PERKIN 2

Mechanistic studies of direct and sensitized photolysis of methyl (4-nitrophenyl)diazoacetate in the presence of an electron-donating amine: photochemical generation of the diazoalkane radical anion

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The direct and perylene-sensitized photolysis of methyl (4-nitrophenyl)diazoacetate (**1**) in the presence of an electron-donating amine was investigated by the characterization of reaction products and by the direct observation of reactive species using a laser flash photolysis technique. In the direct photolysis of **1** in the presence of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD), electron transfer from TMPD occurs and the photoproducts are obtained through an intermediate other than the carbene **3**, which we suppose to be the carbene radical anion $\mathbf{3}^{-\bullet}$. In the perylene-sensitized photolysis of **1** in the presence of an amine having a large electron-donating ability such as *N*,*N*-dimethylaniline and TMPD, the radical anion of **1** can be generated by perylene-mediated electron transfer from the amine to **1**. The resulting $\mathbf{1}^{-\bullet}$ appears to undergo extrusion of dinitrogen to give $\mathbf{3}^{-\bullet}$ smoothly, the behavior of which is dependent on the amine employed as an additive. The product studies revealed that $\mathbf{3}^{-\bullet}$ reacts readily with O_2 to give the ketoester **5** or abstracts hydrogen atoms to give the ester **7**, which is not inconsistent with the theoretical prediction that $\mathbf{3}^{-\bullet}$ has a σ radical character in its electronic structure.

Introduction

One-electron reduction is an attractive method for the decomposition of diazoalkanes, in which their radical anions are generated as the first-formed reactive intermediate. The behavior of diazoalkane radical anions is the subject of great interest, particularly in that a loss of dinitrogen gives rise to the corresponding carbene radical anions, which are expected to have unique structural properties and chemical reactivities. The research on one-electron reduction of diazoalkanes was initiated in 1963 by Kauffmann and Hage, who reported that the reduction of diphenyldiazomethane (Ph_2CN_2) with sodium gave its radical anion.[1] Moreover, Webster proposed the formation of carbene radical anion in the polarographic reduction of tetracyanodiazocyclopentadiene.[2] The intervention of the parent methylene radical anion, as well as cyclopentadienylidene radical anion, was suggested in one-electron reduction of the corresponding diazoalkane in the gas phase.[3,4]

In the 1980s, the electrochemical reduction of diazoalkanes was extensively investigated. McDonald and Hawley reported that the electrochemical reduction of Ph_2CN_2 in DMF afforded benzophenone azine through the carbene radical anion, $Ph_2C^{-\bullet}$, produced from electrogenerated $Ph_2CN_2^{-\bullet}$ by rapid loss of dinitrogen.[5] However, Bethell and his co-workers proposed that the azine was formed by the reaction of $Ph_2CN_2^{-\bullet}$ with Ph_2CN_2 or $Ph_2CN_2^{-\bullet}$ on the basis of the data obtained by using their skilful cyclic voltammetric experiments, which ruled out the intervention of $Ph_2C^{-\bullet}$.[6] Based on the results of electrochemical reduction of various diazoalkanes,[7–9] they established that a unimolecular loss of dinitrogen from the diazoalkane radical anion giving the corresponding carbene radical anion occurred in the diazoalkanes having a carbonyl group at the position adjacent to the diazo group, such as azibenzil and diethyl diazomalonate.[7,10]

In contrast to this research on chemical and electrochemical one-electron reduction of diazoalkanes, no attempt has been reported so far to generate diazoalkane radical anions photochemically. Tomioka and his co-workers found that the irradiation of (4-nitrophenyl)diazomethane in diethylamine afforded 4-nitrotoluene predominantly, and they explained its formation by a mechanism involving the radical anion of the diazomethane produced from an electron transfer from diethylamine to the diazomethane.[11] To our knowledge, this is the sole example of the photoreaction in which the intervention of the diazoalkane radical anion was proposed. It seems possible that the photolysis of a diazoalkane having an electron-deficient group in the presence of an electron-donating substance results in an electron transfer from the substance to the diazoalkane, which gives rise to the diazoalkane radical anion. In this paper, we report our mechanistic studies of direct and sensitized photolysis of methyl (4-nitrophenyl)diazoacetate (**1**) in the presence of an electron-donating amine, in which we wish to propose a reaction scheme involving the radical anion of **1** formed from an electron transfer from an amine to **1**.[12]

Results

Direct photolysis of the diazoacetate 1 in the presence of an amine

(1) Dependence of photoproducts on amines. The photochemistry of the diazoacetate **1** was reported by Tomioka and his co-workers, in which the irradiation of **1** in methanol afforded methyl α-methoxy-(4-nitrophenyl)acetate (**2**).[13] This product was formed by the insertion of the photolytically generated carbene **3** into the OH bond of methanol, which is known as an excellent trapping agent for carbene.[14] A mechanism for the formation of **2** involving the Wolff rearrangement of **3** into the ketene, followed by reaction with methanol, was excluded, because the irradiation of **1** in methanol-d_4 gave **2** deuterated not at the methyl group of the methoxycarbonyl moiety (δ 3.75) but at that of the α-methoxy moiety (δ 3.47).

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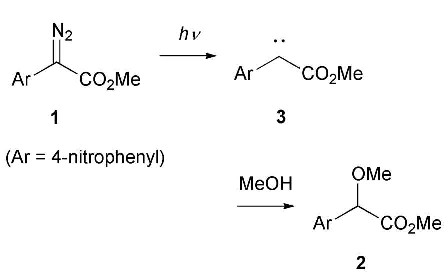
Table 1 Dependence of the photoproducts on additives in the photolysis of **1** in acetonitrile–methanol (9 : 1)[a]

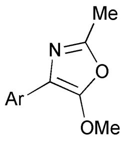
	Yield (%)[b]					
Additives	**2**	**4**	**5**	**7**	E_{ox}[c]/V *vs.* SCE	ΔG[d]/kcal mol^{-1}
None	34	12	10	< 1	—	—
TEA	38	14	< 1	11	1.07	−4.3
ClDMA	29	16	11	2	0.89	−8.5
DMA	26	15	12	5	0.79	−11
MeODMA	23	17	17	13	0.55	−16
TMPD	< 1	10	19	13	0.12	−26
TMPD[e]	< 1	11	< 1	29	0.12	−26

[a] [**1**] = 5 mM, [Additive] = 50 mM. [b] Yield based on the reacted material (30–40%). [c] Oxidation potential of the additive. [d] Free-energy change for the electron transfer from the additive to **1*T**, the excitation of which is assumed to be 58 kcal mol^{-1}. [e] Degassed by three freeze–thaw cycles. TEA = triethylamine, ClDMA = 4-chloro-*N*,*N*-dimethylaniline, DMA = *N*,*N*-dimethylaniline, MeODMA = 4-methoxy-*N*,*N*-dimethylaniline, TMPD = *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine.

Since the reaction of carbene is very complicated in the absence of a trapping agent, and it is reasonable to think that an electron transfer occurs favorably in a polar solvent, we selected acetonitrile containing 10% (v/v) methanol as a solvent to employ in the study of the photolysis of **1**.



