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Electron-Transfer-Initiated Photoreactions of 1-Methyl-2-phenyl-1-pyrrolinium Perchlorate with α-Heteroatom-Substituted Alkanoate Anions

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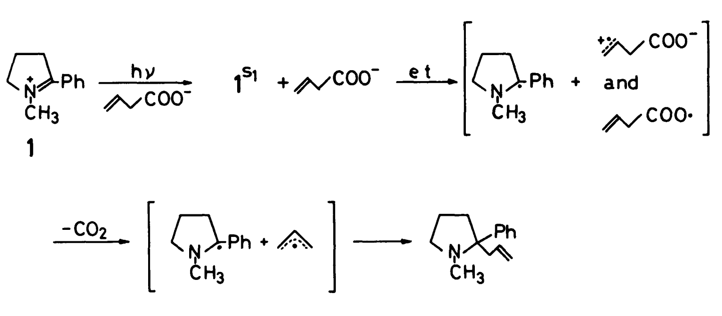
The irradiation of aqueous solutions of 1-methyl-2-phenyl-1-pyrrolinium perchlorate (**1**) in the presence of α-hydroxyalkanoate anions led to the formation of 2-(hydroxyalkyl)pyrrolidine adducts and a reduction product, 1-methyl-2-phenylpyrrolidine. Mechanistic studies demonstrated that photoaddition reactions were induced by one-electron transfers from the carboxylato groups of alkanoates to the excited singlet state of **1** ($\mathbf{1}^{S_1}$), followed by an efficient decarboxylation. Furthermore, the photoreaction of **1** with ethoxyacetate was found to give a 2-(ethoxymethyl)pyrrolidine adduct in preference to the reduction product. For photoreactions with 2-mercaptopropionate and α-amino acids, the reduction product was detected. *N*-Acetylglycinate gave a 2-(acetylaminomethyl)pyrrolidine adduct in fairly high yield (80%). The features of these photoreactions with α-heteroatom-substituted alkanoates are discussed in terms of fluorescence-quenching efficiencies and the properties of radicals formed through electron transfers to $\mathbf{1}^{S_1}$.

Carboxylic acids are known to undergo electron-transfer-initiated photodecarboxylations in the presence of such electron acceptors as heterocyclic[1)] and carbonyl[2)] compounds and 1-cyanonaphthalene.[3)] The reactions are facile in the case of acetic acid derivatives of the type $RXCH_2CO_2H$(R=aryl, X=O, S, and NH). When aliphatic analogues (R=H or alkyl), except for the S compound, are employed as electron donors, however, electron transfers to the excited states of the acceptors were either not observed[2)] or took place with a lower efficiency[1d)] due to their higher ionization potentials. Consequently, few details are known about an electron-transfer-initiated photoreaction in which the α-heteroatom-substituted alkanoic acids participate.

On the other hand, various types of photoaddition reactions involving iminium cations have been systematically investigated by Mariano and his coworkers from mechanistic[4)] and synthetic[5)] points of view. A proposed mechanism involves one-electron transfers from a variety of donors to the excited singlet states of the cations as important primary steps. For example, 2-phenyl-1-pyrrolinium perchlorate and its *N*-methyl derivative (**1**) were converted into 2-pyrrolidinyl radicals by electron transfers. Then, cation radical intermediates derived from π- and *n*-electron donors (such as olefins, allylsilanes, alcohols, and ethers) were transformed into neutral radicals by nucleophilic capture, deprotonation, and desilylation. The coupling of resulting radical pairs afforded 2-substituted 2-phenylpyrrolidines.

Previously, we reported[6)] on the decarboxylative photoaddition of a 3-butenoate anion to the pyrrolinium cation **1** in an aqueous solution. The photoaddition follows, on the whole, the above-mentioned mechanism. Moreover, fluorescence-quenching experiments and an estimation of the free-energy change have suggested that a mechamism which rationalizes this photoaddition involves electron-transfer processes from both the vinyl and carboxylato groups (Scheme 1). This implies that the carboxylato group possesses a reducing ability comparable to those of mono-substituted olefins and that the excited singlet state of the cation **1** ($\mathbf{1}^{S_1}$) behaves as an effective electron acceptor for the carboxylato group. In the present research, we employed this aqueous pyrrolinium-cation system in order to elucidate the chemical behavior of α-heteroatom-substituted alkanoic acids in an electron-transfer-initiated photoreaction.



Scheme 1.

Results and Discussion

Fluorescence Quenching. The fluorescence of **1** was quenched by various aliphatic carboxylate anions (Table 1). All measurements were made on aqueous solutions with a pH of 6; thus, all the acids existed exclusively in carboxylate anionic forms. The solutions contained 0.5 M (1 M=1 mol dm^{-3}) $NaClO_4$ in order to minimize a salt effect (described later). Also, solutions containing **1** and the acids were stable while standing in the dark. The fluorescence and absorption spectra of **1** revealed an absence of the excited- or ground-state complex formation. Stern-Volmer plots yielded straight lines with intercepts equal to 1. The quenching constants ($k_q\tau$) obtained from the least-squares slopes of the plots are given in Table 1.

α-Hydroxyalkanoate anions, which can be seen in the first three rows, had quenching efficiencies similar to each other. On the other hand, no effective quenching was observed at a lower pH where the acids exist in undissociated forms. The oxidation potentials of aliphatic carboxylate anions in acetonitrile are normally lower (ca. 1.6 V vs. SCE)[7] than those of alcohols (ca. 2.5—3.8 V vs. SCE)[8] which are known to serve as quenchers for the fluorescence of the pyrrolinium cation **1**.[8] This leads us to infer that the fluorescence quenching by the hydroxyalkanoate anions is induced by electron transfers from the carboxylato groups to 1^{S_1}, although the Stern-Volmer quenching-rate constants (k_q, estimated to be ca. 6—8$\times10^8$ M^{-1} s^{-1} using the singlet lifetime (τ=1 ns)[8] of **1** in 10% aqueous acetonitrile) are slightly less than a diffusion-controlled rate constant (6.64$\times10^9$ M^{-1} s^{-1}).[9]

A more precise evaluation of the energetics of this electron transfer with the aid of Eq. 1 proposed by

$$\Delta G_{et}(\text{eV}) = E(D/D^+) - E(A^-/A) - e^2/\varepsilon\alpha - E_{0,0} \qquad (1)$$

