Photochemical Dissociation of *p*-Nitrobenzyl Sulfonate Esters *via* an Intramolecular Electron Transfer

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The photochemistry of *p*-nitrobenzyl sulfonate esters, *p*-nitrobenzyl 5-dimethylaminonaphthalene-1-sulfonate (NDS) and *p*-nitrobenzyl pyrene-1-sulfonate (NPS) has been investigated by both steady-state and laser flash photolysis techniques. These sulfonates are photochemically dissociated to give the parent sulfonic acids. Quantum yields for photodissociation of NDS and NPS with excitation at 365 nm in degassed acetonitrile solution are 0.20 ± 0.05 and 0.16 ± 0.04, respectively. Photodissociation of these sulfonates is considered to proceed *via* an intramolecular electron transfer from the excited singlet state of the 5-dimethylaminonaphthalene or pyrene moiety to the *p*-nitrobenzyl moiety from the fact that the transient absorption bands at 390 and 550 nm due to the radical cation of the 5-dimethylaminonaphthalene moiety, 420 and 450 nm due to the radical cation of the pyrene moiety, and at 340 nm due to the radical anion of the *p*-nitrobenzyl moiety are detected in laser spectroscopy. Intramolecular-electron-transfer-induced bond cleavage is observed at the oxygen–carbon bond of these sulfonate esters, producing the organic strong acids. Although photodissociation of *o*-nitrobenzyl esters of carboxylic and sulfonic acids is known, that of *p*-nitrobenzyl esters has not been previously reported. From the mechanistic point of view, the photochemical behaviour of these *p*-nitrobenzyl sulfonate esters is quite different from that of *o*-nitrobenzyl esters. While the latter involves a photoinduced intramolecular rearrangement, the former involves a photoinduced intramolecular electron transfer.

It is well known that the light-induced rearrangement of *o*-nitrobenzyl esters of carboxylic acids[1] and sulfonic acids leads to formation of the parent acids and *o*-nitrosobenzaldehyde. Photochemical acid-generating agents have been attracting interest in terms of photoremovable protecting groups in synthetic chemistry,[2] and recently in the field of cationic polymerization, as well as lithographic resist materials.[3,4,5] The *o*-nitrobenzyl functionality has been successfully used as a photosensitive protecting group in the chemistry of carbohydrates[6] and amino acids.[7]

Although photolabile esters based upon *o*-nitrobenzyl photochemistry have been reported,[3,4] reports of the direct photodissociation of *p*-nitrobenzyl esters are limited. We have recently reported our results on photochemical dissociation of *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate (abbreviated hereafter to NAS)[8] and other *p*-substituted benzyl 9,10-dimethoxyanthracene-2-sulfonate derivatives[9] to give 9,10-dimethoxyanthracene-2-sulfonic acid, and suggested that this dissociation proceeds through an intramolecular electron transfer from the 9,10-dimethoxyanthracene moiety to the *p*-substituted benzyl moiety. The quantum yield for the photodissociation of NAS with excitation at 365 nm in degassed acetonitrile is 0.14 ± 0.04.[9] Though this quantum yield is much higher than those of *o*-nitrobenzyl esters, we have attempted to design more efficient photo-acid generators on the mechanistic basis of our previous study.[8] In this study, we have prepared two *p*-nitrobenzyl sulfonate esters with better electron-donating ability than NAS, namely, *p*-nitrobenzyl 5-dimethylaminonaphthalene-1-sulfonate (NDS) and *p*-nitrobenzyl pyrene-1-sulfonate (NPS).

The photochemical behaviour of NDS and NPS has been investigated by both steady-state and laser flash photolysis techniques. Herein we report a unique photochemical reactivity associated with photoinduced intramolecular electron transfer in NDS and NPS. A possible mechanism for photodissociation of these sulfonates is detailed below.

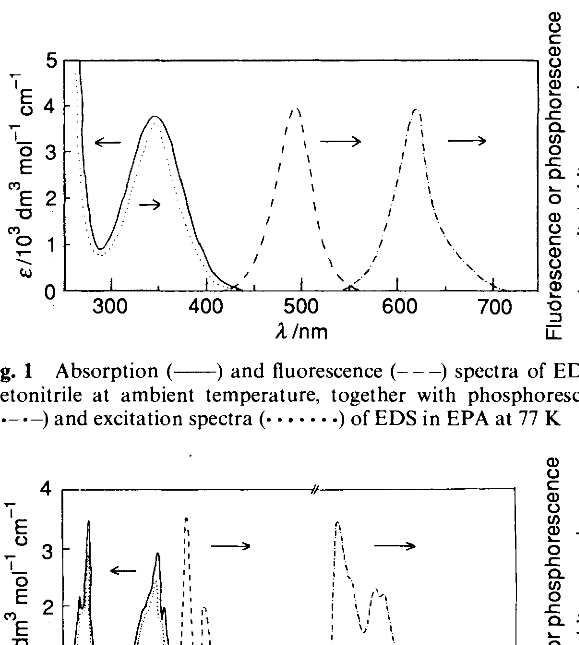

Fig. 1 Absorption (——) and fluorescence (– – –) spectra of EDS in acetonitrile at ambient temperature, together with phosphorescence (–•–•–) and excitation spectra (••••••) of EDS in EPA at 77 K

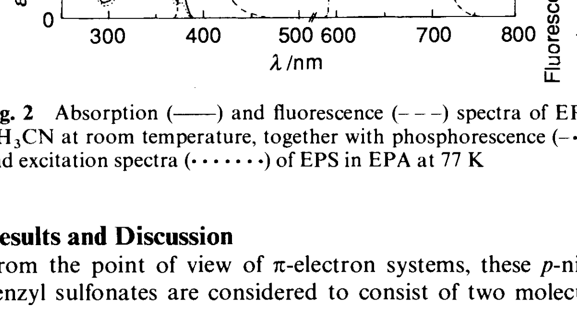

Fig. 2 Absorption (——) and fluorescence (– – –) spectra of EPS in CH_3CN at room temperature, together with phosphorescence (–•–•–) and excitation spectra (••••••) of EPS in EPA at 77 K

