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Fragmentation of Benzyl Esters with an Electron-Withdrawing Group by Photo-Induced Electron Transfer. Analogy with Fragmentation in Secondary Ion Mass Spectrometry

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The analogy between negative secondary ion mass spectrometry and photo-induced electron transfer reactions has been seen in the fragmentation of radical anions of esters. The photochemical reaction may provide a new method of the protection of carboxylic acids.

Recent investigations on the fragmentation of radical cations generated in mass spectrometry and photo-induced electron transfer have revealed that good agreement exists between the two processes.1) Similar agreement would be expected in the fragmentation of radical anions generated in negative chemical ionization (CI) or secondary ion mass spectrometry (SIMS) and in photo-induced electron transfer reactions. In negative ion mass spectrometry, the fragmentation of esters has been reported to give the corresponding carboxylate anion usually as a major peak.2) On the other hand, the formation of a carboxylate anion has not been reported so far in photo-induced electron transfer reactions of esters with amines.3) In this paper, we report the analogy observed in the fragmentation of radical anions of esters generated by both processes.

Benzyl esters with an electron-withdrawing group (1-3) were easily prepared from the corresponding carboxylic acid and benzyl bromide in 90-100% yields.4) In negative secondary ion mass spectrometry5) in a triethanolamine matrix, 1-3 gave the corresponding carboxylate anion as a base peak, as exemplified in Fig. 1.

On irradiation of an acetonitrile solution of the ester (1-3, 0.02 M) and triethylamine (0.2 M) with a low-pressure mercury lamp (1a, 2a, and 3a)

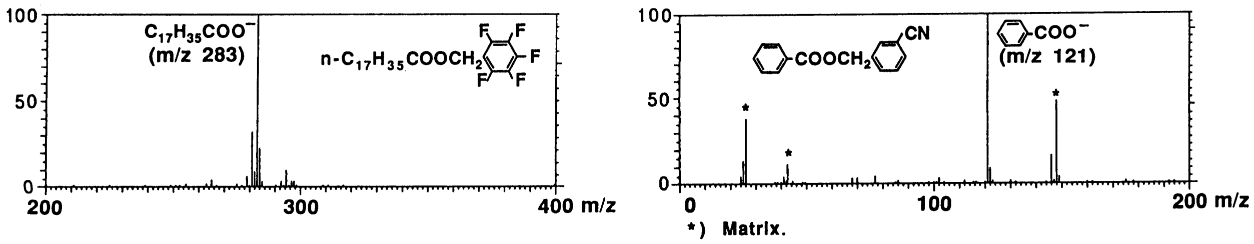
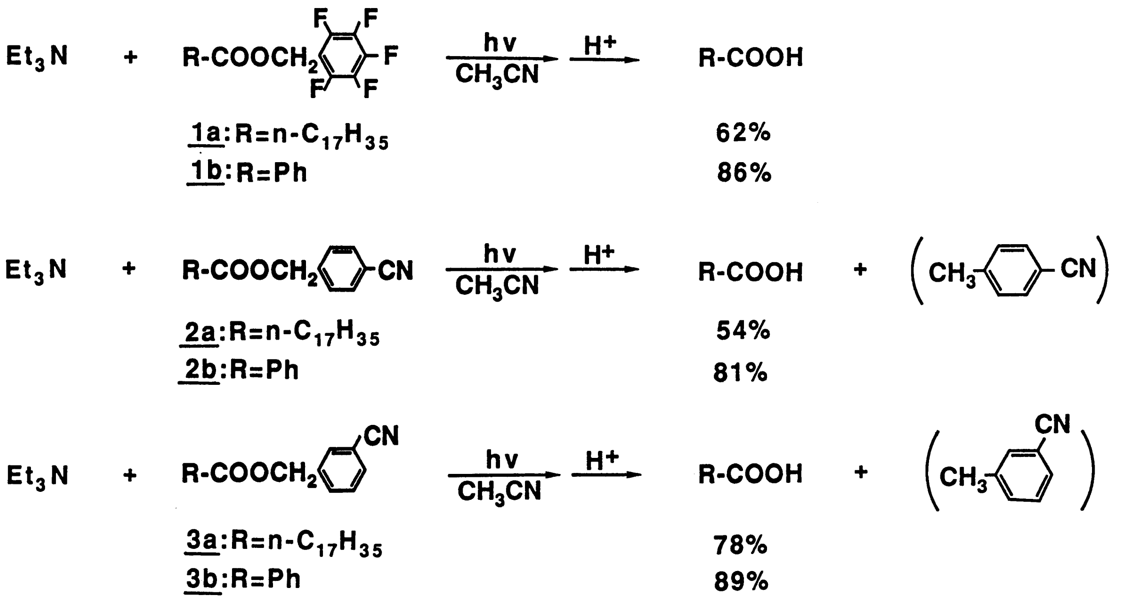