Rehm and Weller[10] requires knowledge of the electrochemical and spectroscopic data of **1** and the anions in an aqueous solution. The reduction potential, $E(A^-/A)$, and the singlet energy, $E_{0,0}$, of **1** were found to be −0.95 V (vs. SCE) and 3.9 eV, respectively. The oxidation potentials ($E(D/D^+)$) of the α-hydroxyalkanoates could not be obtained since discrete oxidation waves were difficult to observe in aqueous solutions;[11] thus, the critical potential of acetate (1.9 V vs. SCE)[12] was employed as the oxidation potential. The coulombic attraction term ($e^2/\varepsilon\alpha$) may be neglected since the two radical species generated by the one-electron transfer are neutral in the present systems. The free-energy change, ΔG_{et}, obtained in this way is −1.1 eV, and supports the idea that a one-electron transfer is energetically feasible. Furthermore, the $k_q\tau$ values for the anions were almost the same as those for acetate (0.57±0.03 M^{-1}) and propionate (0.62±0.02 M^{-1}) anions and the fluorescence of **1** was little quenched by 2-propanol ($k_q\tau$<0.04). These findings agree with the suggestion that electron transfers from the hydroxyl groups are not appreciably responsible for the quenching.

In the case of sulfur-substituted alkanoic acids, a more efficient quenching can be predicted by the high HOMO energies of analogous S compounds.[13] The quenching efficiency of 2-mercaptopropionate was high as shown in Table 1; the estimated k_q value

Table 1. Fluorescence Quenching Constants, Product Yields, and Quantum Yields for 1-Methyl-2-phenyl-1-pyrrolinium Cation **1**–Carboxylate Anion Systems

Carboxylate anion	$k_q\tau$[a)]/M^{-1}	Product yields/%		Quantum yields[b)]		
		Adduct	Reduction product **7**	ϕ_{dis}	ϕ_a	ϕ_r
$HOCH_2COO^-$	0.61±0.02	**2** 44	15	0.15	0.062±0.007	0.017
$HOCH(CH_3)COO^-$	0.59±0.02	**3** 31[c)]	28		0.056[c)]	
$HOC(CH_3)_2COO^-$	0.76±0.03	**4** 25	34	0.13	0.041	0.036
$C_2H_5OCH_2COO^-$	—[d)]	**5** 42	<3		0.064	
$HSCH(CH_3)COO^-$	4.8±0.2	—[e)]	37			
$H_3N^+CH_2COO^-$	<0.05	—[e)]	5			
$H_3N^+C(CH_3)_2COO^-$	0.22±0.01	—[e)]	8.5			
$CH_3CONHCH_2COO^-$	1.03±0.05	**6** 80[f)]	Trace			

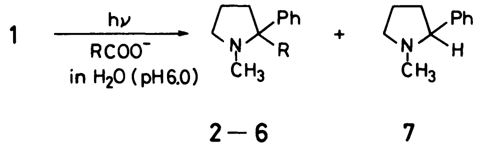
a) Obtained from Stern-Volmer plots at pH 6.0. b) ϕ_{dis}, ϕ_a, and ϕ_r are quantum yields for the **1** disappearance, the adduct formation, and the reduction product formation, respectively, and were obtained using aqueous solutions (pH 6.0) containing **1** of 1.00$\times10^{-3}$ M, carboxylate of 0.5 M, and $NaClO_4$ of 0.5 M. The quantum yields in blank spaces were not determined. c) Total yields of two diastereomers. d) It was difficult to purify this carboxylic acid up to a grade acceptable for quenching experiments. e) No major products other than the reduction product **7** were detected by means of GLC. f) Isolated yield. Other yields were determined by GLC analyses.

using the singlet lifetime of **1** was $4.8\times10^9\,\mathrm{M^{-1}\,s^{-1}}$ and near the diffusion-controlled limit. Moreover, this efficiency was nearly equal to that of the free mercaptopropionic acid ($k_q\tau=4.33\pm0.09\,\mathrm{M^{-1}}$), indicating a predominant electron transfer from the mercapto group. In conformity with these findings, the free acid and the carboxylate anion were found to have almost the same and much lower oxidation potentials: 0.79 V (vs. SCE) for the free acid, 0.66 V (vs. SCE) for the anion.

Glycine and α-aminoisobutyric acid exhibited less quenching-efficiencies than those of the α-hydroxyalkanoates and acetate since the α-amino acids exist as *N*-protonated forms at pH 6 and probably since the strongly electron-withdrawing $\mathrm{NH_3^+}$ groups diminish an electron transfer from the carboxylato groups. Increasing the pH of the solution increased the efficiencies: e.g., a $k_q\tau$ value with glycine was $5.9\pm0.1\,\mathrm{M^{-1}}$ at pH 12. This demonstrates an efficient electron transfer from the unprotonated amino group, as predicted by the generally recognized low ionization potentials of alkylamines.[14]

A *N*-acetylglycinate anion, not subject to *N*-protonation, afforded a somewhat large $k_q\tau$ value ($1.03\,\mathrm{M^{-1}}$). Its free carboxylic acid also had a quenching ability, though the efficiency was fairly low ($k_q\tau=0.19\pm0.02\,\mathrm{M^{-1}}$). This appears to imply that an electron transfer from the acetylamino group can take place to some extent in competition with that from the carboxylato.

Photoreactions of 1 in the Presence of Alkanoate Anions. The pyrrolinium cation **1** was irradiated in aqueous solutions adjusted to pH 6.0 with NaOH and contained carboxylic acids (0.08—0.69 M (listed in Table 1)) to give photoadducts **2**—**6** and a reduction product **7**. 2-Mercaptopropionic acid and two α-amino acids showed no formation of major products other than **7** in GLC analyses of the photolysates. The irradiations were carried out through a Pyrex glass permitting light absorption exclusively by **1** (λ_{max}=258 nm, ε=12050). The progress of a reaction was followed by the UV spectra. The irradiations were allowed to continue until ca. 90% of **1** disappeared. The products were isolated after being extracted with chloroform followed by either preparative TLC or preparative GLC.



