Photochemical Dissociation of *p*-Nitrobenzyl 9,10-Dimethoxyanthracene-2-sulphonate *via* Intramolecular Electron Transfer

Tsuguo Yamaoka,[a,*] **Hiroshi Adachi,**[a] **Kazuo Matsumoto,**[a] **Hiroo Watanabe,**[b] **and Tsutomu Shirosaki**[b]
[a] *Department of Image Science and Technology, Chiba University, 1-33 Yayoi-cho, Chiba 260, Japan*
[b] *Nippon Kayaku Co. Ltd., 3-26-8, Shimo, Kita-ku, Tokyo 115, Japan*

While *o*-nitrobenzyl aromatic sulphonates are known to photodissociate *via* an intramolecular rearrangement, photodissociation of *p*-nitrobenzyl aromatic sulphonates has not been reported. In this study, we report that *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulphonate is photochemically dissociated to give 9,10-dimethoxyanthracene-2-sulphonic acid, 9,10-dimethoxy-2-(*p*-nitrobenzyl)-anthracene, and *p,p'*-dinitrobibenzyl. The dissociation is considered to proceed *via* an intramolecular electron transfer from the 9,10-dimethoxyanthracene moiety to the *p*-nitrobenzyl moiety. The quantum yield of the photodissociation in acetonitrile is 0.11 and the spectral response extends to 450 nm. The quantum yield is much higher than those of *o*-nitrobenzyl esters.

It is well known that *o*-nitrobenzyl esters of carboxylic acids[1] and sulphonic acids photochemically dissociate to generate the parent acid and *o*-nitrobenzaldehyde. Photochemical generation of acids from *o*-nitrobenzyl esters has been attracting interest in terms of photoremovable protecting groups in synthetic chemistry,[2] and recently as a photochemical acid-generating agent in the field of cationic polymerization and lithographic resist materials.[3–6]

Although extensive studies have been reported on the photodissociation of *o*-nitrobenzyl esters and the sensitized photodissociation of *p*-nitrobenzyl esters, reports of the direct photodissociation of *p*-nitrobenzyl esters are limited. Busman reported[7] that *p*-nitrobenzyl esters of alkylsulphonic acids dissociate by the aid of a photosensitizer such as 9,10-dimethoxy-2-ethylanthracene, and that an electron-transfer mechanism is involved in the photodissociation process. Nishida *et al.* reported[8] that photochemical hydrolysis of some sulphonic acid esters proceeds smoothly *via* electron transfer in the excited state in the presence of electron-donating sensitizers such as 1,4-dimethoxynaphthalene.

In the present study, the direct photodissociation of *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulphonate (abbreviated hereafter to NBAS) without the use of sensitizers was investigated. The photochemical behaviour of NBAS and the products of its photochemical reactions are detailed below.

Experimental

Preparation of p-*Nitrobenzyl* 9,10-*Dimethoxyanthracene*-2-*sulphonate*.—Sodium 9,10-dioxo-9,10-dihydroanthracene-2-sulphonate (0.05 mol), zinc powder (5 g), and ethanol (10 cm^3) were dissolved in 20 wt.% aq. sodium hydroxide (20 cm^3) at 80 °C, and dimethyl sulphate (30 cm^3) was added dropwise to this solution. After cooling to room temperature, the precipitates were separated by filtration and were washed with 10 wt.% aq. sodium hydrogensulphite (a mixture of $NaHSO_3$ and $Na_2S_2O_5$) to remove the unchanged sodium 9,10-dioxo-9,10-dihydroanthracene-2-sulphonate. Sodium 9,10-dimethoxy-anthracene-2-sulphonate was obtained by dissolution of the precipitate in water to separate the insoluble zinc powder and zinc hydroxide, and finally by evaporation of the water.

Sodium 9,10-dimethoxyanthracene-2-sulphonate (10 g) and PCl_5 (10 g) were dispersed in toluene (100 g), and stirred and allowed to react at 40 °C for 1 h. The solution, after filtration, was washed with water and evaporated to obtain 9,10-dimethoxyanthracene-2-sulphinyl chloride. The chloride (6.1 g), *p*-nitrobenzyl alcohol (3.5 g), and trimethylamine (1.1 g) were dissolved in toluene 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 *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulphonate. The product was purified by repeated recrystallization from benzene, m.p. 147 °C differential scanning calorimetry (DSC); δ_H 4.1 (6 H, d, OMe), 5.3 (2 H, s, CH_2), and 7.3–8.8 (7 H, m, ArH); *m*/*z*, 453 (M^+); ν_{max} 2 800–3 000 (OMe, CH_2), 1 100 (SO_3), and 1 480 cm^{-1} (NO_2).

