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Intra-ion-pair Electron Transfer Mechanism for Photolysis of Diphenyliodonium Salt Sensitized by 9,10-Dimethoxyanthracene-2-sulfonate Counteranion

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Diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate is photochemically dissociated to give 9,10-dimethoxyanthracene-2-sulfonic acid. The dissociation is considered to proceed via an intra-ion-pair electron transfer from 9,10-dimethoxyanthracene moiety to iodonium moiety. The counteranion acts as both spectral sensitizer for diphenyliodonium ion and precursor for photo-acid generator.

It is well known that onium salts, especially diaryliodonium$^{1)}$ and triarylsulfonium salts,$^{2)}$ are useful as photoinitiator of both radical and cationic polymerization. From the technological aspect it is required that the photolyses of onium salts are spectrally sensitized to near visible wavelengths using electron-donating species, since the absorbption of most onium salts are in the wavelengths shorter than ca. 300 nm. A photoinduced electron transfer mechanism is usually proposed for these sensitization.$^{3)}$ Recently, Schuster et al. reported that triphenylalkylborates of cyanine dyes initiate free-radical photopolymerization due to a novel intra-ion-pair electron transfer mechanism.$^{4)}$

On the other hand, the authors reported$^{5)}$ that 4-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate photodissociates to generate 9,10-dimethoxyanthracene-2-sulfonic acid, and that this dissociation is considered to proceed via an intramolecular electron transfer from the excited state of 9,10-dimethoxyanthracene moiety to 4-nitrobenzyl moiety. By combining diphenyliodonium ion with 9,10-dimethoxyanthracene-2-sulfonic acid as electron acceptor and donor, respectively, we found a novel category of diphenyliodonium salt whose counteranion acts as spectral sensitizer. Herein we report the photochemical behavior associated with photoinduced intra-ion-pair electron transfer in diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate ($\underline{1}$).

The compound $\underline{1}$ was prepared by the reaction of sodium 9,10-dimethoxyanthracene-2-sulfonate ($\underline{2}$) with diphenyliodonium chloride ($\underline{3}$) in a hot water followed by purification by repeated recrystallization from water.$^{6)}$ The electronic absorption spectra of $\underline{2}$, $\underline{3}$ and $\underline{1}$ in CH_3CN solutions are shown in Fig. 1, together with the fluorescence spectrum of $\underline{2}$ in oxgen-free CH_3CN. From these spectra, the lowest excited singlet energy of $\underline{2}$ is estimated to be

290 kJ mol^{-1}. The absorption spectrum of 1 is essentially the sum of the spectra of 2 and 3. No broadening or red-shifting of the spectrum due to ground-state interactions between 2 and 3 was observed. While the spectral response of 3 extends only to 300 nm, the absorption of 1 extends to longer wavelengths than that of 3. Experimentally it has been confirmed that 1 reacts by exciting only 9,10-dimethoxyanthracene moiety with the longer wavelength light which diphenyliodonium cation does not absorb.

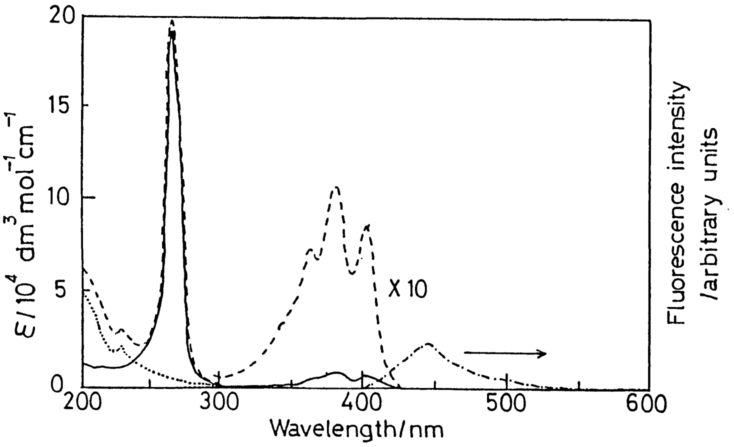

Fig. 1. The absorption spectra of 1 (- - - - -), 2 (———) and 3 (··········) in acetonitrile, together with the fluorescence spectrum of 2 (—·—·—).