2, R = $-\mathrm{CH_2OH}$
3, R = $-\mathrm{CH(CH_3)OH}$
4, R = $-\mathrm{C(CH_3)_2OH}$
5, R = $-\mathrm{CH_2OC_2H_5}$
6, R = $-\mathrm{CH_2NH\overset{}{\underset{\displaystyle O}{\underset{\Vert}{C}}}CH_3}$

The identification of the photoadduct **2** obtained from irradiation in the presence of glycolate was made by a direct comparison of the ^{1}H NMR and IR spectra with those of an authentic sample.[8] The other photoadducts were identified on the basis of comparisons of the characteristic spectroscopic properties of structurally related substances[4] and elemental analyses of 2,4,6-trinitroresorcinolate (styphnate) derivatives. The photoadduct **3** from lactate was a mixture (1 : 1.2) of two diastereomers, separable by silica-gel TLC. The structure of the reduction product **7** was verified by a direct spectroscopic comparison with an authentic sample.[15] The yields of the reduction product and photoadducts are summarized in Table 1 together with the quantum yields obtained for [carboxylates] of 0.5 M.

Mechanistic Studies. In order to unravel the mechanistic features of these photoreactions, the glycolic acid system was investigated in greater detail. Figure 1 shows that the quantum yields for the disappearance of **1** (ϕ_{dis}), for the formation of **2** (ϕ_a), and for the formation of **7** (ϕ_r) depend significantly on the concentration of $\mathrm{NaClO_4}$. The quantum yields were reduced by an addition of $\mathrm{NaClO_4}$, but exhibited no further decrease at $\mathrm{NaClO_4}$ concentrations above ca. 0.4 M. A similar salt effect was observed regarding the fluorescence quenching. Thus, the fluorescence intensity of **1** in the presence of the quencher (glycolate) increased (namely, the quenching efficiency decreased) upon increasing the concentration of $\mathrm{NaClO_4}$. The intensity remained unchanged in the $\mathrm{NaClO_4}$ concentration range of 0.4 to 0.5 M, as shown in Fig. 2. Accordingly, the

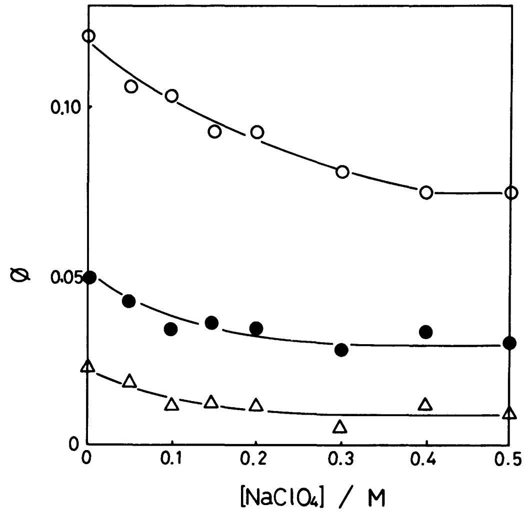


Fig. 1. Dependence of quantum yields, ϕ_{dis}(○), ϕ_a (●), and ϕ_r(△), on the concentration of $\mathrm{NaClO_4}$ in a glycolate system (pH 6.0, [**1**] = 1.00×10^{-3} M, [glycolate] = 0.2 M).

mechanistic studies described in the present paper were made regarding aqueous solutions containing 0.5 M $NaClO_4$ (unless otherwise noted).

Figure 3 shows changes in the quantum yields as a function of the solution pH. ϕ_{dis} and ϕ_a increased steeply around pH 3.5 and remained, substantially, unchanged above pH 4.5. The pK_a of glycolic acid is 3.83; thus, Fig. 3 demonstrates that the disappearance of **1** and the formation of **2** took place more efficiently in the presence of the glycolate anion than in the presence of the free glycolic acid. This corresponds to the above-mentioned fact that the effective quenching of the fluorescence of **1** was observed with the anion, but not with the free acid. This suggests that the photoaddition reaction proceeds mainly via $\mathbf{1}^{S_1}$ by an electron transfer from the anion. Similar pH dependencies of the quantum yields were also observed in the case of an α-hydroxyisobutyric acid system (Fig. 4).

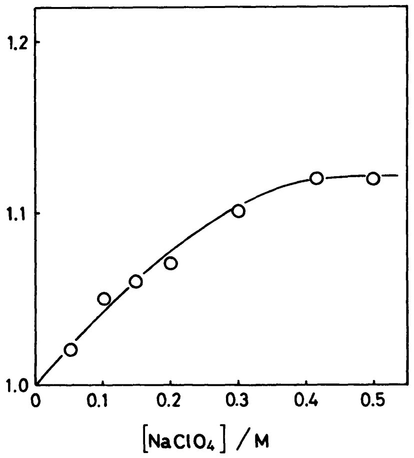


Fig. 2. Dependence of the fluorescence intensity of **1** (I) on the concentration of $NaClO_4$ in the presence of glycolate of 0.2 M. I_0 is the intensity in the absence of $NaClO_4$. The solution pH was 6.0 and [**1**] 1.00×10^{-3} M.

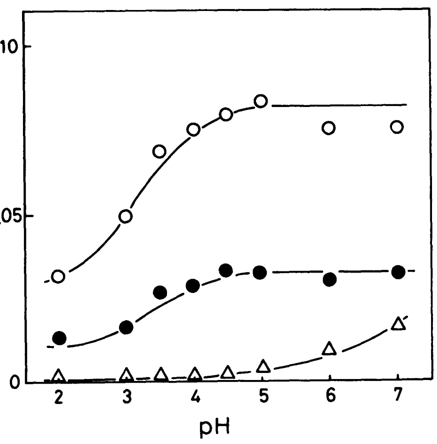
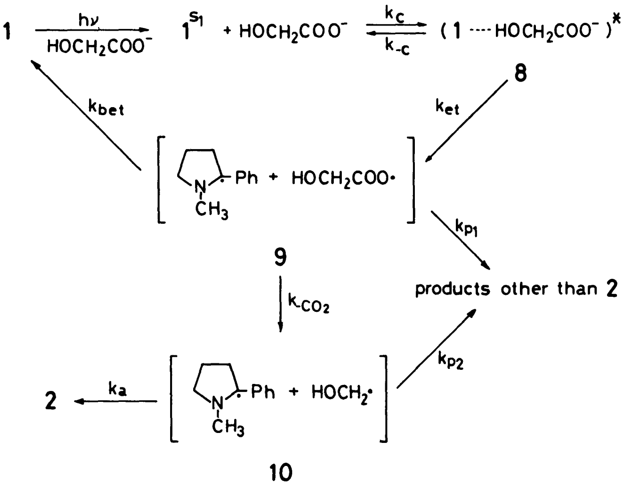


Fig. 3. Dependence of quantum yields, ϕ_{dis}(○), ϕ_a (●), and ϕ_r(△), on pH in a glycolic acid system([**1**]= 1.00×10^{-3} M, [glycolic acid]=0.2 M, [$NaClO_4$]= 0.5 M).