A solution of **1** in acetonitrile containing methanol was purged with argon, and irradiated with a xenon arc lamp (> 390 nm). Chromatographic separation of the reaction mixture gave three products, the α-methoxyacetate **2**,[13] the oxazole **4**,[15] and the ketoester **5**,[16] which were identified by comparison of their ^{1}H NMR spectra with those of authentic samples. The formation of the oxazole **4** is reasonably interpreted in terms of the intramolecular cyclization of the nitrile ylide **6**. Nitrile ylides are accepted as reactive intermediates in the photolysis of diazo compounds in acetonitrile, direct spectroscopic observation of which has been recently achieved by using a laser flash photolysis technique.[17] It seems that the ketoester **5** is produced by the reaction of the carbene **3** in its triplet state with O_2 remaining in the solution, because the formation of **5** was suppressed in the photolysis of the solution degassed strictly by freeze–thaw cycles.



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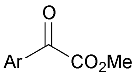

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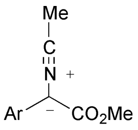

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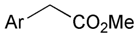

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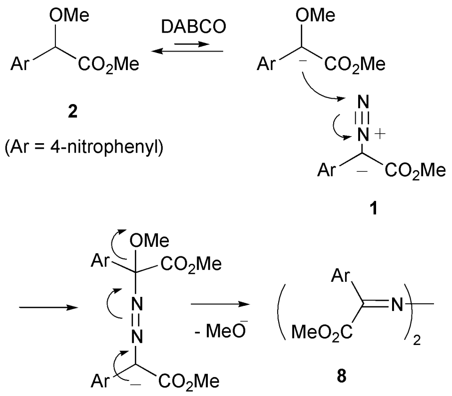
(Ar = 4-nitrophenyl)

When irradiation of **1** was carried out in the presence of an amine (50 mM), a mixture composed of **2**, **4**, and **5** was obtained, but the product distribution varied with the amine employed as an additive. The results are shown in Table 1. In the presence of triethylamine (TEA), methyl (4-nitrophenyl)-acetate (**7**) was obtained instead of **5**. This observation seems to be explained in terms of the hydrogen abstraction of the carbene **3** in its triplet state from TEA to give **7** in preference to the reaction with O_2 to give **5**. However, we found that an increase in the electron-donating ability of the amine, which is evaluated by a lowering of its oxidation potential (Table 1), caused an increase in the yields of **5** and **7** at the expense of **2**. Especially, it should be noted that the formation of **2** was quenched completely in the photolysis of **1** in the presence of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD). This result implies that a reactive intermediate other than the carbene **3** would intervene in the photolysis of **1** in the presence of TMPD. As shown in the table, when the photolysis was carried out after the strict removal of O_2, **5** was not detected but the yield of **7** significantly increased instead. This result indicates that the reactive intermediate generated in the presence of TMPD could afford not **2** but both **5** and **7**. The oxazole **4** could be produced when the formation of **2** was quenched, suggesting that **4** is at least partly formed through a pathway in which the carbene **3** does not participate.

When 1,4-diazabicyclo[2.2.2]octane (DABCO) was employed as an additive, the azine **8** was obtained predominantly. It is known that azines are produced by electrochemical reduction of diazoalkanes through diazoalkane radical anion as a reactive intermediate.[5–8] However, it is found that the azine **8** was formed when the photoreaction mixture obtained by the irradiation of **1** in the presence of DABCO was concentrated by evaporation of the solvent. Moreover, the photolysis in an NMR sample tube confirmed that the irradiation of **1** in the presence of DABCO in methanol-d_4 gave not the azine **8** but the ether **2**. Probably, the azine **8** was produced through the deprotonation of **2** by DABCO, followed by the attack of the resulting carbanion on the terminal nitrogen atom of the starting material **1** remaining in the reaction mixture and the elimination of methoxide ion (Scheme 1). The similar conversion of diazo compounds into the corresponding azines induced by carbanions was reported by Bethell and McDowall.[18]



Scheme 1

(2) Dependence of the product distribution on TMPD concentration. Table 1 shows that the formation of the ether **2** is retarded completely in the photolysis of **1** in the presence of 50 mM of TMPD. We examined the dependence of the product distribution on the TMPD concentration, [TMPD], which would provide information about the reactive species quenched by TMPD. As [TMPD] was increased from 0 to 5 mM, the yield of **2** decreased simply from 34% to 1%, while the yield of **5** increased simply from 4% to 24%. The yield of the oxazole **4** depended in a complicated manner on [TMPD]; the yield of **4** increased from 12% to 19% upon addition of TMPD (0.5 mM), and decreased gradually to 15% with increasing [TMPD] to 5 mM. Fig. 1 illustrates a plot of $\Phi(\mathbf{2})_0/\Phi(\mathbf{2})$ against [TMPD], in which $\Phi(\mathbf{2})_0$ and $\Phi(\mathbf{2})$ are the yields of **2** in the absence and the presence of TMPD, respectively. As shown in the figure, the plot gives a curve deviating upward from a straight line predicted by a Stern–Volmer type relationship. This observation implies that a reaction scheme in which a single reactive species leading to the formation of **2** is quenched by TMPD cannot be applicable to this photoreaction. The analysis of these data is shown in a subsequent section.

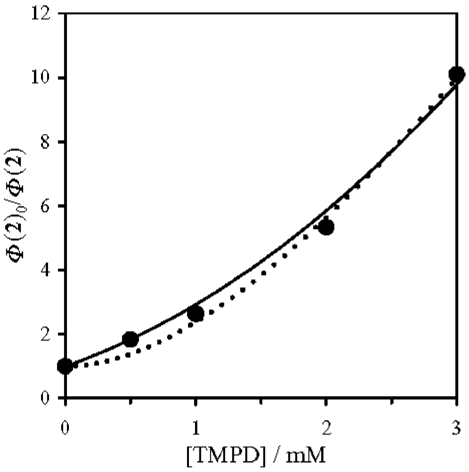


Fig. 1 Dependence of the yield of **2** on the TMPD concentration in the photolysis of **1** in acetonitrile–methanol (9 : 1). Solid and dotted lines represent the curves fitted to the experimental data by using the non-linear least-squares analysis according to eqn. (1) and eqn. (2), respectively.

(3) Laser flash photolysis studies. In order to have information about the mechanism of the photochemistry of **1** in the presence of TMPD, we tried a direct observation of transient intermediates using a nanosecond laser flash photolysis technique. Irradiation of **1** in acetonitrile (1.0 mM) degassed by bubbling of N_2 with the laser pulse (390 nm, 20 ns) gave an intense absorption band with a maximum at 445 nm and a weak broad absorption around 580 nm (a dotted line in Fig. 2). The former absorption, the lifetime of which was estimated to be > 5 µs, is assigned to the nitrile ylide **6** for the following three reasons. First, there have been many precedents that the laser flash photolysis of diazoalkanes in acetonitrile gives a transient absorption around 400 nm having a long lifetime of the order of µs, which is thought to be due to the absorption of the corresponding nitrile ylide.[17] Second, the absorption was observed even in an O_2-saturated acetonitrile solution and its lifetime was unchanged, compared with that recorded in the degassed solution, excluding the possibility of species in the triplet state. Finally, the absorption was not observed in a benzene solution. The weak broad absorption around 580 nm, which had a relatively short lifetime of less than 1 µs, was not observed in an O_2-saturated solution. We assigned this absorption to the T–T absorption of the oxazole **4**, which was confirmed by the laser flash photolysis of an authentic sample of **4** in acetonitrile.