Results and Discussion

From the point of view of π-electron systems, these *p*-nitrobenzyl sulfonates are considered to consist of two molecules,

Table 1 Excited state energies, fluorescence lifetimes, quantum yields for fluorescence and intersystem crossing, photophysical parameters and oxidation potentials for EDS and EPS, together with the free-energy changes accompanying the electron transfer

	E_S/ kcal mol^{-1}	E_T/ kcal mol^{-1}	τ_S/ns	φ_f	φ_{isc}	k_f/ 10^7 s^{-1}	k_{isc}/ 10^7 s^{-1}	$k_q/10^{10}$ dm^3 mol^{-1} s^{-1}	$E_{ox}{}^a$/ V *vs.* SCE	$\Delta G^{S\,b}$/ kcal mol^{-1}	$\Delta G^{T\,c}$/ kcal mol^{-1}
EDS	66.8	51.8	19.4	0.46	0.54	2.4	2.8	1.9	0.94	−17.7	−2.88
EPS	75.3	48.0	18.0	0.61	0.39	3.4	2.2	1.6	1.40	−15.6	11.7

[a] Oxidation potential. [b] Rehm–Weller equation $\Delta G^S = 23.06\,(E_{ox} - E_{red}) - E_S$; $E_{red} = -1.19$ V *vs.* SCE for PNT. [c] $\Delta G^T = 23.06\,(E_{ox} - E_{red}) - E_T$.

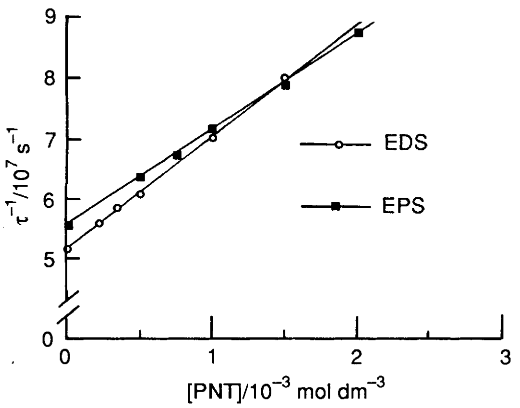

Fig. 3 Stern–Volmer plots of fluorescence quenching of EDS and EPS by PNT at room temperature in oxygen-free acetonitrile solution. The reciprocal of the fluorescence lifetime was plotted as a function of PNT concentration.

owing to separation of the π-electron conjugation at the sulfonyl ester group. Prior to the study on *p*-nitrobenzyl sulfonate derivatives, the intermolecular interaction of ethyl sulfonate esters with *p*-nitrotoluene (PNT) was studied as a model reaction.

Absorption, Fluorescence and Phosphorescence Spectra and Fluorescence Quenching.—Figs. 1 and 2 show the absorption and fluorescence spectra of ethyl 5-dimethylaminonaphthalene-1-sulfonate (EDS) and ethyl pyrene-1-sulfonate (EPS). EDS has a broad absorption band centred at 345 nm and a broad and structureless fluorescence spectrum in the wavelength region 420–560 nm. EPS exhibits strong absorptions at 278 and 350 nm and a vibrational structured fluorescence spectrum in the wavelength region 370–470 nm. From these spectra, the lowest excited singlet energies (E_s) of EDS and EPS are estimated to be 66.8 kcal mol^{-1} (1 cal = 4.184 J) and 75.3 kcal mol^{-1}, respectively. The fluorescence lifetimes (τ_s) and fluorescence quantum yields (φ_f) of EDS and EPS are 19.4 ns, 0.46, 18.0 ns and 0.61, respectively (listed in Table 1). If the energy gap between the lowest excited singlet state and the ground state is more than 50 kcal mol^{-1}, an internal conversion process is unlikely to compete favourably with fluorescence or intersystem crossing processes. With the assumption that the sum of quantum yields of fluorescence and intersystem crossing (φ_{isc}) is unity for EDS and EPS, the quantum yield for intersystem crossing is given by eqn. (1), and the rate constants for fluorescence (k_f) and intersystem crossing (k_{isc}) are expressed as eqns. (2) and (3) respectively.

$$\varphi_{isc} = 1 - \varphi_f \qquad (1)$$

$$k_f = \varphi_f/\tau_s \qquad (2)$$

$$k_{isc} = \varphi_{isc}/\tau_s. \qquad (3)$$

Phosphorescence spectra of EDS and EPS were measured at 77 K in an EPA (a 5:5:2 mixture of diethyl ether, isopentane and ethanol) matrix and are shown in Figs. 1 and 2 together with their phosphorescence excitation spectra. For both ethyl sulfonate esters the excitation spectra are in good agreement with the corresponding absorption spectra. The excited triplet energies (E_T) for EDS and EPS are estimated to be 51.8 kcal mol^{-1} and 48.0 kcal mol^{-1}, respectively from the onset (552 nm) of the EDS phosphorescence spectrum and the 0, 0 band (596 nm) of EPS phosphorescence emission. While the spectral response of PNT extends only to *ca.* 350 nm in acetonitrile, the absorptions of EDS and EPS extend to longer wavelength than that of PNT. In acetonitrile solution, it is expected that light absorbed by the naphthalene and pyrene chromophores of NDS and NPS initiates reactions of these sulfonates photochemically.

The fluorescence quenching rate constants k_q of EDS and EPS by PNT were determined from eqn. (4) where τ and

$$1/\tau' = 1/\tau + k_q[\text{PNT}] \qquad (4)$$

τ' are the fluorescence lifetimes in the absence and presence of PNT, respectively and [PNT] is concentration of PNT. Stern–Volmer plots of the fluorescence quenching of EDS and EPS by PNT in Fig. 3 show that the fluorescences of EDS and EPS are efficiently quenched by PNT. The fluorescence quenching rate constants of EDS and EPS by PNT were determined to be 1.9 × 10^{10} dm^3 mol^{-1} s^{-1} 1.6 × 10^{10} dm^3 mol^{-1} s^{-1}, respectively (Table 1).