A plausible mechanism for the formation of the photoadduct **2** from the glycolate anion analogous to that for the 3-butenoate system[6] (as depicted in Scheme 2) involves the radical-pair intermediates **9** and **10**. **9** is formed by an electron transfer from the glycolate donor to $\mathbf{1}^{S_1}$ presumably through the intervention of an encounter complex **8** and is returned to the ground state of **1** and glycolate by a back electron transfer. The intermediate **10** is formed by the decarboxylation of **9** and is transformed into **2** by a radical coupling within the solvent cage. In addition, the formation processes of the reduction product **7** and other products, as yet unidentified, from **9** and **10** should be taken into consideration. The rate constants of these processes are appended in Scheme 2.



Scheme 2.

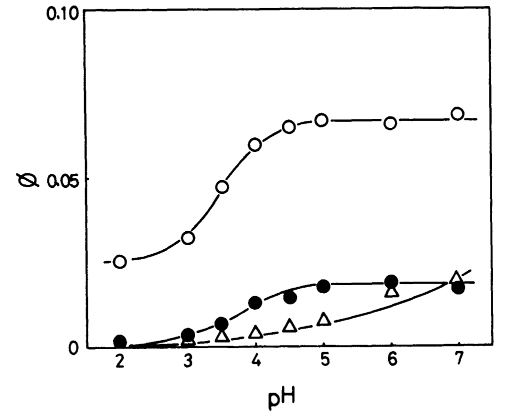


Fig. 4. Dependence of quantum yields, ϕ_{dis}(○), ϕ_a (●), and ϕ_r(△), on pH in an α-hydroxyisobutyric acid system([**1**]= 1.00×10^{-3} M, [$NaClO_4$]=0.5 M). In this case, ϕ_a represents a quantum yield for the formation of **4**.

A steady-state analysis of the sequence gives

$$\phi_a = \alpha_a k_q \tau[\mathrm{HA}]/(1 + k_q \tau[\mathrm{HA}]) \tag{2}$$

or

$$\phi_a^{-1} = \alpha_a^{-1} + (\alpha_a k_q \tau[\mathrm{HA}])^{-1} \tag{3}$$

where [HA] and α_a represent the concentration of the glycolate anion and the limiting quantum yield (ϕ_a at [HA]→∞), $\{k_{-CO_2}/(k_{-CO_2}+k_{bet}+k_{p1})\}\{k_a/(k_a+k_{p2})\}$, respectively. k_q is mathematically equivalent to $k_c k_{et}/(k_{et}+k_{-c})$. The ratio ($k_q\tau$) of the intercept to the slope of a linear plot of ϕ_a^{-1} vs. $[\mathrm{HA}]^{-1}$ (Fig. 5) was 0.66±0.27 M^{-1}. This value agreed with the $k_q\tau$ value (Table 1, 0.61 M^{-1}) obtained from the fluorescence quenching. This result also supports the idea that the photoaddition is an excited singlet-state process of **1**.

If, in this manner, both the reaction and the fluorescence-quenching processes can be considered together under a unified mechanism, the limiting quantum yield α_a can be estimated to be 0.27 (from Eq. 2) using $k_q\tau$ from the fluorescence quenching and the ϕ_a obtained at [HA] of 0.5 M. The limiting quantum yield α_{dis} $(=(k_{-CO_2}+k_{p1})/(k_{-CO_2}+k_{bet}+k_{p1}))$ for the disappearance of **1** can also be calculated using the ϕ_{dis} denoted in Eq. 4 and is given in Table 2

$$\phi_{dis} = \alpha_{dis} k_q \tau[\mathrm{HA}]/(1 + k_q \tau[\mathrm{HA}]) \tag{4}$$

together with the limiting quantum yields estimated in a similar manner for the α-hydroxyisobutyrate system. The α_{dis} (0.64) for the glycolate system indicates that the fraction of the back electron transfer in the total disappearance pathways of **9** was 36%. Furthermore, the ratio $(=\{k_a/(k_a+k_{p2})\}\{k_{-CO_2}/(k_{-CO_2}+k_{p1})\})$ of α_a to α_{dis} implies that $k_{-CO_2}/(k_{-CO_2}+k_{p1})>0.42$. Thus, the decarboxylation of **9** takes place in a proportion of over 27% and the decarboxylation of the hydroxyacetoxyl radical partner in **9** is a sufficiently rapid pathway to compete with the back electron transfer.[16] This reflects the fact that the α_a and α_{dis} were fairly large; namely, the photoreaction of **1** in the presence of the glycolate anion was appreciably efficient.

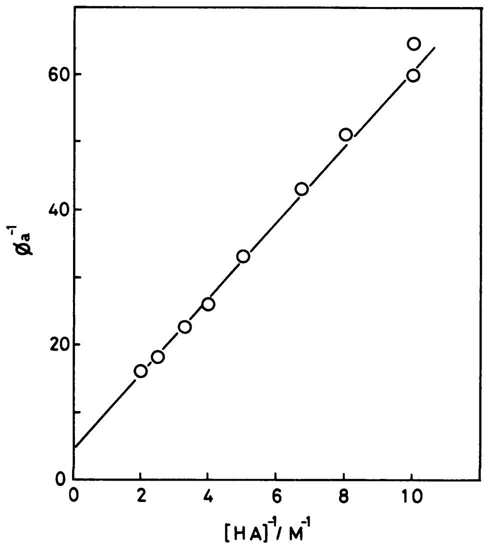


Fig. 5. Double reciprocal plot of the quantum yield for the formation of **2**(ϕ_a) vs. the concentration of glycolate([HA]).