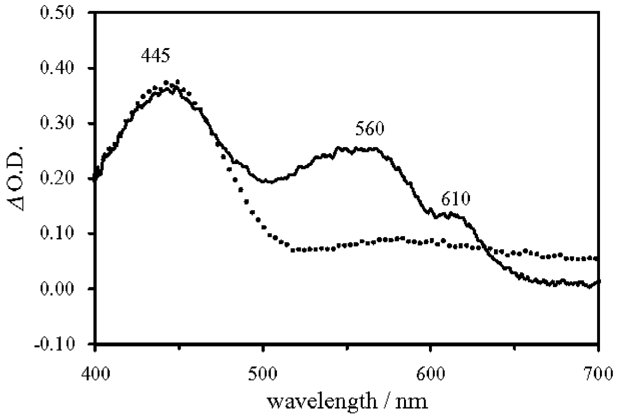


Fig. 2 Transient absorption spectra of a solution of **1** (1.0 mM) in acetonitrile recorded in the presence (solid line) and absence (dotted line) of TMPD (10 mM) at the delay time of 300 ns after a laser pulse (390 nm, 20 ns).

On the other hand, the transient absorption spectrum recorded in the photolysis of **1** in the presence of TMPD (10 mM) exhibited additional bands with maxima of 560 and 610 nm (a solid line in Fig. 2). The intensity of these bands increased until 300 ns after the laser pulse, and decreased slowly with a lifetime of > 5 µs. These bands were observed even in an O_2-saturated acetonitrile solution. We identified the transient species having these bands as TMPD radical cation, $\text{TMPD}^{+\bullet}$, by comparison with an authentic spectrum reported in the literature.[19] Since the diazoacetate **1** is excited exclusively under the conditions of laser flash photolysis, the direct observation of $\text{TMPD}^{+\bullet}$ provides unambiguous evidence for the involvement of a single electron transfer process in the photolysis of **1** in the presence of TMPD.

Sensitized photolysis of the diazoacetate 1 in the presence of an amine

Even if an electron transfer occurs from the amine employed as an additive to the photochemically excited diazoacetate **1**, the efficiency of the generation of $\mathbf{1}^{-\bullet}$ would be low because the extrusion of dinitrogen giving the carbene **3** competes with the electron transfer process. However, when an electron is transferred from a sensitizer radical anion, which is generated by the electron transfer from an amine to the excited sensitizer, to **1**, this problem could be overcome. Moreover, the charge recombination between the resulting amine radical cation and $\mathbf{1}^{-\bullet}$, which reduces the practical efficiency of the electron transfer, could be suppressed in the sensitized photolysis, compared with the direct irradiation, because these radical ions are generated separately from each other. Thus, the electron transfer from the photochemically generated sensitizer radical anion to **1** is thought to be a more reliable approach to the generation of $\mathbf{1}^{-\bullet}$, compared with the electron transfer from an amine to the excited state of **1**.

We selected perylene as a sensitizer, because perylene has an absorption with a large absorptivity in the range of 400 to 450 nm, in which the diazoacetate **1** has a very weak absorption. Moreover, perylene has a relatively large reduction potential of −1.67 V (*vs.* SCE),[20] which is favorable for an electron transfer from an electron-donating amine. Unfortunately, because of low solubility of perylene in acetonitrile–methanol, the selective excitation of perylene cannot be achieved. However, under our irradiation conditions ([perylene] = 0.3 mM, [**1**] = 5 mM), it is estimated that 83% of the incident light (at 440 nm) is absorbed by the sensitizer.

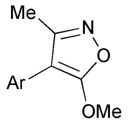
(1) Dependence of photoproducts on amines. Irradiation (> 440 nm) of a solution of **1** (5 mM) in acetonitrile containing 10% methanol in the presence of perylene (0.3 mM) afforded a

Table 2 Dependence of the photoproducts on additives in the perylene-sensitized photolysis of **1** in acetonitrile–methanol (9 : 1)[a]

	Yield (%)[b]					
Additives	**2**	**4**	**5**	**7**	k_q[c]/10^{10} M^{-1} s^{-1}	ΔG[d]/kcal mol^{-1}
None	43	17[e]	11	< 1	—	—
TEA	46	5	4	< 1	0.23	−3.3
ClDMA	39	19	9	< 1	1.2	−7.5
DMA	34	18	5	2	1.3	−9.8
MeODMA	13	20	27	< 1	1.6	−15
TMPD	< 1	9	37	< 1	2.0	−25

[a] [**1**] = 5 mM, [perylene] = 0.3 mM, [Additive] = 50 mM. [b] Yield based on the reacted material (30–40%). [c] Rate constant for quenching of perylene fluorescence by the additive. [d] Free-energy change for the electron transfer from the additive to singlet excited perylene. [e] The isomer of **4** was obtained, which was tentatively identified as **9**. TEA = triethylamine, ClDMA = 4-chloro-*N*,*N*-dimethylaniline, DMA = *N*,*N*-dimethylaniline, MeODMA = 4-methoxy-*N*,*N*-dimethylaniline, TMPD = *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine.

mixture of the products, which were practically identical to those obtained in the direct photolysis of **1**. It was noteworthy that the isomerization of the oxazole **4** occurred under these irradiation conditions. The product was tentatively identified as the isoxazole **9** by considering the ring current effect of the 4-nitrophenyl moiety. The signal assigned to the methyl group on the five-membered ring of **9** appeared in the more shielding area (δ 2.17), compared with the corresponding methyl signal of **4** (δ 2.44). A similar photochemical isomerization of the related oxazoles was reported by Buu and Edward.[21]



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(Ar = 4-nitrophenyl)

Table 2 shows the dependence of the photoproduct distribution on the amine employed as an additive (50 mM). In contrast to the irradiation in the absence of additives, the oxazole **4** was obtained instead of **9**, suggesting that an energy transfer from excited perylene to **4** which causes its isomerization is suppressed by quenching of excited perylene by additives. Moreover, in contrast to the direct irradiation, methyl (4-nitrophenyl)acetate (**7**) was hardly obtained. Similarly to the results obtained in the direct irradiation, the product distributions were very dependent on the additive. It was found that the photoproducts originating from the carbene **3** were obtained even in perylene-sensitized photolysis of **1** in the presence of an amine having a relatively high oxidation potential, such as TEA and *N*,*N*-dimethylaniline (DMA). However, it should be emphasized again that as the electron-donating ability of the additive was increased, the yield of the ether **2** decreased and the ketoester **5** was predominantly obtained instead. Thus, the addition of an amine having a large electron-donating ability, such as TMPD, resulted in the complete suppression of the formation of the ether **2**, which is a unique product derived from the carbene **3**, indicating the intervention of a reactive intermediate other than **3**.

(2) Quenching of perylene fluorescence by amines. In order to have a clue to disclosing the mechanism of the perylene-sensitized photodecomposition of **1** in the presence of amines, quenching of the perylene fluorescence by the amines employed as additives was examined next. We obtained Stern–Volmer constants, $K_{SV} = k_q\tau_0$, for the quenching of perylene fluorescence by the amines. The rate constants for the quenching of singlet excited perylene by the amines, k_q, which are evaluated by employing the reported lifetime of perylene fluorescence in acetonitrile (τ_0 = 6 ns),[20] are collected in Table 2. It is clearly demonstrated that the rate constant for the quenching of perylene fluorescence by the amine increases with a decrease in its oxidation potential. This result strongly suggests that the quenching occurs by a mechanism involving electron transfer from the amine to singlet excited perylene. The negative free-energy changes for this electron transfer process calculated by the Rehm–Weller equation,[22] which are also collected in Table 2, support this assumption.