Identification of Photodissociation Products of NBAS.—A 10^{-4} mol dm^{-3} acetonitrile solution of NBAS in a glass ampoule was degassed with a vacuum line, sealed, and irradiated with 436 nm light from a high-pressure mercury lamp with a sharp-cut glass filter L-42 (Toshiba Co.). The products were observed with a Hitachi liquid chromatography Model 634 with ethanol as eluant. The products were separated by column chromatography using Wakogel C-300 (Wako Chemicals Co.) and chloroform. Each product was characterized with electron-impact mass spectrometry (EIMS), field-desorption mass spectrometry (FDMS), and ^1H NMR spectroscopy.

Quantum-yield Measurement.—A degassed acetonitrile solution of NBAS in a sealed ampoule was irradiated by 436 or 254 nm light and the intensity change in the electronic spectrum was measured at 436 nm where the absorption of NBAS is quenched by the irradiation. The intensity of the incident light was determined by an Epplay Model E-6 thermopile. The photodissociation rate of NBAS was plotted against the incident light energy based on equation (10) and the quantum yields were determined by calibration of the slope of the straight line in Figure 9 as described below.

Results and Discussion

Electronic Spectrum and Change by Photoirradiation.—Figure 1 shows the electronic spectrum of NBAS in oxygen-free acetonitrile and the change due to photoirradiation. NBAS has a strong absorption at 267 nm and a broad absorption with vibrational structures in the wavelength region 330–450 nm. With photoirradiation, both absorption peaks shift to shorter

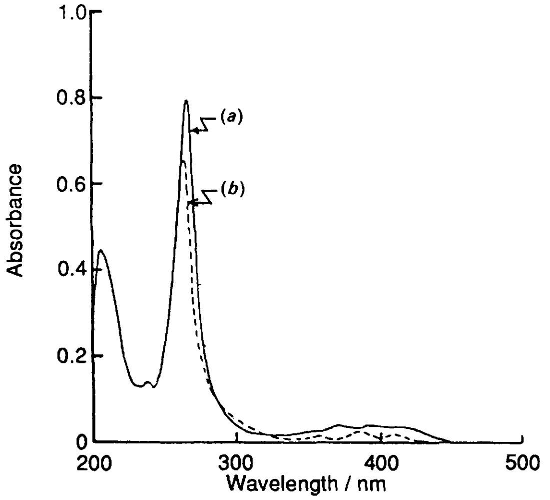


Figure 1. The electronic absorption spectrum of NBAS and its change due to irradiation by 436 nm light (1.57 × 10^{-6} mol dm^{-3} in degassed acetonitrile). (*a*) Before irradiation, (*b*) after irradiation.

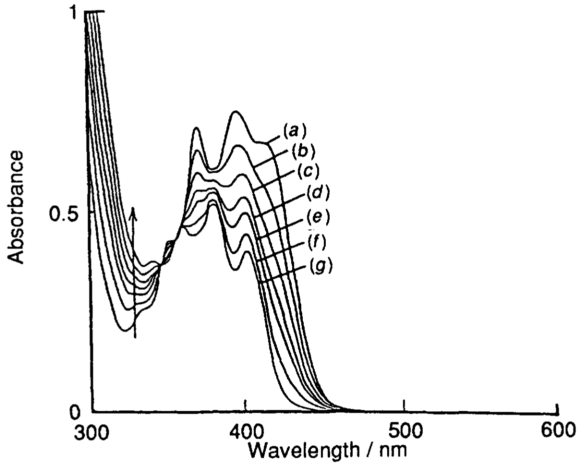


Figure 2. Change of the electronic spectrum of NBAS due to irradiation by 436 nm light (1.50 × 10^{-4} mol dm^{-3} in degassed acetonitrile). The solution, in a quartz cell, was irradiated by 436 nm monochromatic light from a filtered, high-pressure mercury lamp (450 W) at a distance of 30 cm. Photoirradiation time (*a*) 0, (*b*) 10, (*c*) 20, (*d*) 40, (*e*) 40, (*f*) 60, (*g*) 120 min.