Likewise, the fraction of decarboxylation for the α-hydroxyisobutyrate system can be estimated to be greater than 15%. However, it should be pointed out that a smaller α_a/α_{dis} value for this system, probably due to the formation of the reduction product **7** via the intermediate **10** in a higher quantum yield than that for the glycolate system (see Table 1), allowed us to underestimate k_{-CO_2}.

All the quantum yields, ϕ_{dis}, ϕ_a, and ϕ_r for the glycolate system were decreased by an addition of $\mathrm{NaClO_4}$ (Fig. 1). Moreover, the degrees of the decreases were almost the same when considering at least two cases of ϕ_{dis} and ϕ_a: for example, ϕ_{dis} exhibited a 38% decrease at [$\mathrm{NaClO_4}$] of 0.5 M; ϕ_a a 39% decrease. In addition, a decrease of the fluorescence-quenching efficiency upon an addition of the salt was also observed (Fig. 2). It is important to note that in the absence of the glycolate quencher, the salt did not affect the intensity of the fluorescence of **1**. This signifies that the singlet lifetime was not affected by the salt. Thus, it seems likely that the term k_q[HA], which is common to the two quantum yields (Eq. 2 and 4), and the fluorescence quantum

Table 2. Limiting Quantum Yields for the **1** Disappearance(α_{dia}) and for the Photoadduct Formation(α_a) and Fractions of Pathways from the Intermediate **9**

Carboxylate anion (R-COO⁻) R-	α_{dis}	α_a	$\frac{\alpha_a}{\alpha_{dis}}$	Fractions of pathways		
				Back electron transfer	Decarboxylation	Formation of other products
$\mathrm{HOCH_2}$-	0.64	0.27 (0.26)[a]	0.42	0.36	>0.27	<0.37
$\mathrm{HOC(CH_3)_2}$-	0.47	0.15	0.32	0.53	>0.15	<0.32

a) Determined from the intercept(α_a^{-1}) of a linear plot shown in Fig. 5.

yield (ϕ_f) denoted in Eq. 5, was reduced by an addition of $\mathrm{NaClO_4}$.

$$\phi_f = k_f\tau/(1 + k_q\tau[\mathrm{HA}]), \tag{5}$$

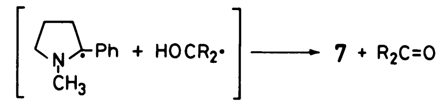
where k_f is a rate constant for the fluorescence of **1**. Hence, the relationships between the increased rates of the quantum yields ($\phi/\phi^\circ-1$) and the decreased rate of the fluorescence intensity in the presence of the quencher ($1-I/I^\circ$), based on the quantum yields (ϕ°) and the intensity (I°) at [$\mathrm{NaClO_4}$] of 0.5 M, can be expressed as

$$1 - I/I^\circ = k_q^\circ\tau[\mathrm{HA}](\phi/\phi^\circ - 1). \tag{6}$$

Here, k_q° is the quenching-rate constant at a [$\mathrm{NaClO_4}$] of 0.5 M.

Linear plots of $1-I/I^\circ$ vs. $\phi_{dis}/\phi_{dis}^\circ-1$ and $\phi_a/\phi_a^\circ-1$ having slopes of $k_q^\circ\tau[\mathrm{HA}]$ (Fig. 6) gave $k_q^\circ\tau=0.87\pm0.07\ \mathrm{M^{-1}}$ from a plot against $\phi_{dis}/\phi_{dis}^\circ-1$ and $0.77\pm0.15\ \mathrm{M^{-1}}$ from that against $\phi_a/\phi_a^\circ-1$, respectively. These $k_q^\circ\tau$ values are in satisfactory agreement with the $k_q\tau$ ($0.61\ \mathrm{M^{-1}}$) obtained from fluorescence-quenching experiments at a [$\mathrm{NaClO_4}$] of 0.5 M, within the experimental limits of error. They verify the salt effect on the k_q[HA] term. The addition of $\mathrm{NaClO_4}$ probably causes an instability in the postulated encounter complex **8**, which is formed from a cation and an anion; thus, it is reasonable to assume that the salt effect involves (in part) a decrease in the k_q value.

It is again worth noting that a higher quantum yield for the formation of **7** was observed in the case of α-hydroxyisobutyrate compared to the case of glycolate (Table 1). This suggests that the α-hydrogen of the α-hydroxyalkanoate anions did not serve as a hydrogen source for the formation of **7**. On the other hand, ketyl radicals are known to be active reducing agents;[17)] e.g., the radicals can transfer hydrogen atoms to aryl ketones.[17b)] It thus seems reasonable to propose that a major pathway for the formation of **7** involves a disproportionation of the radical pairs formed after the decarboxylation (for the glycolate system, **10**), even though a mechanism for the formation was not investigated as thoroughly as that for the adduct formation. In particular, the reason why the yields of **7** increased with an increase in pH (Figs. 3 and 4) remains obscure. Formaldehyde (15%), acetaldehyde (18%), and acetone (32%) were formed in reasonable yields in the glycolate, lactate, and α-hydroxyisobutyrate systems, respectively. **7** was formed in a very low yield (<3%) for the case of an ethoxyacetate having no hydroxyl group. These findings support the idea of this disproportionation pathway. Furthermore, the results that a successive substitution of a methyl group at the α position induced a decrease in ϕ_a and, on the contrary, induced an increase in ϕ_r (Table 1) could be interpreted in terms of a simple steric hindrance of the methyl group during the radical pair combination which produced the photoadducts.



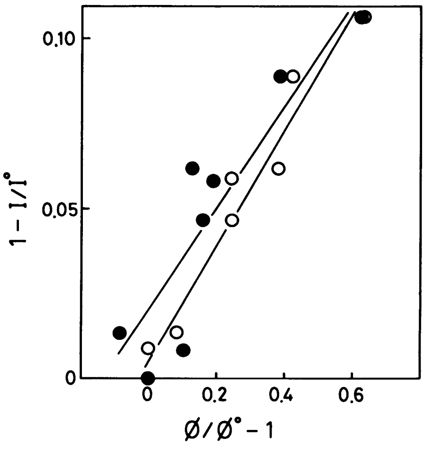
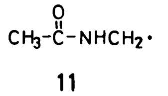


Fig. 6. Relationships between dependencies of the **1** fluorescence intensity(I) and the quantum yields, ϕ_{dis}(○) and ϕ_a(●), on the concentration of $\mathrm{NaClO_4}$ in the presence of glycolate of 0.2 M. ϕ° and I° represent the quantum yields and the fluorescence intensity at [$\mathrm{NaClO_4}$] of 0.5 M.