(3) Laser flash photolysis studies. The transient absorption spectrum was recorded by the laser excitation (434 nm, 40 ns) of a deoxygenated solution of perylene (0.2 mM) in the presence of DMA (50 mM), which is shown with a solid line in Fig. 3. A transient species having an intense absorption band with a maximum at 575 nm was detected, which can be characterized as perylene radical anion, Pe$^{-\bullet}$, by comparison with its authentic spectrum.[23] This observation clearly shows that an electron transfer occurs from DMA to excited perylene, supporting the assumption made on the basis of perylene fluorescence quenching data. A weak broad absorption around 480 nm could be assigned to the overlap of absorptions of triplet excited perylene[23] and DMA$^{+\bullet}$.[24]

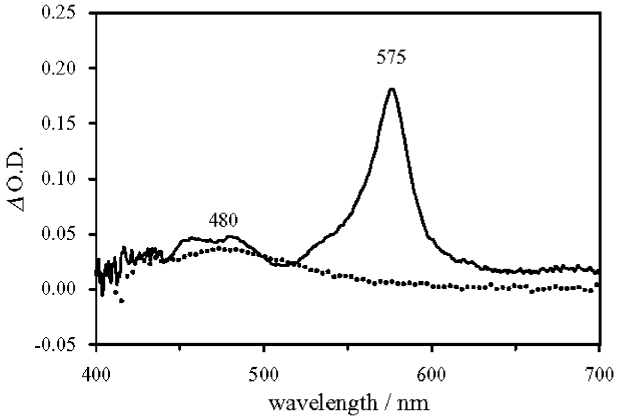


Fig. 3 Transient absorption spectra of a solution of perylene (0.20 mM) in acetonitrile containing DMA (50 mM) recorded in the absence (solid line) and presence (dotted line) of **1** (2.0 mM) at the delay time of 400 ns after a laser pulse (434 nm, 40 ns).

On the other hand, in the transient absorption spectrum recorded by the laser excitation of the solution identical to that described above, except for the presence of **1** (2 mM), no transient absorption band assigned to Pe$^{-\bullet}$ could be detected, which is demonstrated with a dotted line in Fig. 3. Taking into account the rate constants for the quenching of the perylene fluorescence by DMA and **1** (*vide infra*) and their concentrations, it is reasonable to think that singlet excited perylene formed by the laser excitation is predominantly quenched by DMA. Therefore, this result strongly suggests that Pe$^{-\bullet}$

produced by the electron transfer from DMA to singlet excited perylene is immediately quenched by **1**.

Cyclic voltammetric measurement of the diazoacetate 1

The cyclic voltammogram of **1** recorded in acetonitrile at a scan rate of 0.2 V s^{-1} is exhibited in Fig. 4. The electrochemical reduction of **1** is irreversible, showing the reduction peak at $E_{p,c} = -1.26$ V (*vs.* Ag/Ag^{+}). No corresponding peak for the reoxidation was detected even at a scan rate of 5 V s^{-1}. As shown in Fig. 4, on the reoxidation sweep, two peaks were observed at $E_{p,a} = -0.43$ and 0.01 V. Although the cyclic voltammetric measurement was carried out on the products obtained by the photolysis of **1** in acetonitrile, that is, the oxazole **4**, the ketoester **5**, and the ester **7**, their redox peaks were not in agreement with the anodic peaks observed in the measurement of **1**. However, the cyclic voltammetric measurement of the carbanion **10**, which could be generated by the addition of tetramethylammonium hydroxide in a solution of **7**, afforded an oxidation peak at 0.01 V. This observation implies that one of the products formed in the electrochemical reduction of **1** is the carbanion **10**. The formation of the corresponding carbanion was reported in the electrochemical reduction of various diazoalkanes, such as diphenyldiazomethane[6] and diethyl diazomalonate.[7]

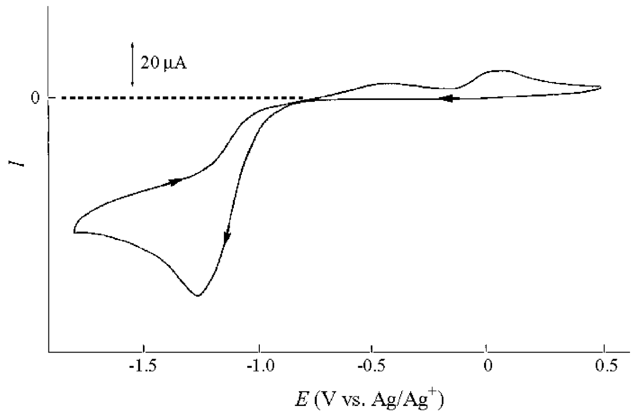
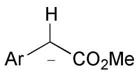


Fig. 4 Cyclic voltammogram for the reduction of **1** (4.4 mM) recorded in acetonitrile containing tetrabutylammonium perchlorate (0.1 M) at a scan rate of 0.2 V s^{-1}.



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(Ar = 4-nitrophenyl)

Structure and reactivity of the diazoacetate radical anion $1^{-\bullet}$ and the carbene radical anion $3^{-\bullet}$ based on the theoretical studies

The electronic structure of carbene radical anions has been of interest theoretically in recent years. Davidson and Hudak carried out molecular orbital calculations using the UHF/STO-3G method on the parent methylene radical anion, $CH_2^{-\bullet}$.[25] They showed that $CH_2^{-\bullet}$ was similar in geometrical structure to singlet methylene, and had the $\sigma^2\pi^1$ electronic structure. Recently, Seburg and his co-workers drew the same conclusion from density functional theory (DFT) calculations using the UB3LYP/6-31+G(d) method on phenylcarbene radical anion, in which the $\sigma^2\pi^1$ electronic structure was more stable than the $\sigma^1\pi^2$ structure by 11–12 kcal mol^{-1}.[26] On the other hand, the semi-empirical calculation on cyclopentadienylidene radical anion done by McDonald and his co-workers predicted that this radical anion had the $\sigma^1\pi^2$ electronic structure in its ground state.[4] The stabilization of the $\sigma^1\pi^2$ electronic structure is probably due to the delocalization of two π electrons on the cyclopentadiene π system to achieve the 6π aromaticity.

In order to gain information about the structure and reactivity of the diazoalkane radical anion $1^{-\bullet}$ and the carbene radical anion $3^{-\bullet}$, we carried out DFT calculations on these reactive species. The geometry was optimized by using the UB3LYP/6-31G(d) method. Figs. 5 and 6 depict the optimized geometries of $1^{-\bullet}$ and $3^{-\bullet}$, respectively, together with the charge and spin densities on the selected atoms. It is noteworthy that the diazo moiety of $1^{-\bullet}$ is significantly bent with a C–N–N angle of 132.7°, and that the bond angle of the divalent carbon atom of $3^{-\bullet}$ is 135.7° which is nearly identical to that of the carbene in its triplet state **3T** (134.9°) calculated by the use of the same method.