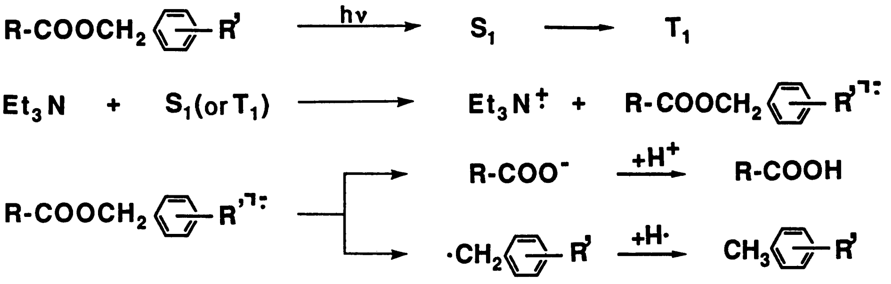
Fig.1. Partial negative SIMS spectra of 1a (left) and 3b (right) in a triethanolamine matrix.

or a medium-pressure mercury lamp through a Pyrex filter (1b, 2b, and 3b) followed by acidification with hydrochloric acid, octadecanoic acid or benzoic acid was isolated in a good yield. In the cases of 2 and 3, a substantial amount of p- or m-tolunitrile was formed in the course of reaction, which decomposed gradually and disappeared at the end of the reaction. The photocleavage of esters in high yields might be used as a new method of the protection of carboxylic acids together with the convenient synthesis of benzyl esters with an electron-withdrawing group (or groups).



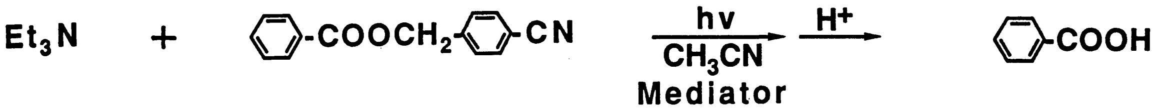
The fluorescence of 2a and 3a was quenched by triethylamine nearly at the diffusion-controlled limit. The free energy changes for the electron transfer processes from the amine to the excited singlet states of 2a and 3a were found to be negative on the basis of the calculation by the Rehm-Weller equation.[6)] On the other hand, 1b, 2b, and 3b have very weak fluorescence and strong phosphorescence, and photocleavage of 1b, 2b, and 3b did not proceed in acetonitrile saturated with oxygen. The calculated free energy changes for the electron transfer from triethylamine to the excited triplet states of 1b, 2b, and 3b are all negative. Therefore, electron transfer occurs mainly from triethylamine to the excited singlet states of 2a and 3a and the excited triplet states of 1b, 2b, and 3b. In the case of 1a, the diffusion-controlled fluorescence quenching by the amine and a decrease in the rate of the photocleavage to one-fifth in acetonitrile saturated with oxygen indicate that both the excited singlet and triplet states of 1a participate in the electron-transfer processes.

From these results, the mechanism for the photocleavage of the esters is proposed in Scheme 1. The electron transfer from triethylamine to the excited singlet and/or triplet states of 1-3 affords the radical anions of the esters. The radical anion dissociates to the carboxylate anion and the benzyl radical, which abstract proton and hydrogen to yield the carboxylic acid and the toluene derivative, respectively.



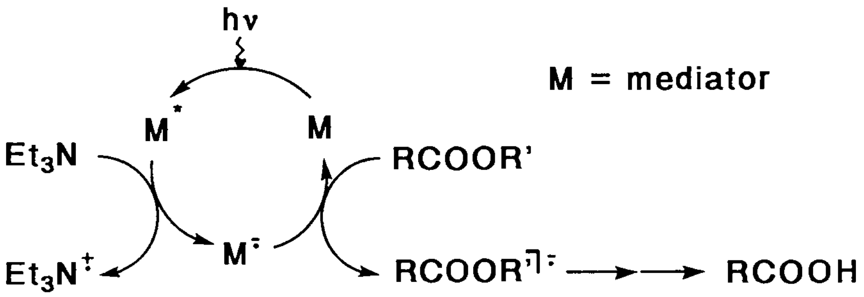
Scheme 1.

In the presence of a mediator,[7)] photocleavage of the esters proceeds smoothly with light of a longer wavelength. Thus, in the presence of a small amount of phenanthrene or pyrene, 2b yielded benzoic acid in good yields on irradiation with 334 or 366 nm light, respectively. The mediators were chosen on the basis of oxidation and reduction potentials. The oxidation potentials of phenanthrene ($E_{1/2}^{ox}$ = 1.58 V) and pyrene ($E_{1/2}^{ox}$ = 1.27 V) are larger than that of triethylamine (E_{p}^{ox} = 0.79 V). The reduction potentials of phenanthrene ($E_{1/2}^{red}$ = -2.50 V) and pyrene ($E_{1/2}^{red}$ = -2.13 V) are smaller than that of 2b ($E_{1/2}^{red}$ = -1.82 V).[8)] In this situation, the excited state of the mediator can accept an electron from triethylamine and donate it to 2b. The order that the mediator donates or accepts an electron is obscure, but in the absence of triethylamine, photocleavage of 2b with the mediator did not proceed efficiently. Therefore, in the initial



Mediator = phenanthrene (17 mol%) λ = 334 nm 76%
Mediator = pyrene (38 mol%) λ = 366 nm 95%

stage, electron transfer occurs from the amine to the excited state of the mediator.[9] The mechanism for photocleavage in the presence of the mediator is illustrated in Scheme 2.



Scheme 2.

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