The electrochemical behaviour has been studied in acetonitrile solution with tetrabutylammonium perchlorate as the supporting electrolyte. The reduction potential of PNT is −1.9 V *vs.* SCE.[9] Oxidation of EDS and EPS gives reversible cyclic voltammetric waves with peaks at 0.94 V and 1.40 V *vs.* SCE, respectively. Based on these values of redox potentials, the free-energy changes (ΔG) accompanying the electron transfer from the lowest excited state of EDS and EPS to PNT can be calculated according to the Rehm–Weller equation[10] (5) (Table 1).

$$\Delta G = 23.06\{E(\text{D/D}^+) - E(\text{A}^-/\text{A}) - C\} - E_{0,0} \qquad (5)$$

where $E(\text{D/D}^+)$ stands for the oxidation potential of the electron donor, $E(\text{A}^-/\text{A})$ the reduction potential of the acceptor, $E_{0,0}$ the electronic energy corresponding to the excited state of the donor and C for the coulombic interaction between the radical ions. The coulombic interaction energy is generally 1–2 kcal mol^{-1} in a polar solvent. This value was neglected in the present study. The fact that fluorescence quenching rate constants k_q of EDS and EPS by PNT are well related to the large negative values of free energy changes (ΔG^s) associated with electron transfer from the excited singlet state of EDS and EPS to PNT strongly suggests that the electron transfer takes place efficiently from the excited singlet state of EDS and EPS to PNT.

On the other hand, the absorption spectrum of NDS in acetonitrile can be considered to be the superposition of the spectra of the corresponding PNT and EDS chromophores. No broadening or red-shifting due to ground-state interactions between EDS and PNT was observed, providing evidence for the absence of ground-state interactions between the 5-di-

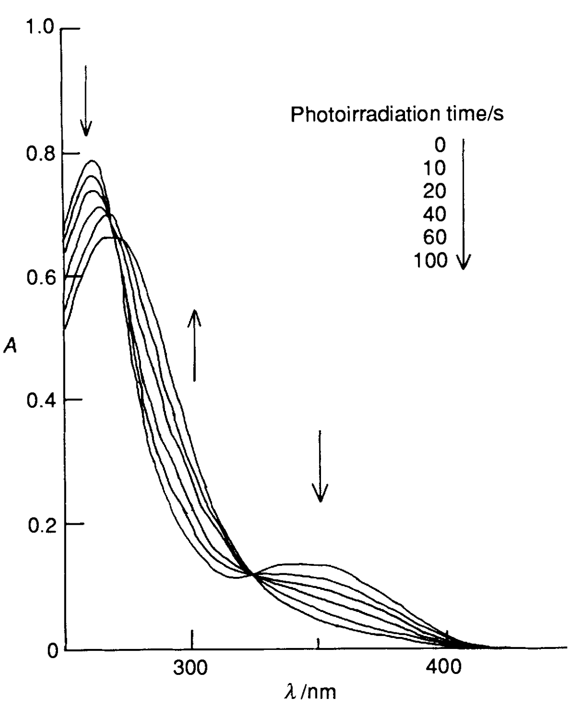

Fig. 4 Change of the absorption spectrum of NDS due to irradiation by 365 nm light (5.5 × 10^{-5} mol dm^{-3} in oxygen-free acetonitrile). The intensity of the incident light was 0.58 mW cm^{-2}.

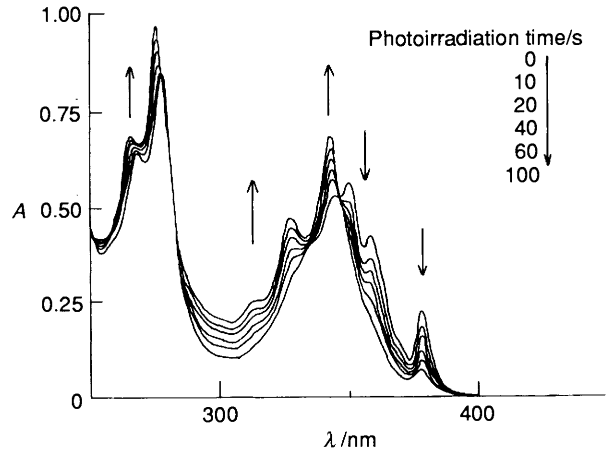

Fig. 5 Change in the absorption spectrum of NPS (2.0 × 10^{-5} mol dm^{-3}) in degassed acetonitrile due to 365 nm light irradiation. The intensity of the incident light was 0.46 mW cm^{-2}.

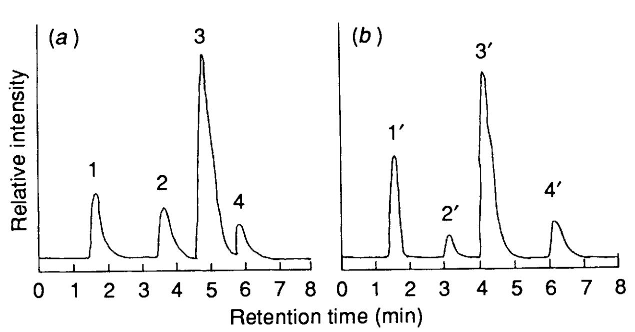

Fig. 6 High-pressure liquid chromatograms of the photodissociation products of NDS (*a*) and NPS (*b*). (*a*) Analysis at 245 nm. Eluent: CH_3CN-H_2O (9:1), 1 cm^3 min^{-1}. (*b*) Analysis at 242 nm. Eluent: CH_3CN-H_2O (8:2), 1 cm^3 min^{-1}

methylaminonaphthalene moiety and the *p*-nitrobenzyl moiety for NDS. This observation also applies to NPS. Moreover, the redox potentials of NDS and NPS are the same as those of the corresponding intermolecular model compounds.