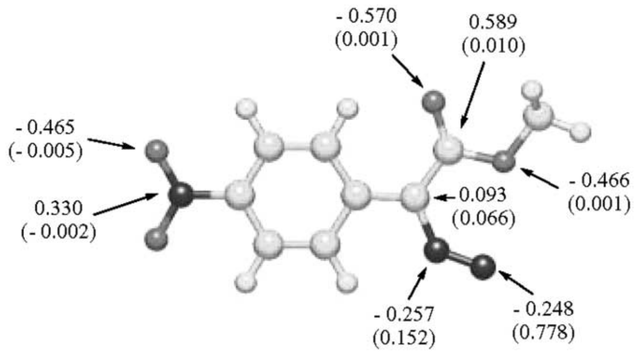


Fig. 5 Structure of $1^{-\bullet}$ calculated at the UB3LYP/6-31G(d) level of theory. Charge and spin densities (in parentheses) on the selected atoms are given in the structure drawing.

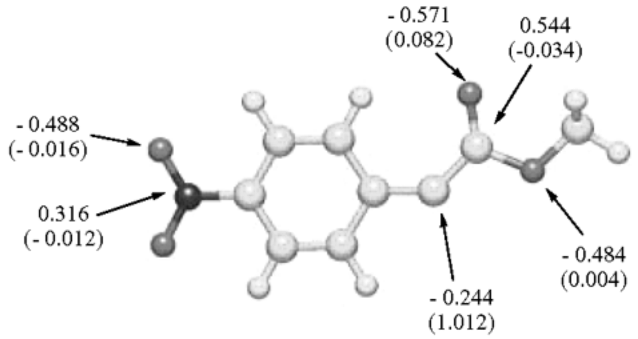
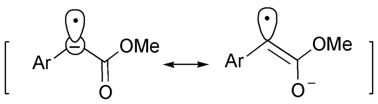


Fig. 6 Structure of $3^{-\bullet}$ calculated at the UB3LYP/6-31G(d) level of theory. Charge and spin densities (in parentheses) on the selected atoms are given in the structure drawing.

It is found that the negative charge of both $1^{-\bullet}$ and $3^{-\bullet}$ exists mainly on the nitro group and the methoxycarbonyl moiety, implying that the negative charge is delocalized on the π conjugated system of the molecule. On the other hand, the spin of $1^{-\bullet}$ and $3^{-\bullet}$ is almost perfectly localized on the dinitrogen moiety and on the divalent carbon, respectively. Especially, it should be pointed out that the molecular orbital occupied by an unpaired electron of $3^{-\bullet}$, which is localized on the divalent carbon, has a σ character, indicating that the electronic structure of $3^{-\bullet}$ is essentially described as $\sigma^1\pi^2$. Thus, $3^{-\bullet}$ can be predicted to be the species represented as the conjugate base of 1-(4-nitrophenyl)-2-methoxy-2-hydroxyvinyl radical **11**. On the basis of its σ radical character, it is expected that $3^{-\bullet}$ can react readily with O_2 and abstract hydrogen atoms.

Furthermore, the enthalpy change for the extrusion of dinitrogen from $1^{-\bullet}$ to yield $3^{-\bullet}$, $\Delta\Delta H_f$, was estimated from their electronic energies calculated by using the UB3LYP/6-31+G(d) method. On the basis of our calculations, $\Delta\Delta H_f$ for the transformation of $1^{-\bullet}$ into $3^{-\bullet}$ and dinitrogen is evaluated to be +2.7 kcal mol^{-1}. Thus, the endothermicity for the extrusion of dinitrogen of $1^{-\bullet}$ is found to be considerably smaller, compared with that of the neutral diazoalkane **1** to yield the carbene **3T**



$3^{-\bullet}$ **11**

(Ar = 4-nitrophenyl)

and dinitrogen, which was calculated to be +20.4 kcal mol^{-1} by the use of the same method. On the basis of the small endothermicity, it is expected that $\mathbf{1}^{-\bullet}$ is a thermally labile species, which is readily decomposed to give $\mathbf{3}^{-\bullet}$. To validate this expectation, however, estimation of the activation energy for the extrusion of dinitrogen is required.

Discussion

Mechanism of the direct photolysis of the diazoacetate 1 in the presence of an amine

As described in the previous section, the distribution of the products obtained in the photolysis of **1** in acetonitrile–methanol was dependent on the amine employed as an additive. It should be noted again that an increase in the electron-donating ability of the amine resulted in a decrease in the yield of the ether **2**, which is the unique product originating from the carbene **3**. Especially, **2** could not be afforded by the irradiation of **1** in the presence of TMPD, which has the lowest oxidation potential of the amines employed in this study. The mechanism of the photodecomposition of **1** in the presence of an additive having a large electron-donating ability is now discussed.

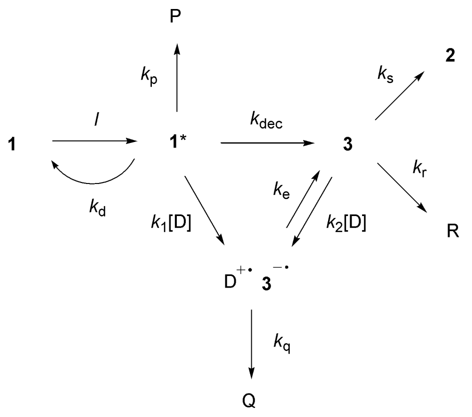
The most plausible one is the mechanism involving an electron transfer process. As mentioned in the introductory part, Tomioka's group proposed that an electron transfer occurred in the photolysis of (4-nitrophenyl)diazomethane in amines.[11] Moreover, in the field of azide photochemistry, the participation of an electron transfer was proposed in the photolysis of 4-nitrophenyl azide in amines.[27,28] It is reasonable to think that the diazoacetate **1** having an electron-withdrawing methoxycarbonyl moiety has a larger electron-accepting ability than (4-nitrophenyl)diazomethane. Thus, it is conceivable that an electron transfer process participates in the photolysis of **1** in the presence of an electron-donating amine. The direct observation of $\text{TMPD}^{+\bullet}$ in the photolysis of **1** in the presence of TMPD affords strong evidence in support of this assumption.

There are two candidates for an electron acceptor in the photolysis of **1** in the presence of TMPD: the electronically excited diazoacetate **1*** and the carbene **3**. Upon excitation of **1**, **1*** is initially produced in its singlet excited state (**1*S**), which undergoes intersystem crossing to its triplet excited state (**1*T**). It is likely that the lifetime of **1*S** is extremely short, because the nitro group, as well as the methoxycarbonyl moiety, is expected to accelerate the intersystem crossing.[29] Thus, **1*S** can be ruled out as a candidate for the electron acceptor. The free-energy change for the electron transfer from TMPD to **1*T** is calculated by the Rehm–Weller equation to be −26 kcal mol^{-1}, assuming that the energy level of **1*T** is estimated by that of nitrobenzene (58 kcal mol^{-1}). Therefore, it appears that the electron transfer from TMPD to **1*T** is an energetically favorable process, which is expected to proceed with a diffusion-controlled rate constant ($1.9 \times 10^{10}\ M^{-1}\ s^{-1}$ in acetonitrile).[20]

The carbene **3** is another candidate for an electron acceptor in the photolysis of **1** in the presence of TMPD. The extrusion of dinitrogen from **1*S** and **1*T** gives the carbene in its singlet state **3S** and triplet state **3T**, respectively. It is known that phenylcarbenes are energetically more stable in their triplet state than in their singlet state, but a rapid interconversion occurs between these two spin states.[14] Moreover, it is generally accepted that singlet carbene reacts with methanol to give the product derived from the insertion of the carbene into the OH bond, while triplet carbene is readily trapped with O_2 to yield the corresponding ketone or abstracts hydrogen atoms to give the methylene compound.[14] Therefore, it is reasonable to think that the ether **2** and the ketoester **5** obtained by the irradiation of **1** in the absence of TMPD originate from **3S** and **3T**, respectively. The formation of the nitrile ylide is reported in the photolysis of diazoalkanes in acetonitrile,[17] so that it is likely that the oxazole **4** is also derived from **3**. However, we propose that a portion of **4** produced in the photolysis of **1** arises directly from the electronically excited state of **1** on the basis of the following two reasons. First, **4** was obtained even in the photolysis of **1** in the presence of TMPD, in which the formation of **2** was completely quenched. Secondly, the T–T absorption of **4** was observed immediately after the irradiation of **1** with the laser pulse.