Photoreactions of 1 with Sulfur- and Nitrogen-Substituted Alkanoates. In the case of 2-mercaptopropionate, only the reduction product **7** was detected as a major product (Table 1). As described above, an electron transfer from 2-mercaptopropionate (predominantly from the mercapto group) to $\mathbf{1}^{S_1}$ takes place more efficiently than those from α-hydroxyalkanoates. Accordingly, a primary event for this photoreaction can be reasonably assumed to be an electron transfer leading to the formation of a 1-methyl-2-phenylpyrrolidinyl radical and the ensuing, predominant formation of a radical $\mathrm{H\overset{+\cdot}{S}CH(CH_3)}$-$\mathrm{COO^-}$. On the other hand, S–H bonds possess relatively low dissociation energies and are, consequently, subject to a hydrogen-atom abstraction. Thus, **7** is quite likely to be formed through a hydrogen-atom abstraction of pyrrolidinyl radical within a solvent cage from $\mathrm{H\overset{+\cdot}{S}CH(CH_3)COO^-}$ or a mercaptoalkyl radical $\mathrm{HS\dot{C}HCH_3}$ resulting after decarboxylation, or through an out-of-cage hydrogen-atom abstraction from the mercaptopropionate anion, in preference to the formation of an adduct analogous to the photoadducts from the α-hydroxyalkanoates.

In cases of glycine and α-aminoisobutyric acid, **7** was also detected as a very low-yield product (Table 1). This is apparently due to a quite inefficient electron transfer at pH 6 (vide supra). A photolysis at a higher pH (where the NH_3^+ groups of the α-amino acids are deprotonated) was impossible to perform since the higher pH brought about a thermal instability of **1**.[18]

On the other hand, *N*-acetylglycinate gave an adduct **6** in fairly high yield (80%, Table 1). A reasonably efficient electron transfer from the glycinate (vide supra) can induce the formation of an acetylaminoacetoxyl radical $CH_3CONHCH_2COO\cdot$ via an electron transfer from the carboxylato group and of a radical zwitterion $CH_3CO\overset{+\cdot}{N}HCH_2COO^-$ via an electron transfer from the acetylamino group. Both these radicals could be transformed into an acetylaminomethyl radical **11** via decarboxylation.



$$CH_3-\overset{O}{\overset{\|}{C}}-NHCH_2\cdot$$

11

This is rather efficiently induced since the methyl radical **11** is stabilized by a conjugation with the acetylamino group. Thus, the formation of **6** in high yield is understandable in terms of the formation of this stable radical as well as in terms of the efficient primary electron-transfer pathway.

Experimental

General. Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. UV spectra were obtained with a Shimadzu UV-202 or JASCO UVIDEC-610A spectrophotometer. Fluorescence emission and IR spectra were recorded on a Shimadzu RF-510 spectrometer and a Hitachi 285 spectrophotometer, respectively. Mass spectra were taken with a JEOL JMS-01SG-2 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-24B spectrometer with TMS as the internal standard. GLC (PEG-20M) was performed using a Shimadzu GC-3BF or a Hitachi 263-30 chromatograph with a flame-ionization detector. Preparative TLC was performed on silica-gel plates (Merck Kieselgel 60 PF_{254}).

Materials. **1** was prepared and purified according to a method from the literature:[8] mp 117.5—119.0 °C. *N*-Acetylglycine (Aldrich, 99%) was treated with an activated carbon, then recrystallized four times from methanol. The other reagents were all purchased from commercial sources and purified by recrystallization or vacuum distillation just before use.

Fluorescence Quenching Experiments. The relative intensities of the fluorescence at 380 nm of **1** (1.00×10^{-3} M) were measured at 25±1 °C. The excitation wavelength (at which the quenchers do not absorb light) was 305 nm. Aqueous solutions were adjusted to pH 6.0 with 4 M NaOH when carboxylate anions were used as quenchers. The slopes of Stern-Volmer plots were determined by a least-squares analysis of the obtained data for solutions containing 0.5 M $NaClO_4$. Concentrations of the quenchers were in the 0.05—0.5 M ranges.

Preparative Irradiations. Preparative irradiations were carried out using a 400 W high-pressure mercury lamp (Riko-Sha UVL-400HA) equipped with a Pyrex water jacket under an argon atmosphere. The lamp was immerged in the reaction solutions (200 cm^3, pH 6.0) and photolysates were acidified (pH 1) with HCl and then concentrated to 20 cm^3 in vacuo, unless otherwise noted. The acidic solutions were made basic (pH 10) with NaOH, saturated with NaCl, and extracted with three 40-cm^3 portions of chloroform. The extracts were dried over anhydrous Na_2SO_4 and then concentrated in vacuo to give oily residues. These were subjected to GLC analyses. Photoproducts were isolated by preparative GLC or TLC. Styphnate derivatives of the photoadducts and of reduction product **7** were separated out from equimolar solutions of the photoproducts and 2,4,6-trinitroresorcinol in ethanol, and recrystallized from ethanol.

The yields of the photoproducts were determined by GLC analyses (except for the *N*-acetylglycine photosystem) and are summarized in Table 1. The internal standards used were 9,10-dihydroanthracene for **2**, acenaphthene for **3**, **4**, and **5**, and naphthalene for **7**.