Table 2 The assignment of peaks in the mass spectra of the photoproducts for peak 4 in Fig. 6(*a*) (left) and peak 4′ in Fig 6(*b*) (right)

m/z	Fragment	*m/z*	Fragment
306	Parent peak of DANN:M	337	Parent peak of NBP:M
291	$M - CH_3$	322	$M - CH_3$
276	$M - (CH_3 \times 2)$	307	$M - (CH_3 \times 2)$
260	$M - NO_2$	291	$M - NO_2$
245	$M - (CH_2 + NO_2)$	276	$M - (CH_3 + NO_2)$
230	$M - (CH_3 \times 2 + NO_2)$	261	$M - (CH_3 \times 2 + NO_2)$

No fluorescence of NDS and NPS was detected with excitation at 365 nm in deaerated acetonitrile solution, indicating that the fluorescence from the naphthalene and pyrene nuclei in NDS and NPS was quenched by the *p*-nitrobenzyl moiety more efficiently than that in the corresponding intermolecular model compounds. Taking into consideration the fact that the rate constant of fluorescence is competitive with that of intersystem crossing in EDS and EPS as listed in Table 1, it is inferred that intersystem crossing to their triplet state does not occur in the NDS and NPS molecules.

Photochemical Reaction and Assignment of Photoproducts.— Fig. 4 shows the change of absorption spectrum of NDS in oxygen-free acetonitrile in the wavelength region 250–450 nm. The absorption band decreases in intensity with irradiation at 365 nm and is finally converted into the absorption band with the weaker absorption intensity. The final spectrum is analogous to that of 5-dimethylaminonaphthalene-1-sulfonic acid (DNSA). Fig. 5 shows the absorption spectral changes during photolysis of NPS in degassed acetonitrile solution. New strong peaks centred at 279, 323 and 344 nm appeared according to the progress of irradiation. The final spectrum is similar to that of pyrene-1-sulfonic acid (PSA). These results suggest that photochemical reactions of NDS and NPS result in the formation of the corresponding parent acids.

A solution of NDS in degassed acetonitrile was irradiated with 365 nm light and the photoproducts were characterized. The HPLC of the products from photolysis of NDS shows four peaks at different retention times as shown in Fig. 6(*a*). Among these peaks, peak 1 and 3 agree with those of DNSA and unchanged NDS in retention time. All photoproducts were identified by separation on a preparative GPC column followed by electron impact mass spectroscopy (EIMS) or ^1H NMR spectroscopy. Based on the strong peaks at *m/z* 251 and 386 in each EIMS spectra, the products for peak 1 and 3 were identified as DNSA and NDS. The EIMS spectrum of the product for peak 2 shows a peak at *m/z* 136 which corresponds to the mass of a nitrobenzyl radical. In addition, the ^1H NMR spectrum for peak 2 provided further information for the chemical structure of this product. The spectrum (500 MHz, $CDCl_3$) for peak 2 shows δ 8.14 (d, 4 H), 7.28 (d, 4 H) and 3.08 (s, 4 H). From these results, the photoproduct for peak 2 was concluded to be *p,p′*-dinitrobibenzyl. The EIMS spectrum of the product for peak 4 exhibits a strong peak at *m/z* 306. The peaks of the fragments are summarized in Table 2 (left). These results indicate that the product for peak 4 is 1-dimethylamino-5-(*p*-nitrobenzyl)-naphthalene (DANN). A similar photofragmentation has been observed for NPS as shown in the liquid chromatogram in Fig. 6(*b*) and the peaks of the fragments for peak 4′ in Table 2 (right).

The mechanism for the photoreaction of *o*-nitrobenzyl esters involves insertion of an excited nitro group oxygen into a benzylic carbon–hydrogen bond. Subsequent rearrangement and cleavage generates *o*-nitrosobenzaldehyde and the corresponding organic acids from *o*-nitrobenzyl carboxylates[3] and sulfonates,[4] respectively. These substrates contain a benzylic

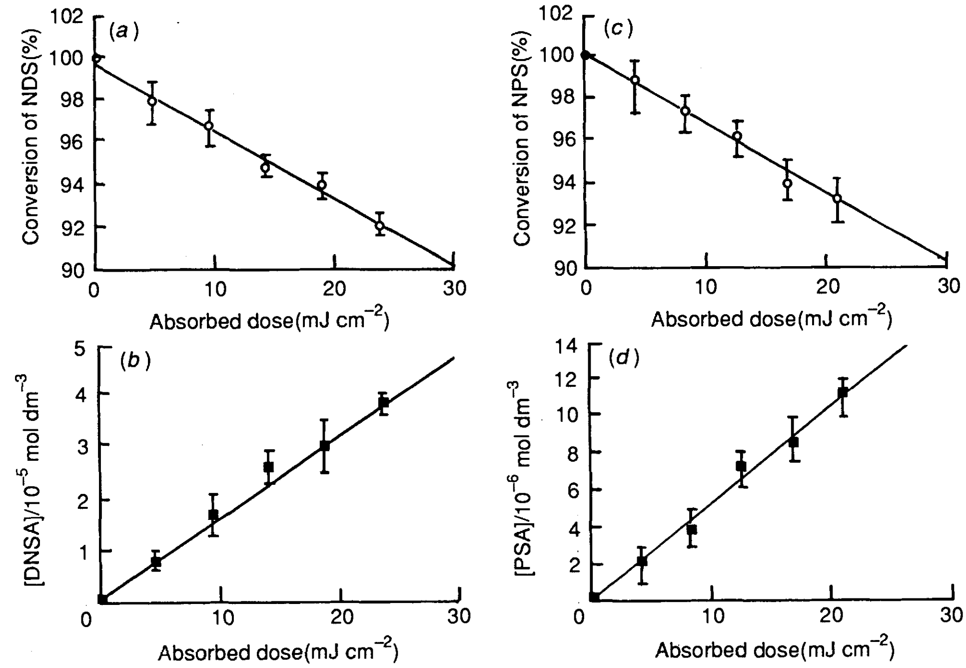

Fig. 7 Plots of conversion of NDS (*a*) and NPS (*c*) and concentration of photo-generated acid (*b* and *d*) *vs.* absorbed dose with excitation at 365 nm in degassed acetonitrile