Because it is known that the reaction of singlet carbene with methanol is diffusion-controlled and the concentration of TMPD employed as an additive is much smaller than that of methanol, **3S** is ruled out as a candidate for an electron acceptor in the photolysis of **1** in the presence of TMPD. Although it is difficult to estimate the free-energy change for the electron transfer from TMPD to **3T**, this should be an endothermic process. As discussed in the following section, the oxidation potential of the carbanion **10** (0.01 V *vs.* Ag/Ag^{+}) can be employed to estimate the reduction potential of **3T**, which is equal to the oxidation potential of $\mathbf{3}^{-\bullet}$, leading to a value of +3 kcal mol^{-1} for the free-energy change for the electron transfer from TMPD to **3T**. Thus, it cannot be expected that this electron transfer process proceeds at a rate comparable to that of the reaction of **3T** with O_2 or solvent. However, it seems possible that an encounter of **3T** with TMPD in a solution leads to the formation of the complex, in which an electron is partially transferred from TMPD to **3T**.

It should be emphasized that the dependence of the yield of **2** on [TMPD] shown in Fig. 1 suggests that a reaction scheme where a single reactive species leading to the formation of **2** is simply quenched by TMPD cannot be acceptable, no matter which is the reactive species, **1*** or **3**. We wish to propose the following two schemes which explain the nonlinear relationship between the yield of **2** and [TMPD]. The first is a reaction scheme in which both **1*** and **3** are quenched by TMPD, which is illustrated in Scheme 2. In the scheme, for the sake of simplicity, a mixture of **1*S** and **1*T** is shown by **1***, and **3** represents an interconverting mixture of **3S** and **3T**. Moreover, $D^{+\bullet}\mathbf{3}^{-\bullet}$ shows the radical ion pair produced by the electron transfer, in which D stands for TMPD, assuming that $\mathbf{1}^{-\bullet}$ extrudes rapidly dinitrogen to give $\mathbf{3}^{-\bullet}$ (*vide infra*). P and Q represent the products originating from the electronically excited state of **1** and $D^{+\bullet}\mathbf{3}^{-\bullet}$, respectively. The products derived from **3** other than **2** are depicted by R. In the scheme, k_d, k_{dec}, and k_e represent unimolecular rate constants for nonradiative deactivation of **1***, decomposition of **1*** to give **3**, and charge recombination of the radical ion pair $D^{+\bullet}\mathbf{3}^{-\bullet}$ to reproduce **3**,



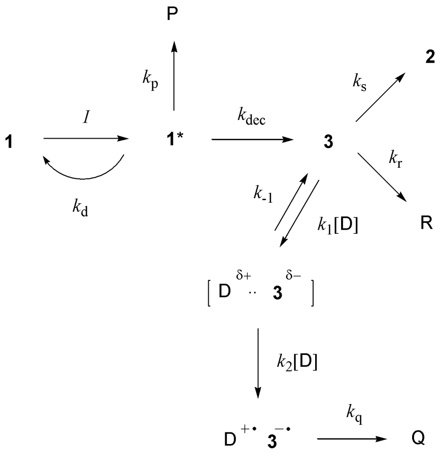
Scheme 2

while k_p, k_q, k_r, and k_s show pseudo-first-order rate constants for the reactions giving P, Q, R, and **2**, respectively. The second-order rate constants for the electron transfer from TMPD to **1*** and **3** are depicted by k_1 and k_2, respectively. The ratio of the yield of **2** in the absence of TMPD to that in the presence of TMPD, $\Phi(\mathbf{2})_0/\Phi(\mathbf{2})$, is given by eqn. (1) by using a steady-state approximation.

$$\Phi(\mathbf{2})_0/\Phi(\mathbf{2}) = (1 + \alpha[\mathrm{D}])(1 + \beta[\mathrm{D}])/(1 + \gamma[\mathrm{D}]) \qquad (1)$$

In this equation, α, β, and γ are equal to $k_1/(k_p + k_d + k_{dec})$, $k_2k_q/(k_r + k_s)(k_e + k_q)$, and $k_1k_e/k_{dec}(k_e + k_q)$, respectively. The non-linear least-squares analysis revealed that the experimental data shown in Fig. 1 were reproduced by eqn. (1) with $\alpha = 0.70$, $\beta = 0.72$, and $\gamma = 0$, as shown with a solid line in Fig. 1. As mentioned above, the electron transfer from TMPD to **1*T** is expected to be diffusion-controlled ($k_1 = 1.9 \times 10^{10}$ M^{-1} s^{-1}). Therefore, if this mechanism is correct, the lifetime of **1*T** in acetonitrile–methanol, which is equal to $1/(k_p + k_d + k_{dec})$, is evaluated to be 37 ps. Unfortunately, the experimental information on the lifetime of **1*T** which would serve to validate this mechanism is not available at the present stage.

The second scheme we propose to explain the nonlinear relationship between $\Phi(\mathbf{2})_0/\Phi(\mathbf{2})$ and [TMPD] is illustrated in Scheme 3, in which the complex formed from **3** and TMPD is further quenched by TMPD to yield the free carbene radical anion $\mathbf{3}^{-\bullet}$. In this scheme, k_1 and k_2 represent the second-order rate constants for the charge transfer from TMPD to **3** to afford the complex $[\mathrm{D}^{\delta+}\cdot\cdot\mathbf{3}^{\delta-}]$ and for the reaction of TMPD with the complex, respectively. Moreover, k_{-1} represents the rate constant for the dissociation of the complex to regenerate **3**. The steady-state treatment leads to eqn. (2) for $\Phi(\mathbf{2})_0/\Phi(\mathbf{2})$,



Scheme 3

$$\Phi(\mathbf{2})_0/\Phi(\mathbf{2}) = 1 + \alpha[\mathrm{D}]^2/(1 + \beta[\mathrm{D}]) \qquad (2)$$

where α and β are depicted by $k_1k_2/k_{-1}(k_r + k_s)$ and k_2/k_{-1}, respectively. By non-linear least squares analysis, it was found that the experimental data were also fitted to eqn. (2) with $\alpha = 1.70$ and $\beta = 0.23$, which is demonstrated with a dotted line in Fig. 1. At the present stage, we have no decisive evidence to determine which mechanism is appropriate for the photolysis of **1** in the presence of TMPD. In order to establish the mechanism, further kinetic data on the reaction of **1*** and **3** are required.

