addition, the Li salt of **1** in THF or the Na salt in MeOH did not quench the fluorescence of CN at all. Thus, the present photodecarboxylation is effective only for naked carboxylate ions, that is, in the absence of ion-pairing with a countercation or hydrogen-bonding with protic solvents.

Sensitizations with 1,4-dicyanonaphthalene (DCN) and 9-cyanoanthracene (CA) resulted in less selectivity (runs 2 and 3), where substantial amounts of sensitizers were consumed during the photooxidation but the corresponding products could not be identified. The CN-sensitized photooxidation took place in benzene as well (run 4). When the photoreaction was carried out under an oxygen atmosphere, $Ph_2C{=}O$ was obtained in 39% yield, but Ph_2CH_2 was still formed as the major product in 57% yield (run 6). Thus, the predominant pathway is not affected by molecular oxygen, a well-known radical scavenger,[25] indicating that most of $Ph_2CH^\bullet$ is reduced instantaneously within the geminate radical ion pair.

We were interested in the sensitization with 9,10-dicyanoanthracene (DCA) because the one-electron reduction of $R^\bullet$ by $DCA^{-\bullet}$ is estimated to be endothermic by 0.25 eV. Contrary to the prediction, the DCA-sensitized photooxidations of **1a** proceeded similarly, affording Ph_2CH_2 as the major product in addition to a small amount of 1,1,2,2-tetraphenylethane ($(Ph_2CH)_2$). An interesting point about this observation will be discussed later.

(b) Substituted Phenylacetates (2b and 3b). The photooxidations were also investigated for substituted phenylacetates. The 1,2,4,5-tetracyanobenzene (TCB)- or DCA-sensitized photooxidations of K/18-crown-6 salts of *p*-chloro- (**2b**) and *p*-methoxyphenylacetates (**3b**) in benzene also gave *p*-chloro- and *p*-methoxytoluene, respectively, but in much lower yields (Table 2, runs 10, 11, 14, and 15). A substantial amount of bibenzyl, (p-$MeOC_6H_4CH_2)_2$, was detected for the reaction of **3b**. The low mass balance in these cases might be due to coupling reactions of benzyl radicals with the cyanoaromatic radical anion;[26] in fact, a coupling product was actually identified in the products from **2b** (see run 11 in Table 2). These coupling reactions may be avoided by use of sterically hindered sensitizers,[17d,27] such as 1,4-dicyano-2,5-dimethylbenzene (DMDCB) or 1,4-dicyano-2,3,5,6-tetramethylbenzene (TMDCB). It was found that the selectivities for formation of the toluenes were significantly improved (runs 12, 13, 16, and 17) with these hindered sensitizers. The remarkable effect of TMDCB as the sensitizer might be, in addition to the steric hindrance, due to its more negative reduction potential facilitating electron transfer from $TMDCB^{-\bullet}$ to benzyl radicals.

(c) 1-Naphthylacetates (4). Similar sensitized photolyses of the K/18-crown-6 salt of 1-naphthalenecarboxylate ($NpCH_2CO_2^-$, **4b**), which has an absorption band at ∼340 nm, were carried out with both CA and DCA as sensitizer using a filter solution (i.e., >350 nm). The photooxidations of **4b** were effective, affording 1-methylnaphthalene ($NpCH_3$ (**10**)) as the major product (runs 18 and 19), and the dimeric product, $(NpCH_2)_2$, was not detected. When anthracene was employed as the sensitizer, no reaction took place, **4b** being recovered quantitatively.

The predominant formation of $NpCH_2$-H in the DCA sensitization seems to be anomalous because the one-electron

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Table 2. Products on the Continuous Irradiation of Carboxylate and Sensitizer Systems[a]