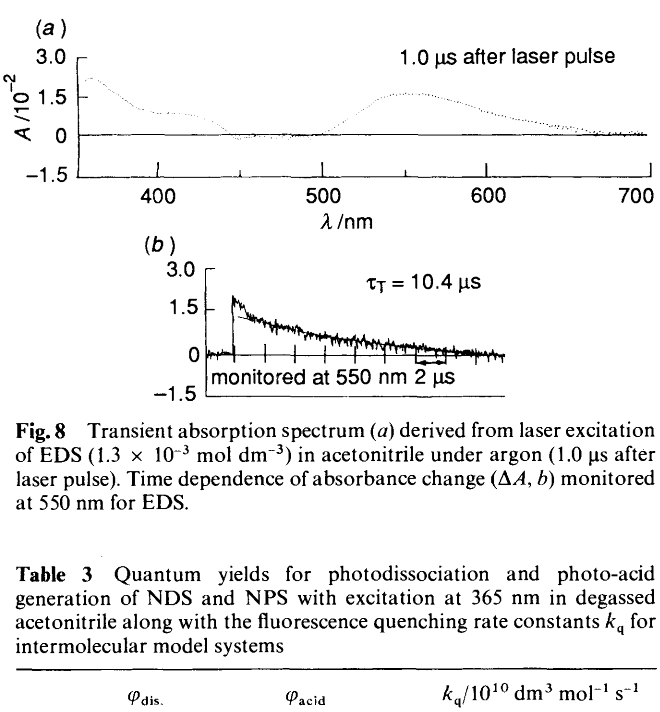

Fig. 8 Transient absorption spectrum (*a*) derived from laser excitation of EDS (1.3 × 10^{-3} mol dm^{-3}) in acetonitrile under argon (1.0 μs after laser pulse). Time dependence of absorbance change (ΔA, *b*) monitored at 550 nm for EDS.

Table 3 Quantum yields for photodissociation and photo-acid generation of NDS and NPS with excitation at 365 nm in degassed acetonitrile along with the fluorescence quenching rate constants k_q for intermolecular model systems

	$\varphi_{dis.}$	φ_{acid}	$k_q/10^{10}$ dm^3 mol^{-1} s^{-1}
NDS	0.20 ± 0.05	0.16 ± 0.04	1.9
NPS	0.16 ± 0.04	0.13 ± 0.02	1.6

carbon–hydrogen bond *ortho* to a nitro group, which is a necessary structural requirement for their photolability.

Unlike *o*-nitrobenzyl esters, however, the *p*-nitrobenzyl ester is unable to dissociate with direct excitation since a nitro group at the *para*-position is too far from a benzylic carbon–hydrogen bond to interact with it. On the other hand, Busman *et al.* have reported[11] that *p*-nitrobenzyl sulfonates dissociate with the aid of an electron-donating photosensitizer to release the corresponding sulfonic acid, and that photodissociation proceeds through an electron transfer from the sensitizer to the sulfonates. As described in a previous paper,[8] NAS incorporates an electron-donating sensitizer within its structure and the photodissociation proceeds spontaneously *via* an intramolecular electron transfer from the 9,10-dimethoxyanthracene moiety to the *p*-nitrobenzyl moiety. From the fact that NDS and NPS have lower oxidation potentials in the excited singlet state than NAS, more efficient photochemical dissociation may take place in NDS and NPS.*

Quantum Yields for Photodissociation ($\varphi_{dis.}$) *and Photo-acid Generation* (φ_{acid}).—Quantum yields were measured at low conversion (less than 10%) by irradiating the degassed acetonitrile solution with 365 nm light. The concentrations of the starting materials and sulfonic acids formed by photolysis were determined by HPLC and quantum yields were estimated based on the absorbed dose. Fig.7(*a*) and (*c*) show typical plots of conversion of NDS and NPS *vs.* absorbed dose, indicating that the photodissociation rate as a function of the absorbed dose is a single straight line under our experimental conditions. In addition, quantum yields for photodissociation of NDS and NPS are independent of the concentration of the starting materials (5.0 × 10^{-5}–1.0 × 10^{-3} mol dm^{-3}), suggesting that the photodissociation of these sulfonates proceeds *via* a unimolecular reaction. The obtained values for $\varphi_{dis.}$ and φ_{acid} of NDS and NPS are tabulated in Table 3 along with k_q values.

In an electron transfer mechanism, the lower the oxidation potential is, the more efficiently electron transfer occurs. Comparison of intermolecular fluorescence quenching rate constant k_q and quantum yield $\varphi_{dis.}$ values show that an electron transfer process may be involved in the photochemical dissociation of NDS and NPS.

Laser Flash Photolysis.—Evidence for the electron transfer process was obtained by laser flash photolysis (LFP) experiments. LFP was performed in deaerated acetonitrile solution by irradiating with a 355 nm laser pulse at room temperature.

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* The oxidation potentials in the excited singlet state ($E_{ox} - E_s$) for NAS, NPS and NDS are −41.0 kcal mol^{-1} (in ref. 9), −43.0 kcal mol^{-1} and −45.0 kcal mol^{-1}, respectively.

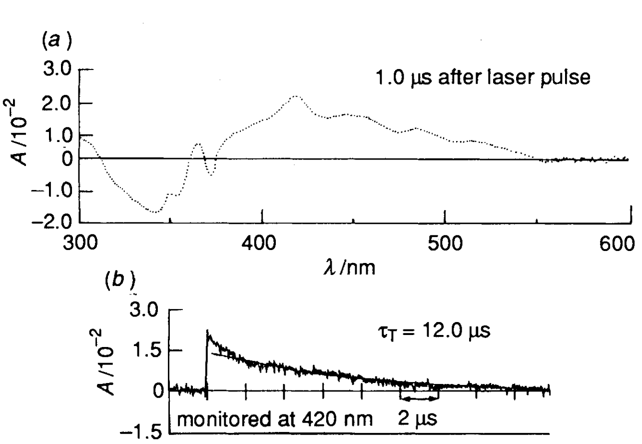

Fig. 9 Transient absorption spectrum (*a*) derived from laser irradiation of EPS (1.5×10^{-4} mol dm^{-3}) in acetonitrile under argon (1.0 μs after laser pulse). Time dependence of absorbance change (*b*) monitored at 420 nm for EPS