Photolysis of 1 with Glycolic Acid: An aqueous solution containing **1** (400 mg, 7.7 mM) and glycolic acid (10.5 g, 0.69 M) was irradiated for 120 min. Then, the photolysate was worked up by the above-mentioned method to give a crude oil (435 mg). A GLC analysis of the oil showed the formation of two major products: 1-methyl-2-hydroxymethyl-2-phenylpyrrolidine **2** and 1-methyl-2-phenylpyrrolidine **7**. These were isolated by preparative GLC. Spectral data for **2** and **7** were as follows and were identical with those of authentic samples.[8,15] **2**: ^{1}H NMR ($CDCl_3$) δ=1.65—3.4 (6H, m, ring methylenes), 2.11 (3H, s, N-CH_3), 2.85 (1H, s, OH), 3.77, 3.93 (2H, d and d, J=11 Hz, $\underline{CH_2}OH$), 7.1—7.6 (5H, m, ArH); IR (liquid film) 3390 (broad), 2940, 1600, 1445, 1060, 760, and 700 cm^{-1}. **7**: ^{1}H NMR ($CDCl_3$) δ=1.6—3.5 (7H, m, ring protons), 2.17 (3H, s, N-CH_3), 7.1—7.5 (5H, m, ArH).

The identification of **7** was confirmed by a direct comparison of the IR spectrum of a styphnate derivative from **7** with that from the authentic sample and by a melting-point value (184.5—185 °C) for a mixture of the derivatives. IR (KBr disk) of the styphnate derivative: 3425 (broad), 3030, 2760, 1650, 1590, 1540, 1460, 1380, 1345, 1300, 1200, 1090, 760, and 710 cm^{-1}.

Photolysis of 1 with Lactic Acid: The irradiation (190 min) of an aqueous solution of **1** (600 mg, 11.6 mM) containing lactic acid (5.41 g, 0.3 M) gave 760 mg of a crude oil. A GLC analysis of the oil showed the formation of three major products, **7** and two diastereomeric 1-methyl-2-(1-hydroxyethyl)-2-phenylpyrrolidines **3**. The diastereomers were separated by preparative TLC (hexane:diethyl ether=3:7, R_f=0.23 and 0.14).

3(R_f=0.23): ^{1}H NMR ($CDCl_3$) δ=1.05 (3H, d, J=6.4 Hz, $CH(\underline{CH_3})OH$), 1.90 (3H, s, N-CH_3), 1.0—3.2 (6H, m, ring methylenes), 3.84 (1H, s, OH), 4.42 (1H, q, J=6.4 Hz, $\underline{CH}(CH_3)OH$), 7.0—7.5 (5H, m, ArH); IR (liquid film) 3400 (broad), 2980, 1600, 1450, 1120, 765, and 705 cm^{-1}; MS (75 eV) *m/z* (rel intensity) 205 (M^+; 13), 204 (82), 160 (100).

This compound was further characterized as its styphnate derivative (mp 127.3—129.5 °C). Found: C, 50.76; H, 4.97; N, 12.72%. Calcd for $C_{19}H_{22}N_4O_9$: C, 50.67; H, 4.92; H, 12.44%.

3(R_f=0.14): ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, d, J=6.4 Hz, $CH(\underline{CH_3})OH$), 2.14 (3H, s, N-CH_3), 0.85—3.3 (6H, m, ring methylenes), 3.45 (1H, s, OH), 4.06 (1H, q, J=6.4 Hz,

$C\underline{H}(CH_3)OH$), 7.1—7.6 (5H, m, ArH); IR (liquid film) 3400 (broad), 2975, 1600, 1450, 1120, 765, and 705 cm^{-1}; MS (75 eV) *m/z* (rel intensity) 205 (M$^+$; 8.6), 204 (60), 160 (100).

The formation ratio of the isomers (R_f=0.23: R_f=0.14) was 1:1.2.

Photolysis of 1 with α-Hydroxyisobutyric Acid: The irradiation (180 min) of **1** (400 mg, 7.7 mM) in the presence of α-hydroxyisobutyric acid (4.16 g, 0.2 M) gave 374 mg of a crude oil. A GLC analysis of the oil showed the formation of **7** and 1-methyl-2-(1-methyl-1-hydroxyethyl)-2-phenylpyrrolidine **4**. The photoadduct **4** was isolated by preparative TLC (hexane:diethyl ether=3:7).

4: ^{1}H NMR (CDCl$_3$) δ=1.32, 1.44 (6H, s and s, $C(C\underline{H}_3)_2OH$), 2.53 (3H, s, N-CH$_3$), 1.1—3.4 (6H, m, ring methylenes), 3.45 (1H, s, OH), 7.1—7.6 (5H, m, ArH); IR(liquid film) 3440 (broad), 2975, 1600, 1445, 1155, 760, and 705 cm^{-1}; MS (CI) *m/z* (rel intensity) 220 (M+H; 42), 160 (100).

An elemental analysis of the styphnate derivative of **4** (mp 130.8—133.5 °C) was as follows: Found: C, 51.79; H, 5.17; N, 12.23%. Calcd for $C_{20}H_{24}N_4O_9$: C, 51.72; H, 5.21; N, 12.06%.

Photolysis of 1 with Ethoxyacetic Acid: A GLC analysis of a crude oil (416 mg) obtained after the irradiation (120 min) of **1** (7.7 mM) in the presence of ethoxyacetic acid (0.2 M) showed the formation of 1-methyl-2-ethoxymethyl-2-phenylpyrrolidine **5** and a very small amount of **7** (<3%). The photoadduct **5** was isolated by preparative TLC (hexane:diethyl ether=3:7).

5: ^{1}H NMR (CDCl$_3$) δ=1.20 (3H, t, *J*=6.6 Hz, $OCH_2C\underline{H}_3$), 1.7—2.6 (4H, m, methylenes at C-3 and C-4 of ring), 2.28 (3H, s, N-CH$_3$), 2.8—3.3 (2H, m, N-CH$_2$), 3.52 (2H, q, *J*=6.6 Hz, $OC\underline{H}_2CH_3$), 3.6, 3.8 (2H, d and d, *J*=9.0 Hz, $C\underline{H}_2OCH_2CH_3$), 7.1—7.7 (5H, m, ArH); IR (liquid film) 2975, 2865, 1600, 1445, 1115, 765, and 705 cm^{-1}; MS (75 eV) *m/z* (rel intensity) 219 (M$^+$, 3), 160 (100).

An elemental analysis of the styphnate derivative of **5** (mp 137.2—138.5 °C) was as follows: Found: C, 51.63; H, 5.16; N, 12.29%. Calcd for $C_{20}H_{24}N_4O_9$: C, 51.72; H, 5.21; N, 12.06%.