					selectivity (%)		
run no.	RCO_2^-	R−	solvent	sens	R−H	others	$-\Delta G$ (eV)[b]
1	**1a**	Ph_2CH-	THF	CN	100	nd[c]	+0.84
2				CA	21	nd	+0.44
3				DCN	28	nd	+0.14
4			benzene	CN	73	nd	+0.84
5				DCA	55	R−R, 13	−0.25
6			benzene[d]	CN	57	$Ph_2C{=}O$, 39	+0.84
7	**1b**	Ph_2CH-	THF	CN	74	nd	+0.84
8				CA	34	R−R, 1.4	+0.44
9	**1c**	Ph_2CH-	THF	CN	100	nd	+0.84
10	**2b**	$p\text{-}ClC_6H_4CH_2-$	benzene	DCA	26	nd	−0.51
11				TCB	12	**6**,[e] 19	−0.75
12				TMDCB	78	nd	+0.50
13				DMDCB	81	nd	+0.35
14	**3b**	$p\text{-}MeOC_6H_4CH_2-$	benzene	DCA	12	R−R, 23	−0.93
15				TCB	6.1	R−R, 5.2	−1.17
16				TMDCB	52	R−R, 1.2; **7**,[e] 8.9	+0.08
17				DMDCB	21	R−R, 3.2; **8**,[e] 22; **9**,[e] 15	−0.07
18	**4b**	$\alpha\text{-}NpCH_2-$	benzene	CA	64	nd	+0.31
19				DCA	52	nd	−0.38
20			benzene[f]	CA	23[g]	nd	+0.31
21				DCA	44[g]	nd	−0.38
22			benzene[d]	CA	45	NpCHO, 12	+0.31
23				DCA	6.7	NpCHO, 44	−0.38

[a] Argon-saturated solutions of carboxylate salt (0.3−5.0 mM) and sensitizer (0.2−5.0 mM) were irradiated with a 300-W medium-pressure mercury lamp through an appropriate filter (>350 nm for **1**−**3**; >300 nm for **4** and **5**). Conversions of carboxylates were mostly over 60% yield. [b] Estimated from eq 1. [c] nd, not detected (<0.5%). [d] Under oxygen atmosphere. [e] See Chart 2. [f] 1% D_2O was added. [g] 1-Methylnaphthalene-α-*d* ($NpCH_2D$), over 80%.

reduction of $NpCH_2^{\bullet}$ by $DCA^{-\bullet}$ is endothermic by 0.38 eV (see Table 2). Since **10** may be formed either by the protonation of $NpCH_2^-$ or via hydrogen abstraction of $NpCH_2^{\bullet}$, the origin of hydrogen in **10** was examined by deuterium labeling. When 1% D_2O was added to the solvent benzene, 1-methylnaphthalene-α-*d* ($NpCH_2D$) was obtained in over 80% D isotropic purity, indicating the predominance of the reduction of $NpCH_2^{\bullet}$ by $DCA^{-\bullet}$ followed by protonation of $NpCH_2^-$ with water.

It is interesting to note that a large difference in the effects of O_2 on CA- and DCA-sensitized photooxidations was observed. CA-sensitized reaction of **4b** was not significantly affected by the presence of molecular oxygen, affording **10** (45%) as the major product. However, in the case of DCA sensitization, the formation of **10** was suppressed to only one-eighth, and the major product was NpCHO (44%).

Transient Absorption Spectra of Intermediates Generated by Laser Flash. Nanosecond laser flash photolysis (LFP) was carried out in order to clarify the primary photoproduct on the sensitized photooxidation of diphenylacetate salts (**1**). LFP (XeCl, 308 nm, 10 ns) of **1b** (20 mM) and CN (0.2 mM) in THF showed an absorption band of an intermediate with its maximum at 450 nm immediately after the laser pulse, as shown in Figure 1a. The absorption bands of $CN^{-\bullet}$ ($\lambda_{max} = 370$ nm)[28] and of $Ph_2CH^{\bullet}$ ($\lambda_{max} = 325$ nm)[29] were practically absent in this spectrum. The spectrum quite resembles that of $Ph_2CH^-K^+$/18-crown-6 in THF ($\lambda_{max} = 448$ nm),[30] but the assignment was not conclusive because the triplet excited state of CN has a similar T−T absorption band around 450 nm.[31] Next, the LFP experiment was done with TMDCB (0.2 mM), which led to the production of an almost identical transient absorption spectrum (Figure 1b). Thus, in both cases, the diphenylmethyl carbanion (Ph_2CH^-) was actually generated within the pulse duration of excimer laser, i.e., <10 ns. This observation confirms that the reduction of the carbon radical by electron