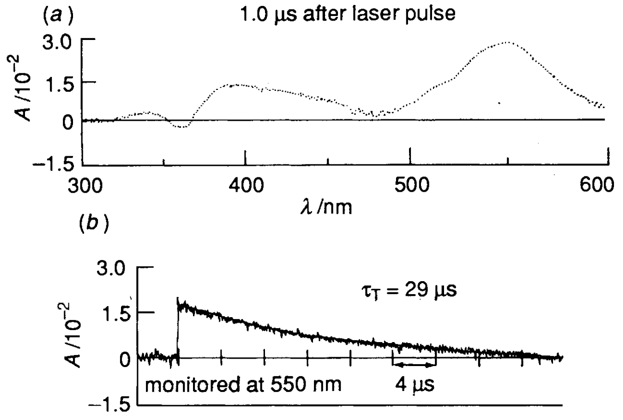

Fig. 10 Transient absorption spectrum (*a*) recorded 1.0 μs after laser irradiation of NDS (1.3×10^{-3} mol dm^{-3}) in acetonitrile solution. The decay profile monitored at 550 nm for NDS (*b*).

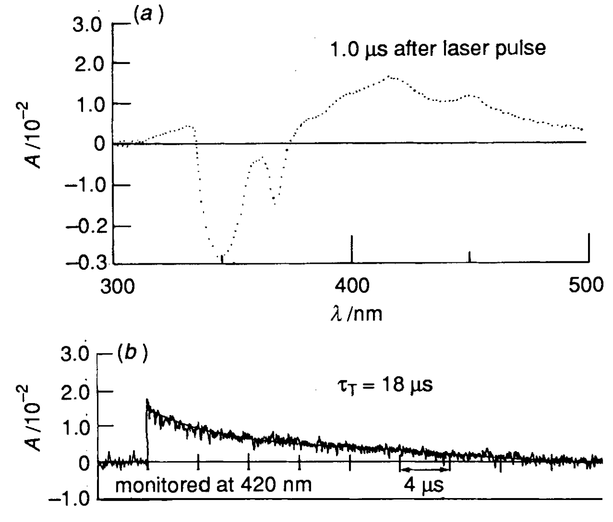

Fig. 11 Transient absorption spectrum (*a*) recorded 1.0 μs after laser excitation of NPS (1.5×10^{-4} mol dm^{-3}) in acetonitrile solution. The decay profile monitored at 420 nm for NPS (*b*)

Laser excitation of an acetonitrile solution of EDS (1.0×10^{-3} mol dm^{-3}) under argon gave the transient absorption spectrum (Fig. 8) which can be assigned to T–T absorption of EDS. This assignment was confirmed by its relatively long lifetime (τ_T = 10.4 μs) and by the fact that it is efficiently quenched by dissolved oxygen. LFP of EPS (1.5×10^{-4} mol dm^{-3}) under an inert atmosphere gave the transient absorption spectrum (Fig. 9) which can be assigned to T–T absorption of EPS on the basis of the above argument (τ_T = 12.0 μs).

Irradiation of an argon-saturated acetonitrile solution of NDS (1.3×10^{-3} mol dm^{-3}) with laser pulse at 355 nm instantaneously gave the transient spectrum shown in Fig. 10. The transient absorption of NDS exhibits both strong absorption bands centred at 390 and 550 nm and a weak absorption band at 340 nm. The former transient species are assigned to the radical cation of the 5-dimethylaminonaphthalene moiety by comparison with the spectrum of the *N*,*N*-dimethyl-2-naphthylamine radical cation.[12] This assignment is also supported by the fact that the excitation of EDS (1.0×10^{-3} mol dm^{-3}) in the presence of *p*-dicyanobenzene (1.0×10^{-3} mol dm^{-3}) as an electron acceptor gave the transient absorption bands at 390 and 550 nm and the absorption of the *p*-dicyanobenzene radical anion whose spectrum has already been assigned (λ_{max} = 340 and 430 nm).[13] These bands at 390 and 550 nm appear instantaneously and decay completely following a first-order rate law with a lifetime of 29 ± 5.2 μs within experimental error. The latter band is assigned to the *p*-nitrobenzyl radical anion by identification with the spectrum independently generated by radiolysis.[14] It was difficult to analyse the decay kinetics of the absorption band at 340 nm accurately because of the small signal changes. The transient behaviour of NPS is analogous to that of NDS. LFP of NPS (1.5×10^{-4} mol dm^{-3}) in argon-purged acetonitrile solution produced broad absorption bands centred at 420 and 450 nm due to the radical cation of the pyrene moiety by comparison with the spectrum of pyrene radical cation[15] and a weak absorption band at 340 nm due to the *p*-nitrobenzyl radical anion (Fig. 11). The former bands decay completely with first-order kinetics to afford a lifetime of 18 ± 1.6 μs. The transient absorption of NPS is the superposition of the spectra of the radical cation of the pyrene moiety and the *p*-nitrobenzyl radical anion. These results reveal that intramolecular electron transfer from the 5-dimethylaminonaphthalene or pyrene moiety to the *p*-nitrobenzyl moiety leads to formation of the radical cation of the 5-dimethylaminonaphthalene or pyrene moiety and the *p*-nitrobenzyl radical anion. Judging from the result that intersystem crossing to the triplet state does not take place in NDS and NPS, electron transfer may occur from the excited singlet state of the 5-dimethylaminonaphthalene or pyrene moiety to the *p*-nitrobenzyl moiety.

The mechanism for photochemical dissociation of NDS and NPS outlined in Scheme 1 accommodates the experimental findings.