The fluorescence of 2 in degassed CH_3CN (0.2 mmol dm^{-3}) decays with a lifetime of 9.8 ns. The fluorescence lifetime of 1 (0.2 mmol dm^{-3}) is 2.4 ns. With assumption that the shorter fluorescence lifetime of 1, relative to that of 2, is due entirely to electron transfer, the rate constant k_{et}^{intra} for intra-ion-pair electron transfer from 9,10-dimethoxyanthracene moiety to diphenyliodonium moiety is given by Eq. 1, where τ_1 and τ_2 are the lifetime of 1 and 2, respectively. Using Eq. 1 and the lifetime given above, we find $k_{et}^{intra} = 3.2\times10^8 s^{-1}$ in CH_3CN.[7)]

$$k_{et}^{intra} = 1/\tau_1 - 1/\tau_2 \qquad (1)$$

In cyclic voltammetry the compound 1 shows irreversible oxidation and reduction waves at 1.09 and -0.23 V vs. SCE, respectively. The calculation of ΔG value accompanied by the electron transfer based on Rehm-Weller equation[8)] reveals that the electron transfer from the excited singlet state of 9,10-dimethoxyanthracene moiety to diphenyliodonium moiety is exothermic by more than 150 kJ mol^{-1}.

Intra-ion-pair electron transfer mechanism is also supported by the results of laser flash photolysis measurements. Excitation of 1 (0.5 mmol dm^{-3}) with the third harmonic pulse (355 nm, 5 ns fwhm) of a Q-swiched Nd:YAG (Quantel international YG660A) in degassed CH_3CN gives instantaneous appearance of transient absorption bands at 310 and 425 nm. This spectrum is essentially identical with that of 9,10-dimethoxyanthracene-2-sulfonate radical cation independently generated.[9)] The transient absorption monitored at 425 nm decays with first-order kinetics to afford a lifetime of 450 ± 34 ns with a similar value at 310 nm within experimental error. These results suggest that this sulfonate should exist as ion pair or at least, solvent separated ion pair state , even in the polar solvent.[10)] In spite of the absence of absorption due to diphenyliodonium radical, the ΔG value mentioned above may support the view of electron transfer process.

Irradiation of a degassed CH_3CN solution of 1 (0.2 mmol dm^{-3}) with 365 nm light leads to formation of the parent acid, iodobenzene and benzene. These photoproducts were characterized by electron impact mass spectroscopy(EIMS) and GC-MS.[11]

Quantum yield for the acid formation from 1 in acetonitrile was measured by a non-aqueous photometric method using 3'-diethylamino-7'-methyl-spiro-[isobenzofuran-1(*3H*),9'-[*9H*]-xanthen]-3-one as an indicator after standardization with 4-toluenesulfonic acid. This leuco dye is a satisfactory indicator which is colorless in nature or basic medium and red in acid medium. Quantum yield for photo-acid generation of 1 was determined to be 0.29 by means of this method(Fig. 2).[12]

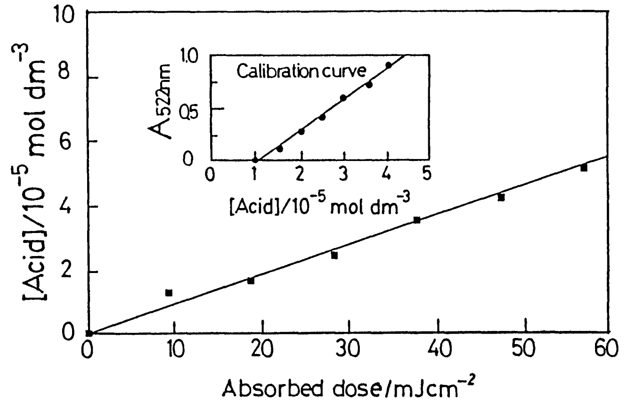

Fig. 2. A plot of acid generation from 1 versus absorbed dose with excitation at 365 nm in degassed acetonitrile solution. Insert. Calibration was made with using 4-toluenesulfonic acid as standard.