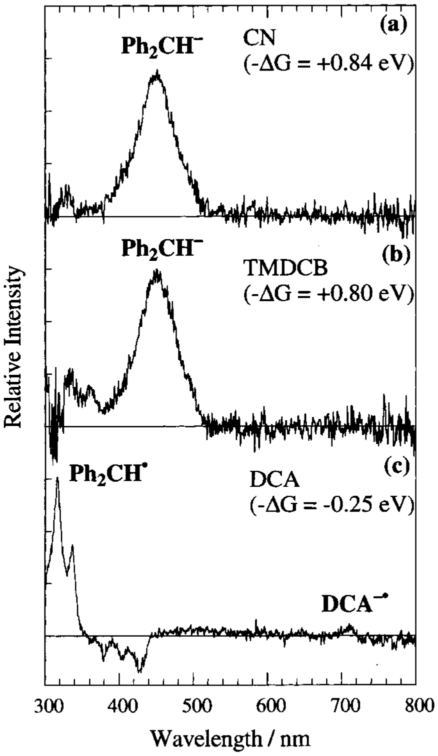

Figure 1. Absorption spectra of transients obtained from laser flash of sensitizers and diphenylacetate salts in solution saturated with argon. (a) 0.2 mM CN and 20 mM potassium diphenylacetate/18-crown-6 (**1b**) in THF at 1 μs after excitation (308 nm, XeCl). (b) 0.2 mM TeMDCB and 20 mM **1b** in THF at 1 μs after excitation (308 nm, XeCl). (c) 0.1 mM DCA and 10 mM tetra-*n*-butylammonium diphenylacetate (**1a**) in benzene at 300 ns after excitation (355 nm, Nd:YAG THG).

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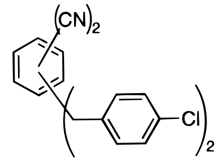
transfer proceeds smoothly in-cage, i.e., within the geminate radical ion pair.

Chart 2



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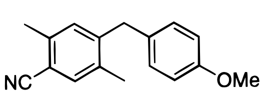

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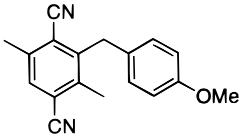

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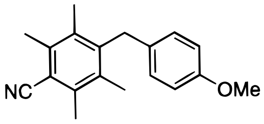

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In contrast, LFP (third harmonic of Nd:YAG laser, 355 nm, ~6 ns) of 10 mM **1a** and 0.1 mM DCA in benzene resulted in a quite different spectrum, as shown in Figure 1c, which indicated the generation of $Ph_2CH^\bullet$ ($\lambda_{max} = 325$ nm) and $DCA^{-\bullet}$ ($\lambda_{max} = 335$, 500, 580, 640, and 700 nm).[28,32] The absorption of Ph_2CH^- was not observed at all, which might be understandable because the reduction of $Ph_2CH^\bullet$ by $DCA^{-\bullet}$ is endothermic, $-\Delta G < 0$. The kinetic trace of diphenylmethyl radical followed a rapid second-order decay due to its dimerization, while $DCA^{-\bullet}$ did not decay within the time window of the experiment, i.e., 100 μs.

Free Energy Change ($-\Delta G$) Dependence of Anion/Radical Selectivities. It was shown that irradiation of argon-saturated solutions of sensitizers in the presence of carboxylate salts ($R-CO_2^-M^+$) led to the predominant formation of R−H, which was formed by protonation of carbanions (R^-) as indicated by the incorporation of deuterium from D_2O. The products of irradiation under oxygen and the LFP study showed that the formation of either carbanion (R^-) or radical ($R^\bullet$) depends on the energy gap of the electron transfer from sensitizer anion radical to $R^\bullet$. When the electron transfer is exothermic ($-\Delta G > 0$), it takes place smoothly within the geminate pair of radical/sensitizer radical anion ($R^\bullet/Sens^{-\bullet}$) and is not affected by the presence of molecular oxygen. In contrast, when $-\Delta G < 0$, the geminate pair of $R^\bullet/Sens^{-\bullet}$ dissociates into free $R^\bullet$ and $Sens^{-\bullet}$, which are trapped effectively by oxygen to afford mainly oxygenated products. Thus, it is apparent that the reduction potentials of sensitizers have a crucial role in determining the in-cage production of carbanions. In other words, the product selectivity depends on the free energy change ($-\Delta G$) for the one-electron reduction of $R^\bullet$ by sensitizer radical anions.

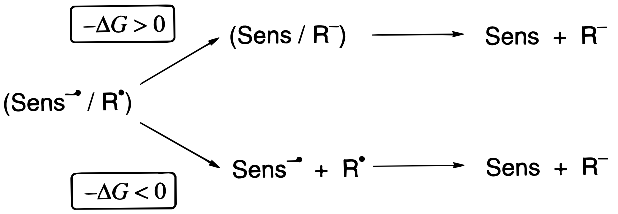
The rate constant of bimolecular electron transfer (k_{et}) can be estimated from the Rehm−Weller relationship[19] according to

$$k_{et} = \frac{k_{diff}}{1 + 0.25[\exp(\Delta G^{\ddagger}/RT) + \exp(\Delta G/RT)]} \tag{4}$$

$$\Delta G^{\ddagger} = \sqrt{(\Delta G/2)^2 + (\Delta G(0))^2} + \Delta G/2 \tag{5}$$