Irradiation by 365 nm light generates an electronically excited singlet state localized on the naphthalene or pyrene chromophores for NDS and NPS, respectively. These excited singlet states undergo electron transfer to the *p*-nitrobenzyl moiety to form radical ions, which may either revert to the starting materials or undergo carbon–oxygen bond cleavage to give ultimately the parent sulfonic acids, *p*,*p*′-dinitrobibenzyl and 1-dimethylamino-5-(*p*-nitrobenzyl)naphthalene and 1-(*p*-nitrobenzyl)pyrene after extrusion of SO_3^{-}.*

Conclusions

We have synthesized photochemically active esters that generate organic acids upon photolysis, namely, *p*-nitrobenzyl

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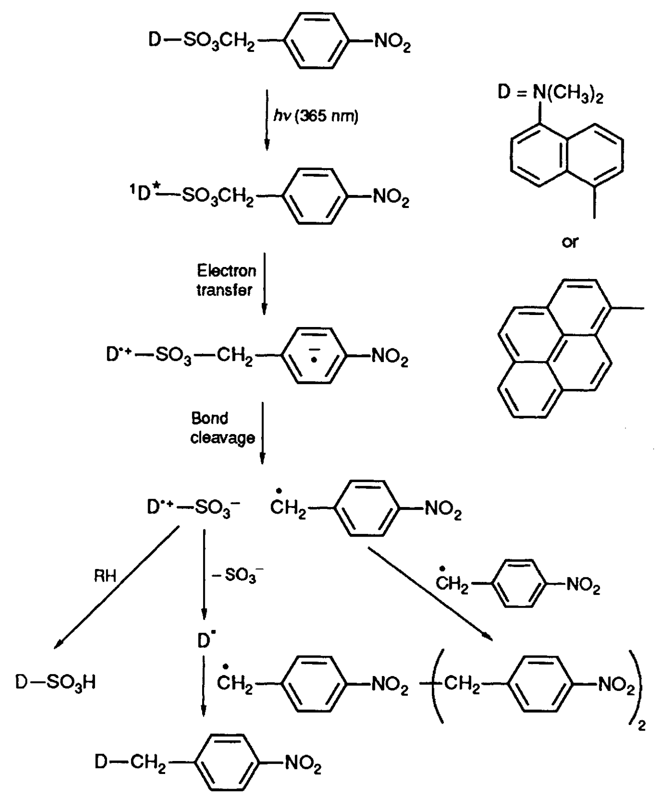
* Judging from the photoproduct analyses, an extrusion of SO_3^{-} may be involved in these photodissociations. Photorearrangement and desulfonation have been observed in α-sulfonyloxy enones. A. Feigenbaum, J. P. Pete and D. Scholler, *J. Org. Chem.*, 1984, **49**, 2355.



Scheme 1

5-dimethylaminonaphthalene-1-sulfonate and *p*-nitrobenzyl pyrene-1-sulfonate on the mechanistic basis of our previous study.[8] Photodissociation of these sulfonates proceeds *via* an intramolecular electron transfer from the excited singlet state of the 5-dimethylaminonaphthalene or pyrene moiety to the *p*-nitrobenzyl moiety. This work reveals an interesting photochemical reactivity associated with photoinduced intramolecular electron transfer in these *p*-nitrobenzyl sulfonate esters. In other words, intramolecular-electron-transfer-induced bond cleavage takes place at the oxygen–carbon bond of these sulfonic acid esters, giving the corresponding parent sulfonic acids. The sulfonic acid formed by the irradiation–electron transfer–bond cleavage sequence may be used in important chemical processes such as the initiation of cationic polymerization and photoremovable protecting groups in synthetic chemistry.

Experimental

Materials.—Where possible, commercially available materials were used in this study. Acetonitrile was distilled over phosphorus pentoxide followed by distillation over calcium hydride. *p*-Nitrotoluene was recrystallized from ethanol. Diethyl ether, isopentane and ethanol (Wako Chemicals) were carefully purified according to the literature.[16]

The following new compounds were synthesized by methods similar to those described in the literature.[8,9]

Ethyl 5-dimethylaminonaphthalene-1-sulfonate (EDS). 5-Dimethylaminonaphthalene-1-sulfonyl chloride (dansyl chloride, Wako Chemicals, 1 g, 4.0 mmol), ethyl alcohol (0.2 g, 4.1 mmol) and triethylamine (Wako Chemicals 0.4 g, 4.2 mmol) were dissolved in dried toluene (20 cm^3) and the solution was stirred for 24 h at room temperature, washed with water, and then evaporated to remove toluene under reduced pressure and to obtain EDS. The product was purified by repeated recrystallization from cyclohexane (0.35 g, 31.4%). M.p. 55–56 °C (Found: C, 60.35; H, 6.15; N, 4.9. $C_{14}H_{17}NO_3S$ requires C, 60.22; H, 6.09; N, 5.02%); δ_H(400 MHz; CDCl$_3$) 1.23 (3 H, t, CH$_3$), 2.88 [6 H, s, N(CH$_3$)$_2$], 4.08 (2 H, q, -CH$_2$-) 7.20–8.60 (6 H, m, ArH); *m/z* 279 (M$^+$, 100%); ν_{max}/cm^{-1} 2800–3000 (CH$_2$, CH$_3$) and 1320, 1180 (SO$_2$).

p-*Nitrobenzyl 5-dimethylaminonaphthalene-1-sulfonate (NDS).* An amount of 1 g (4.1 mmol) of dansyl chloride, 0.63 g (4.1 mmol) of *p*-nitrobenzyl alcohol (Aldrich) and 0.4 g (4.2 mmol) of triethylamine were dissolved in dried toluene (20 cm^3). Stirring at room temperature was continued for 24 h, water was added to wash the reaction mixture, and then evaporated to remove toluene to obtain NDS. Repeated recrystallization from hexane gave NDS (0.65 g, 41.8%). M.p. 91–92 °C. Found: C, 59.2; H, 4.65; N, 7.05. $C_{19}H_{18}N_2O_5S$ requires C, 59.07; H, 4.66; N, 7.25%); δ_H(400 MHz; CDCl$_3$) 2.90 [6 H, s, N(CH$_3$)$_2$] 5.12 (2 H, s, -CH$_2$-), 7.20–8.60 (10 H, m, ArH); *m/z* 386 (M$^+$ 100%) ν_{max}/cm^{-1} 2800–3000 (CH$_2$, CH$_3$), 1520, 1350 (NO$_2$) and 1310, 1170 (SO$_2$).