Mechanism of the sensitized photolysis of the diazoacetate 1 in the presence of an amine

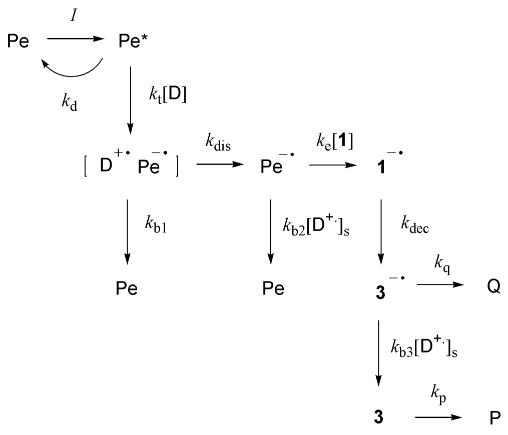
As described in the previous section, the fluorescence of perylene is effectively quenched by amines employed as additives. The rate constants for fluorescence quenching by amines, k_q, are close to the diffusion-controlled limit (1.9×10^{10} M^{-1} s^{-1} in acetonitrile),[20] except for triethylamine. Therefore, taking into account the concentration of the amine (50 mM), it is reasonable to think that the singlet excited perylene is quenched not by **1**, but by the amine predominantly. The large exothermicity of the electron transfer process evaluated by the Rehm–Weller equation,[22] which is shown in Table 2, implies that the quenching of singlet excited perylene by the amines proceeds by the electron transfer mechanism. Moreover, the direct observation of $\mathrm{Pe}^{-\bullet}$ by the irradiation of perylene in the presence of DMA with the laser pulse provides unambiguous evidence supporting the electron transfer mechanism. Therefore, it can be concluded that when the amine having an oxidation potential lower than DMA is employed as an additive, singlet excited perylene is quenched by the amine by the electron transfer mechanism to give $\mathrm{Pe}^{-\bullet}$.

Next, a discussion on the electron transfer process from $\mathrm{Pe}^{-\bullet}$ to **1** is given. The free-energy change for this process is evaluated to be −9.5 kcal mol^{-1}, which implies that the electron transfer is an energetically favorable process. Furthermore, laser flash photolysis studies revealed that accumulation of $\mathrm{Pe}^{-\bullet}$ produced by the electron transfer from DMA to singlet excited perylene was not observed in the presence of **1**. These data strongly suggest that electron transfer from $\mathrm{Pe}^{-\bullet}$ to **1** proceeds in the perylene-sensitized photolysis of **1** in the presence of DMA. Because the exothermicity of the electron transfer process increases with a lowering of the oxidation potential of the amine, we conclude that in the presence of an amine having an oxidation potential lower than DMA, $\mathbf{1}^{-\bullet}$ can be generated by electron transfer from $\mathrm{Pe}^{-\bullet}$ to **1**.

Thus, evidence is obtained supporting the generation of $\mathbf{1}^{-\bullet}$ in the perylene-sensitized photolysis of **1** in the presence of an electron-donating amine such as DMA and TMPD. However, it should be pointed out that the product distribution obtained in the presence of DMA is completely different from that in the presence of TMPD (Table 2). The former is essentially identical to the product distribution for the reaction involving the carbene **3** as a reactive intermediate, while the formation of **2**, which is a unique product originating from **3**, is completely quenched in the presence of TMPD. These results suggest that the reactivity of $\mathbf{1}^{-\bullet}$ generated by electron transfer from $\mathrm{Pe}^{-\bullet}$ to **1** is significantly dependent on the amine used as an electron donor to produce $\mathrm{Pe}^{-\bullet}$.

These results can be explained by a mechanism involving the generation of the carbene **3** by the charge recombination between carbene radical anion $\mathbf{3}^{-\bullet}$ generated by the extrusion of dinitrogen from $\mathbf{1}^{-\bullet}$ and the radical cation of the amine used as an electron donor. The total scheme we propose for the perylene-sensitized photolysis of **1** in the presence of an electron-donating amine D is illustrated in Scheme 4. As mentioned above, it is plausible that $\mathbf{1}^{-\bullet}$ is generated by the quenching of Pe* by D to give the contact ion pair $[\mathrm{D}^{+\bullet}\mathrm{Pe}^{-\bullet}]$, followed by its dissociation into a free radical ion $\mathrm{Pe}^{-\bullet}$ and electron transfer from $\mathrm{Pe}^{-\bullet}$ to **1**. In the scheme, k_{b1}, $k_{b2}[\mathrm{D}^{+\bullet}]_s$, and $k_{b3}[\mathrm{D}^{+\bullet}]_s$ are the rate constants for the charge recombination processes, in which $[\mathrm{D}^{+\bullet}]_s$ stands for the steady-state concentration of the amine radical cation. Moreover, P and Q represent the products originating from **3** and $\mathbf{3}^{-\bullet}$, respectively.

On the basis of theoretical calculations which imply that the endothermicity of the process of the extrusion of dinitrogen from $\mathbf{1}^{-\bullet}$ is very small, we propose that $\mathbf{1}^{-\bullet}$ decomposes immediately to give $\mathbf{3}^{-\bullet}$. Although $\mathbf{3}^{-\bullet}$ reacts smoothly with O_2 to afford **5**, the charge recombination between $\mathbf{3}^{-\bullet}$ and the radical cation of the amine $\mathrm{D}^{+\bullet}$ to produce the carbene **3** should be considered. The rate constant for the charge recombination, k_{b3}, could be dependent on the amine owing to the dependence of the free-energy change for the charge recombination process on its oxidation potential, E_{ox}. As suggested by the theoretical calculations, the electronic structure of



Scheme 4

$3^{-\bullet}$, in which the negative charge is delocalized on the π-conjugated system of the molecule, is similar to that of the corresponding carbanion **10**. If we employ E_{ox} of **10** (0.01 V *vs.* Ag/Ag$^+$) as that of $3^{-\bullet}$, the free-energy change for the charge recombination between $D^{+\bullet}$ and $3^{-\bullet}$ is evaluated to be −19 and −3 kcal mol^{-1} for D = DMA and TMPD, respectively. Because the electron transfer from D to **3** is mediated by excited perylene, the radical ions $D^{+\bullet}$ and $3^{-\bullet}$ are not in contact with each other. Therefore, it is expected that the rate constant for the charge recombination increases with an increase in the exothermicity of the process. Thus, it is reasonable to think that when DMA is employed as an electron donor, the charge recombination between $DMA^{+\bullet}$ and $3^{-\bullet}$ proceeds rapidly to yield the carbene **3**, which undergoes spin interconversion and gives a mixture of products originating from both **3S** and **3T**. On the other hand, the rate of the charge recombination between $TMPD^{+\bullet}$ and $3^{-\bullet}$ is considerably reduced, so that the reaction products derived from $3^{-\bullet}$ are obtained without the formation of the products arising from **3**.