Here, k_{diff} is the diffusion-controlled rate constant, and $\Delta G^{\ddagger}$ and $\Delta G^{\ddagger}(0)$ are the activation free energy and that at $\Delta G = 0$, respectively. If the electron transfer between $R^\bullet$ and aromatic radical ions follows the Rehm−Weller relationship, the bimolecular rate constant will reach the diffusion limit when $-\Delta G \geq +0.5$ eV. This case corresponds to the ET between $Ph_2CH^\bullet$ and $CA^{-\bullet}$ ($-\Delta G = +0.84$ eV) or $TMDCB^{-\bullet}$ ($-\Delta G = +0.80$ eV). On the other hand, the predicted rate constant for the reduction of $Ph_2CH^\bullet$ by $DCA^{-\bullet}$ ($-\Delta G = -0.25$ eV) falls to $\sim 10^7\ M^{-1}\ s^{-1}$. Such a slow electron transfer would not compete with the dissociation of radical ion pairs into, as observed, free radical and ions as depicted in Scheme 2.

Scheme 2



Electron-transfer processes within geminate radical ion pairs have been well studied both by the free ion yields[32,33] and by high-speed time-resolved spectroscopy,[34] demonstrating that the first-order ET rates show the Marcus inverted region[35] and distance dependence.[36] Since the ET in the present case is a charge shift in less polar solvents, some difference may be expected in the behavior of intermediates and in ET parameters from a charge recombination between radical cations and anions. Related cases have been studied by Pincock,[37] Gould et al.,[38] and Schuster el al.[39] More detailed examination of the electron transfer within the $R^\bullet/Sens^{-\bullet}$ pair will be possible if the first-order rate constants are determined, e.g., by picosecond transient absorption spectroscopy.

Finally, some mention should be made here of the out-of-cage ET process. As stated above, the geminate pair of ($R^\bullet$/$Sens^{-\bullet}$) dissociates into free radical and radical ions when the in-cage ET is endothermic ($-\Delta G > 0$). In the case of DCA, the predicted rate for the reduction of $Ph_2CH^\bullet$ by $DCA^{-\bullet}$ is only $\sim 10^7\ M^{-1}\ s^{-1}$ according to the Rehm−Weller equation. A question here is why the slow ET reaction becomes the major one despite quite fast coupling of $R^\bullet$. This could well be explained by the persistent radical ion effect of the relatively stable radical ion $DCA^{-\bullet}$. In fact, the spectra of long-living $DCA^{-\bullet}$ was observed by laser flash spectroscopy (see Figure 1c) and also after 5 min irradiation of DCA and **1a**, as shown in the Supporting Information. Although the ET reduction of $R^\bullet$ by $DCA^{-\bullet}$ is not as fast as the coupling of $R^\bullet$, the steady-state concentration of $DCA^{-\bullet}$ is high enough to suppress the

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dimerization. This is an interesting example of Ingold−Fischer persistent radical effect.[40] The $DCA^{-\bullet}$ has been detected spectroscopically in some PET reactions.[41,42] It should be stressed here that the persistent radical ion effect may play an important role in controlling reaction selectivities.

Conclusion

We have shown that the generation of carbanions from carboxylate ions is achieved by photoinduced electron transfer. This reaction is potentially useful not only in the conversion of arylacetic acids (RCO_2H) to RH but as a method to generate carbanions photochemically. The key process in the formation of either carbanion is the electron transfer from sensitizer anion radical to radical intermediates proceeding in-cage and depending on the free energy changes. When the electron transfer is exothermic ($-\Delta G > 0$), it takes place smoothly within the geminate radical ion pair ($R^\bullet/Sens^{-\bullet}$) and is not affected by external radical scavengers such as oxygen. In contrast, when $-\Delta G < 0$, the ET proceeds in bulk between free radical ($R^\bullet$) and sensitizer radical anion ($Sens^{-\bullet}$). The former in-cage formation of carbanions is clean and may provide a useful method to prepare “naked” benzyl-type carbanions.

Experimental Section

^1H NMR spectra were recorded with a Varian Gemini-200 (200 MHz) NMR spectrometer. GC/MS analyses were carried out with a Shimadzu QP-5000 mass spectrometer using a 0.2-mm × 25-m capillary column of CBP1-M50-025 (Shimadzu). GLC analyses were performed with a Shimadzu GC-14A gas chromatograph, using a 2.5-mm × 1-m column of Carbowax 300M, 2% on Chromosorb WAW (GL Sciences).