Ethyl pyrene-1-sulfonate (EPS). Sodium pyrene-1-sulfonate (Wako Chemicals, 1 g) and PCl$_5$ (Wako Chemicals, 2 g) were dispersed in dichloromethane (50 cm^3), and allowed to react at 40 °C for 1 h. The solution, after filtration, was washed with water and evaporated to obtain pyrene-1-sulfonyl chloride. This chloride (1 g, 3.3 mmol), ethyl alcohol (0.16 g, 3.4 mmol) and triethylamine (0.35 g, 3.5 mmol) were dissolved in dried toluene (20 cm^3) and the solution was stirred for 24 h at ambient temperature, washed with water, and then evaporated to remove the solvent to obtain EPS. EPS was then recrystallized three times from hexane (0.51 g, 50.0%). M.p 127–127.5 °C. (Found: C, 60.4; H, 4.0; N, 3.1. $C_{18}H_{14}O_3S$ requires C, 60.14; H, 3.87; N, 3.19%); δ_H(400 MHz; CDCl$_3$) 1.22 (3 H, t, CH$_3$) 4.13 (2 H, q, –CH$_2$–) 8.15–8.95 (9 H, m, ArH); *m/z* 310 (M$^+$ 100%), ν_{max}/cm^{-1} 2800–3000 (CH$_2$, CH$_3$) and 1350, 1150 (SO$_2$).

p-*Nitrobenzyl pyrene-1-sulfonate (NPS).* The pyrene-1-sulfonyl chloride, *p*-nitrobenzyl alcohol and triethylamine at a ratio of 1.00 mol:1.10 mol:1.50 mol were dissolved in dried toluene and stirred for 24 h at ambient temperature. The solution was washed with water and then evaporated to remove toluene. *p*-Nitrobenzyl pyrene-1-sulfonate was obtained by column chromatography with a Wako gel C-200 column (Wako Chemicals) using chloroform as the eluent (0.40 g, 29.3%). M.p. 133–134 °C. (Found C, 66.0; H, 3.5; N, 3.05. $C_{23}H_{15}NO_5S$ requires C, 66.19; H, 3.60; N, 3.36%); δ_H(400 MHz; CDCl$_3$) 5.14 (2 H, s, –CH$_2$–) 7.24–9.85 (13 H, m, ArH); *m/z* 417 (M$^+$ 100%). ν_{max}/cm^{-1} 2800–3000 (CH$_2$, CH$_3$), 1530, 1350 (NO$_2$) and 1320, 1180 (SO$_2$).

Absorption, Fluorescence and Phosphorescence Measurements.—Absorption spectra were recorded on a Shimadzu UV-2100S UV–VIS recording spectrophotometer at room temperature. Fluorescence spectra were recorded with samples in 1.00 × 1.00 cm quartz cells in a Hitachi F-4010 fluorescence spectrophotometer. Fluorescence quantum yields (φ_f) of EDS and EPS in oxygen-free acetonitrile were estimated by comparing emission intensities integrated between 410 and 700 nm with that of quinine bisulfate in 0.5 mol dm^{-3} H$_2$SO$_4$, for which φ_f is 0.55, as a standard.[17] Fluorescence lifetimes τ were determined at room temperature by means of time-correlated single-photon counting with a Horiba NAES-1100, with a NFL-111 hydrogen flash lamp (*ca.* 2 ns fwhm) as the excitation source. Phosphorescence spectra were measured in EPA matrix at 77 K on a Hitachi F-4010 spectrofluorometer equipped with phosphorescence accessories.

Cyclic Voltammetry.—Cyclic voltammetry was carried out using a three-electrode cyclic voltammetric cell. The working electrode was a platinum wire and the reference electrode was Ag/AgClO$_4$ under an atmosphere of dried argon. Tetrabutylammonium perchlorate (0.1 mol dm^{-3}) was used as a supporting electrolyte. A potentiostat and a function generator were Hokuto HA-301 and Hokuto HB-104, respectively. Calibration was *vs.* ferrocene. All potentials are calculated *vs.* SCE.

Irradiation.—Irradiations at 365 nm were made with the high-pressure mercury lamp with a glass filter UV-33, UV-D2 (Toshiba Co.) and heat absorbing filter HA-30 (Hoya Co.) A Hoya ND filter was used as an attenuation filter when necessary. The intensity of the incident light was measured with an Epply Model E-6 thermophile. Sample solutions for the irradiation were deaerated by five freeze–pump–thaw cycles.

Sample Analysis.—Samples were analysed by reverse-phase high performance liquid chromatography (HPLC) using a system that consisted of a Hitachi L-4000 pump, L-4200 UV–VIS detector and D-2500 chromato-integrator with a Hibar LiChrospher PR-18 endcapped column (250 × φ 4 mm) using a 9:1 or 8:2 mixture of MeCN and H_2O as the eluent at ambient temperature. All samples were HPLC analysed immediately after irradiation, using dansyl chloride and pyrene-1-sulfonyl chloride as an internal standard. The photoproduct separation was performed with a preparative GPC column (ULTRASTYRAGEL 500 Å, Waters) using chloroform as the eluent. The separated products were analysed by EIMS and ^{1}H NMR spectroscopy.

Laser Flash Photolysis.—Laser flash photolyses were performed with the third harmonic pulse (355 nm, 5 ns fwhm) of a Q-switched Nd:YAG (Quantel international YG660A) for excitation, and with a pulsed xenon lamp (Hamamatsu Photonics L2274) as a monitoring light source. The monitoring light was detected by an intensified optical multichannel analyser (Hamamatsu Photonics C-2327) and a photomultiplier (Hamamatsu Photonics R1477) coupled to a monochromator (JASCO CT-25CP) to measure time-resolved absorption spectra and decay curves using an auto digitizer (Autonics MODEL H310). The system was computer-controlled and the output signals were analysed with a personal computer (NEC PC 9801VM). Sample solutions were deaerated by bubbling dried argon for 30 min. A control laser experiment was carried out using pyrene in benzene solution.[18]

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