Conclusions

We report our attempts to produce a diazoalkane radical anion by a photoinduced electron transfer from an electron-donating amine to the diazoalkane **1**. On the basis of the photoproducts and the results obtained by the laser flash photolysis studies, we conclude the following three points concerning the formation and reactivity of $1^{-\bullet}$ and $3^{-\bullet}$. First, in the direct photolysis of **1** in the presence of TMPD in acetonitrile–methanol, electron transfer from TMPD occurs and the photoproducts are obtained through an intermediate other than the carbene **3**, which we suppose to be $3^{-\bullet}$. Second, in the perylene-sensitized photolysis of **1** in the presence of an amine having a large electron-donating ability such as DMA and TMPD, $1^{-\bullet}$ can be generated by perylene-mediated electron transfer from the amine to **1**. It seems that $1^{-\bullet}$ undergoes the extrusion of dinitrogen smoothly to give $3^{-\bullet}$, the behavior of which is very dependent on the amine employed as an additive. When DMA is used the rapid charge recombination between $DMA^{+\bullet}$ and $3^{-\bullet}$ causes the generation of the carbene **3**, while the photoproducts derived from $3^{-\bullet}$ are obtained in the presence of TMPD. Finally, $3^{-\bullet}$ reacts readily with O_2 to give the ketoester **5** or abstracts hydrogen atoms to give **7**. These results imply that $3^{-\bullet}$ has highly radical character in its reactivity, which is not inconsistent with the theoretical prediction that $3^{-\bullet}$ can be represented as the conjugate base of the 2-hydroxyvinyl radical **11**.

Thus, our results have revealed that diazoalkane radical anion, as well as carbene radical anion, can be generated photochemically in solutions. At the present stage the structural requirement of diazoalkanes for the formation of their radical anions is not known, although the methoxycarbonyl moiety, as well as the nitro group, of **1** is thought to be essential for the stabilization of the radical anion species $1^{-\bullet}$ and $3^{-\bullet}$. Work is in progress to elucidate the general scheme for the photochemical generation of diazoalkane radical anions.

Experimental

General methods

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-A500 spectrometer at 500 and 125 MHz, respectively. UV–vis spectra were obtained with a JASCO V-560 spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-777 spectrofluorometer. Gel permeation liquid chromatography (GPLC) was carried out on a JAI LC-08 equipped with a HAIGEL-H column. Preparative thin–layer chromatography (PTLC) was carried out on a Merck kieselgel 60 PF_{254}.

Materials

Methyl (4-nitrophenyl)diazoacetate (**1**) was prepared according to the procedure reported by Schank.[30] Perylene was purchased from Tokyo Kasei Kogyo Co., Ltd., and was recrystallized from benzene before use. Triethylamine, *N*,*N*-dimethylaniline, *N*,*N*-dimethyl-4-chloroaniline, and *N*,*N*-dimethyl-4-methoxyaniline were purified by distillation under reduced pressure. *N*,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine was obtained by treatment of its commercially available hydrochloride with an aqueous dilute sodium hydroxide solution, and purified by recrystallization from ether. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was recrystallized from ether before use. Acetonitrile was refluxed with, and distilled from CaH_2 prior to use. Methanol was purified by distillation.

Irradiation for product identification

In a typical run, a solution of the diazoacetate **1** (5 mM) and amine (50 mM) in acetonitrile–methanol (9 : 1, 3 mL) was placed in a Pyrex tube, and degassed by bubbling of argon for 5 min. The solution was irradiated with a 500-W xenon arc lamp at room temperature through a cutoff glass filter (> 390 nm) for 10 min. After removal of the solvent under reduced pressure, the residue was separated by GPLC with chloroform eluent and PTLC to yield a mixture of the photoproducts: the α-methoxyacetate **2**,[13] the oxazole **4**,[15] the ketoester **5**,[16] and methyl (4-nitrophenyl)acetate (**7**). The products were identified by comparison of the spectroscopic data with those of authentic material. When DABCO was employed as an additive, the azine **8** was obtained in 45% yield. Dimethyl α,α′-azinobis-[(4-nitrophenyl)acetate] (**8**): yellow granules; mp 50–52 °C; ^{1}H NMR ($CDCl_3$) δ 4.40 (6H, s), 7.96 (4H, d, $J = 9.0$ Hz), 8.32 (4H, d, $J = 9.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 52.8, 124.1, 129.1, 136.5, 149.9, 160.0, 164.0; IR (KBr) 1727, 1596, 1589 cm^{-1}. Anal. Found: C, 52.05; H, 3.48; N, 13.43. Calcd for $C_{18}H_{14}N_4O_8$: C, 52.18; H, 3.41; N, 13.53%. Perylene-sensitized photolysis was carried out as follows; a degassed solution of **1** (5 mM) and amine (50 mM) in acetonitrile–methanol (9 : 1, 3 mL) containing perylene (0.3 mM) was placed in a Pyrex tube, and irradiated with a 500-W xenon arc lamp at room temperature through a cutoff glass filter (> 440 nm) for 3 h. The irradiation mixture was treated with a procedure identical to that described for the direct photolysis. In the perylene-sensitized photolysis of **1** in the absence of an amine, not the oxazole **4**, but the isomer of **4** was obtained, together with **2** and **5**. Although the purification of the isomer was not successful, it was tentatively identified as the isoxazole **9**. 5-Methoxy-3-methyl-4-(4-nitrophenyl)isoxazole (**9**); ^{1}H NMR ($CDCl_3$) δ 2.17 (3H, s), 3.82 (3H, s), 7.75 (2H, d, $J = 8.7$ Hz), 8.26 (2H, d, $J = 8.7$ Hz).

Irradiation for analytical experiments

A solution identical to that described in the irradiation for product identification was prepared and irradiated. After removal of the solvent, the residue was dissolved in $CDCl_3$. The consumption of **1** (30–40%) and the yield of the photoproducts were determined by the integration of ^1H NMR in the crude reaction mixture. Identifications of the products were established by the agreement of their ^1H NMR spectra with those of authentic samples.

Fluorescence quenching studies

Solutions of perylene (1.5×10^{-6} M) in acetonitrile containing various amounts of quenchers were placed in 10 mm quartz cells. Fluorescence spectra were measured at room temperature on excitation at 380 nm. When TMPD was used as a quencher, the light of 440 nm was employed for the excitation. Relative fluorescence intensities were determined by measuring the peak heights for the maxima.

Laser flash photolysis studies

The laser flash photolysis experiments were performed by using a pulse Q-switch Nd : YAG laser (SOLAR LF114) and Ti : sapphire laser (SOLAR CF131M) as the excitation source. Transient absorption signals were monitored by using a 10-W xenon flash lamp (HAMAMATSU E2608). A sample solution was placed in a flask, purged with N_2 before and during measurements, and flowed into a quartz cuvette (5 × 10 mm) by a magnetic gear pump. The transient absorption spectra were recorded in the wavelength range of 400 to 700 nm.

Cyclic-voltammetric measurements

Cyclic voltammograms were measured in acetonitrile solution degassed by bubbling of N_2 (2–4 mM) with a platinum electrode, tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte, and a silver/silver chloride reference electrode. Although the electrochemical reduction of **1** is irreversible as shown in Fig. 4, the reversible voltammograms were recorded on the oxazole **4**, the ketoester **5**, and the ester **7**, the half-wave potentials, $E_{1/2}$, of which were determined to be −1.10, −0.73, and −1.13 V (*vs.* Ag/Ag^+), respectively.

Calculations

The DFT calculations were carried out by the program package Gaussian 98 on a DEC Alpha workstation computer. The geometry optimizations were performed at the UB3LYP/6-31G(d) level of theory. The electronic energies calculated by using the UB3LYP/6-31+G(d) level of theory were as follows. $\mathbf{1}^{-\bullet}$: −812.131206, $\mathbf{3}^{-\bullet}$: −702.6027575, **1**: −812.0562134, **3T**: −702.4994941, N_2: −109.5241739 hartree. These values include zero-point energies. The charge distribution was calculated by Mulliken population analysis.

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