Materials. Benzene and THF (Tokyo Kasei) were distilled over sodium. Crown ethers were received from Tokyo Kasei and used without further purification. 1,2,4,5-Tetracyanobenzene (TCB), 1,4-dicyanobenzene (DCB), naphthalene, anthracene, and 9-cyanoanthracene (CA) were received from Tokyo Kasei and recrystallized from ethanol. 1-Cyanonaphthalene (Tokyo Kasei) was distilled under reduced pressure. 1,4-Dicyano-2,5-dimethylbenzene (DMDCB),[43] 1,4-dicyano-2,3,5,6-tetramethylbenzene (TMDCB), 1,4-dicyanonaphthalene (DCN),[44] and 9,10-dicyanoanthracene (DCA)[45] were prepared by the reported procedures. Metal salts of carboxylates were prepared from the corresponding carboxylic acid by adding equimolar base such as LiOH, NaOH, or KOH in MeOH and precipitated by the addition of ether. The precipitate was filtered and washed with ether. ^1H NMR analysis revealed that the purity of salts of carboxylates was ∼100%.

Tetra-*n*-butylammonium Diphenylacetate (1a). Tetra-*n*-butylammonium bromide (13 g, 40 mmol) and sodium diphenylacetate (12 g, 50 mmol, excess) were dissolved in water and stirred with a magnetic stirrer. The solution was extracted three times with CH_2Cl_2 (200 mL). After being dried over anhydrous sodium sulfate, the solvent was removed by rotary evaporation to yield a viscous oil that solidified upon standing, yielding white needle crystals. ^1H NMR (200 MHz) in $CDCl_3$: δ 0.92 (t, $J = 7$ Hz, 12 H), 1.31 (m, 8 H), 1.52 (m, 8 H), 3.16 (m, 8 H), 5.06 (s, 1 H), 7.28 (m, 10 H).

Continuous and Pulse Irradiations. Since all sensitizers should be excited at longer wavelength than carboxylates, the excitation of carboxylate salts or photoproducts was avoided in sensitized photolyses by the use of appropriate filters. Continuous irradiations were done with a 300-W medium-pressure mercury lamp through a Pyrex filter (i.e., >300 nm) or 10% KNO_3 filter solution (i.e., >350 nm). Typically, a 10-mL solution of carboxylate (∼5 mM) including sensitizer (∼3 mM) in a test tube with a septum rubber cap was purged with argon for 10 min and was irradiated at ambient temperature.

Pulse irradiation was done with a SL248G Nd:YAG laser and carried out by flowing the solution through a $3 \times 1 \times 0.1$ cm^3 quartz cell in order to ensure that each laser pulse irradiated a fresh volume of solution.

After irradiation, an internal standard was added to the solutions. Then it was washed with 1 N HCl and treated with diazomethane for the methylation of carboxylates. The products were identified by GC/MS, and the conversion of the carboxylates (methyl esters) and the yield of products were determined at appropriate intervals of time by GLC.

Time-Resolved Absorption Spectroscopy. Laser kinetic spectroscopy experiments were carried out using a nanosecond laser system similar to that previously described.[46] The system consisted of a 150-W Xe flash lamp (XF-80, Tokyo Instruments), a SPEX 270M monochromator, and a Hamamatsu R-1221HA photomultiplier tube. The CCD detector (ICCD-1024-MLΔG-E, Princeton Instruments) was controlled by a detector controller (ST-135, Princeton Instruments) and a pulse generator (PG-200, Princeton Instruments). The system was controlled by a PC-9801 computer which was interfaced (GPIB) to the detector controller. The delay time of this system was controlled by two digital delay/pulse generators (DG-535, Stanford Research system). The excitation source was a Physik MINex XeCl excimer laser (308 nm, ∼10 ns, ∼15 mJ/pulse) or the third harmonic (355 nm, ∼6 ns, ∼25 mJ/pulse) from a Spectron SL248G Nd:YAG laser. The argon-saturated sample solutions were irradiated in a 4×1 cm^2 cell made of quartz.

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Supporting Information Available: Absorption spectrum of benzene solution of 0.15 mM DCA and 3 mM **1a** under argon (Figure 2); $DCA^{-\bullet}$ of 2×10^{-3} mM was detected by the characteristic absorption at 450−750 nm (1 page, print/PDF). See any current masthead page for ordering information and Web access instructions.

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