From these experimental results, the proposed mechanism for the sensitized photolysis of diphenyliodonium salt is that electron transfer occurs from the excited singlet state of 9,10-dimethoxyanthracene moiety to diphenyliodonium moiety to form two radical species, namely, 9,10-dimethoxyanthracene-2-sulfonate cation radical and diphenyliodonium radical. The former radical ultimately forms 9,10-dimethoxyanthracene-2-sulfonic acid by hydrogen abstraction from the solvent, while the homolytic cleavage of the latter gives iodobenzene and benzene as products.

The present study offers a new type of diphenyliodonium salt whose counteranion acts as spectral sensitizer, and which releases the parent sulfonic acid together with the radical species on irradiation of light. Quantitative experiments and application to radical and cationic "hybrid" polymerization with this compound as photoinitiator are on the way. Furthermore, other diphenyliodonium sulfonates are also being investigated as more efficient systems.

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References

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6) The compound 1 gave acceptable elemental analysis and ^{1}H-NMR. Mp 198-9 ℃. Found : C, 56.43; H, 3.87%. Calcd for $C_{28}H_{23}O_5SI$: C, 56.19 ; H, 3.85%. IR(KBr pellet) 2900, 1350, 1200, 750, 680 cm^{-1}. ^{1}H-NMR(500 MHz methanol-d_4) δ 8.79(s, 1H), 8.34(d, 1H), 8.30(t, 2H), 8.15(d, 4H), 7.87(d, 1H), 7.69(d, 2H), 7.53(t, 6H), 4.11(d, 6H).

7) The rate constant k_{et}^{intra} is unexpectingly slow from the view point of intramolecular electron transfer mechanism. The conclusive explanation for this slow rate constant is not evident presently and continued experiments are being carried out.

8) D. Rehm and A. Weller, Isr. J. Chem., 8, 259 (1970).

9) The transient absorption bands at 310 and 425 nm were assigned by identification with these observed in the transient measurement with 1,4-dicyanobenzene as electron acceptor, whose radical anion is known. "Electronic Absorption Spectra of Radical Ions," ed by T. Shida, Elsevier, Amsterdam (1988), p. 240. No transient absorption spectrum of 2 (0.5 mmol dm^{-3}) was observed with direct excitation at 355 nm, indicating that the intersystem crossing of the excited singlet state of 2 to its triplet state may not proceed with measurable yield.

10) This idea is supported by the absence of concentration effect on the fluorescence lifetime of 1. If the ion pair dissociates to free ions in this solvent, no radical absorption will be detected due to deactivation of the excited singlet state of aromatic sulfonate moiety.

11) The photoproducts were separated by a preparative GPC column with chloroform as eluent. These products are assigned to be 9,10-dimethoxyanthracene-2-sulfonic acid (a strong peak at m/z 318 in EIMS), iodobenzene (a peak at m/z 204 in GC-MS) and benzene (a peak at m/z 78 in GC-MS) on the basis of mass spectroscopic data. While it was reported by J. V. Crivello et al. that biphenyl was contained as one of the minor products in the dye-sensitized photolysis of iodonium salt in acetonitrile, we could not detect it in our experiment. J. V. Crivello and J. H. W. Lam, J. Polym. Sci. Poly. Chem. Ed., 16, 2441 (1978). The reason may be due to the difference in our experimental conditions from the reported, especially due to lower exposure energy giving less than 10% conversion of the starting material, although not conclusive.

12) This method is based on coloration of the leuco dye. A similar procedure has been reported. G. Buhr, R. Dammel, and C. R. Lindley, Polym. Mat. Sci. Eng., 61, 269, (1989); S. A. MacDonald and D. R. McKean, J. Photopolym. Sci. Technol., 3, 375, (1990).
The intensity of the incident light was measured with an Epply Model E-6 thermophile.

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