Photolysis of 1 with *N*-Acetylglycine: **1** (400 mg, 7.7 mM) was irradiated in the presence of *N*-acetylglycine (4.68 g, 0.2 M) for 240 min. The GLC analysis of an obtained oil (303 mg) revealed no distinct peak. 1-Methyl-2-(acetylaminomethyl)-2-phenylpyrrolidine **6** was isolated by preparative TLC (acetone) in a high yield (286 mg, 80%).

6: ^{1}H NMR (CDCl$_3$) δ=1.96 (3H, s, CH$_3$CO), 2.10 (3H, s, N-CH$_3$), 1.7—2.4 (4H, m, methylenes at C-3 and C-4 of ring), 2.6—3.2 (2H, m, methylene at C-5 of ring), 3.45, 3.93 (2H, dd and dd, *J*=13.4, 6.8, 3.4 Hz, $C\underline{H}_2NH$), 6.05 (1H, broad s, NH), 7.1—7.5 (5H, m, ArH); IR (liquid film) 3300 (broad), 2960, 1650, 1540, 1440, 760, and 700 cm^{-1}; MS (75 eV) *m/z* (rel intensity) 232 (M$^+$; 0.16), 231 (100), 160 (63).

An elemental analysis of the styphnate derivative of **6** (mp 164.2—166.3 °C) was as follows: Found: C, 50.11; H, 5.00; N, 14.59%. Calcd for $C_{20}H_{23}N_5O_9$: C, 50.32; H, 4.86; N, 14.67%.

Photolysis of 1 with α-Amino Acids: A GLC analysis of a crude oil (250 mg), obtained after the irradiation (300 min) of **1** (400 mg, 7.7 mM) in the presence of α-aminoisobutyric acid (4.12 g, 0.2 M), showed the formation of **7**; other products were not identified.

When glycine was used as a carboxylic acid, **7** was also detected as a product.

Photolysis of 1 with 2-Mercaptopropionic Acid: An argon-purged aqueous solution (20 cm^3) containing **1** (40.0 mg, 7.7 mM) and 2-mercaptopropionic acid (0.425 g, 0.2 M) in a Pyrex glass tube was irradiated using a merry-go-round apparatus (described below) for 300 min. The photolysate was acidified (pH 1) with HCl and concentrated to ca. 2 cm^3 in vacuo. The concentrate was made basic (pH 10) with NaOH and then extracted with 6 cm^3 of chloroform. In this extract, only the reduction product **7** was detected as a major product by means of a GLC analysis.

Identification and Determination of Carbonyl Compounds: Aldehydes and acetone formed during photoreactions of the hydroxyalkanoate systems were isolated as their 2,4-dinitrophenylhydrazone derivatives which were identified by a direct comparison of the IR spectra and melting points with those of authentic samples. These derivatives were determined by means of HPLC (JASCO Familic-100, SC-01, 80% methanol).

Determination of Quantum Yields. The qantum yield for the formation of **2** was measured using a linear optical-bench system equipped with a 500 W super-high-pressure mercury lamp (Ushio USH-500D) at 25±1 °C. The beam of the 280 nm band was isolated with a monochromator (Jarrel Ash JE-25E) and was divided into two portions using a beam splitter tilted at 45° with respect to the beam. The transmitted light was used to irradiate an argon-purged aqueous solution (pH 6.0, [**1**]=1.00×10^{-3} M, [glycolate]=0.5 M, [NaClO$_4$]=0.5 M) in a cyclindrical cell (20×10 mm). It absorbed >96% of the light during photolysis runs. The diverted light (perpendicular to the transmitted light) was received by a UV radiometer (TOPCON UVR-254) in order to monitor the light output. The amount of transmitted light (1.54×10^{14} quanta s^{-1}) absorbed by the sample solution was determined by a calibration of the radiometer against the trioxalatoferrate(III) actinometry (0.006 M potassium trioxalatoferrate(III)).[19]

Product analyses were performed by GLC for the reaction mixtures. These were worked up in the same way as the preparative run using 9,10-dihydroanthracene as an internal standard: ϕ_a=0.057, 0.060, and 0.068 at 1.11, 1.08, and 0.878×10^{18} quanta of absorbed photons.

The quantum yields for the formation of the other photoadducts (**3**, **4**, and **5**), for the formation of reduction product, **7**, and for the disappearance of **1** were determined at 25±1 °C using a merry-go-round apparatus equipped with the same 400 W high-pressure mercury lamp that was employed for the preparative run. Aqueous solutions (20 cm^3) in Pyrex glass tubes containing **1** of 1.00×10^{-3} M, carboxylic acids of 0.5 M and NaClO$_4$ of 0.5 M were adjusted to pH 6.0. The glycolic acid solution employed for the determination of the quantum yield for the formation of **2** was used as an actinometer solution. Photolysates were subjected to a GLC analysis in the same manner as for the determination of the quantum yield of **2**. Internal standards were the same as those used for the determination of chemical yields in the preparative runs. The degrees (<10%) of the disappearance of **1** were obtained from the decrease of the absorbance at λ_{max} of 258 nm.

The relative quantum yields at different concentrations of glycolate and at different concentrations of NaClO$_4$ and the pH dependencies of the quantum yields were also determined using the merry-go-round apparatus as described above.

Cyclic Voltammetry. The CV measurements were carried out using a Yanaco P8-ES unit and a Yanaco P8-PT potentiostat. The working electrode in a three-electrode cell was a platinum disk (3 mm diameter) sealed into a teflon tube and the counter electrode was a pool of mercury. SCE was used as a reference electrode. Current-voltage curves were recorded on a Yokogawa 3078 X-Y recorder. The reduction current of **1** was observed as a discernible shoulder on the large reduction wave of water when an aqueous solution containing **1** of 5.0×10^{-3} M and $NaClO_4$ of 0.1 M was used. The measured value (−0.95 V) was almost the same in magnitude as the value obtained in acetonitrile.[4] For a determination of the oxidation potentials of 2-mercaptopropionic acid and its carboxylate anion, aqueous solutions containing the acid of 4.0×10^{-3} M and $NaClO_4$ of 0.5 M were used. With the carboxylate anion, the pH of the aqueous solution was adjusted to 6.0 with NaOH.

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