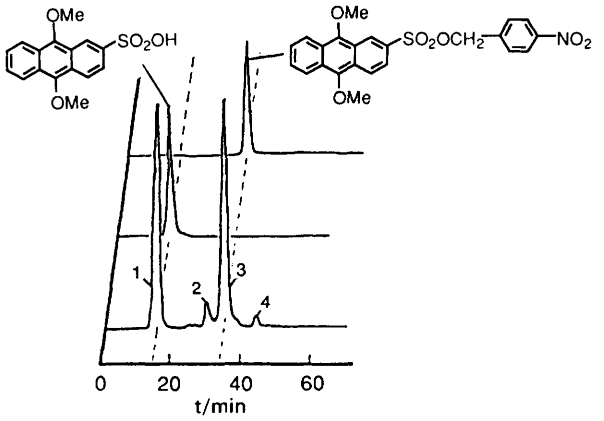


Figure 3. High-pressure liquid chromatogram of photodissociation products of NBAS.

Table. The assignment of peaks in the mass spectrum of the product for peak 4 in the liquid chromatogram.

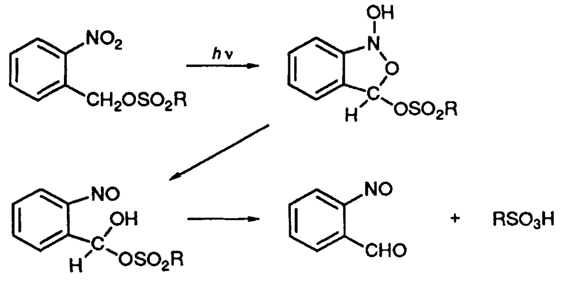
m/*z*	Fragments
373	Parent peak of DNBA: M
358	$M - CH_3$
343	$M - (CH_3 \times 2)$
327	$M - NO_2$
312	$M - (CH_3 + NO_2)$
297	$M - (CH_3 \times 2 + NO_2)$

wavelength and decrease in intensity. Figure 2 shows the absorption spectrum of NBAS in the region 330–450 nm as measured with a solution of higher concentration. The absorption band decreases in intensity upon photoirradiation and is finally converted into the absorption band with the weaker absorption intensity and the blue-shifted peak. The final spectrum agrees with that of 9,10-dimethoxyanthracene-2-sulphonic acid (abbreviated hereafter to AS). The spectral behaviour of NBAS due to photoirradiation suggests that photochemical dissociation of NBAS releases a sulphonic acid moiety.

Photochemical Reaction of NBAS.—A solution of NBAS in degassed acetonitrile was irradiated with 365 nm UV light and the products were characterized. The liquid chromatogram of the products shows four peaks at different retention times as shown in Figure 3. Among these peaks, peaks 1 and 3 agree with those of AS and unchanged NBAS in retention time. The absorption spectra of the four products are shown in Figure 4(*a*)–(*d*). The electronic spectra of the products for peaks 1 and 3 agree with those of AS and NBAS. Based on the strong peaks at *m*/*z* 318 and 454 and FDMS and EIMS, in addition to the spectroscopic identification mentioned above, the products for peaks 1 and 3 were concluded to be AS and NBAS, resepctively. The product for peak 4 gives the electronic spectrum of Figure 4(*d*) which is similar to the absorption spectrum of 9,10-dimethoxyanthracene-2-sulphonic acid in the wavelength region 330–430 nm.

FDMS and EIMS spectra of the product for peak 4 show a strong peak at *m*/*z* 373 and the peaks of the fragments are summarized in the Table. From these results the product was assigned to be 9,10-dimethoxy-2-(*p*-nitrobenzyl)anthracene (abbreviated hereafter to DNBA).

The product corresponding to peak 2 gives the electronic absorption spectrum shown in Figure 4(*b*). The spectrum has no absorption due to the 9,10-dimethoxyanthracene moiety and its FDMS spectrum shows a peak at *m*/*z* 136 which corresponds to the mass of a nitrobenzyl radical. The electronic absorption spectrum of the product agreed with that of *p*,*p*′-dinitrobibenzyl (DNB), which was synthesized from the oxidation of *p*-nitrotoluene.[9] From these results, the product is concluded to be *p*,*p*′-dinitrobibenzyl. It was reported that *o*-nitrobenzyl tosyl ester is photochemically converted into toluene-*p*-sulphonic acid and *o*-nitrosobenzaldehyde as is shown below [equation (1)] through an analogous reaction of a carboxy acid ester of *o*-nitrobenzyl alcohol.[5]



(1)

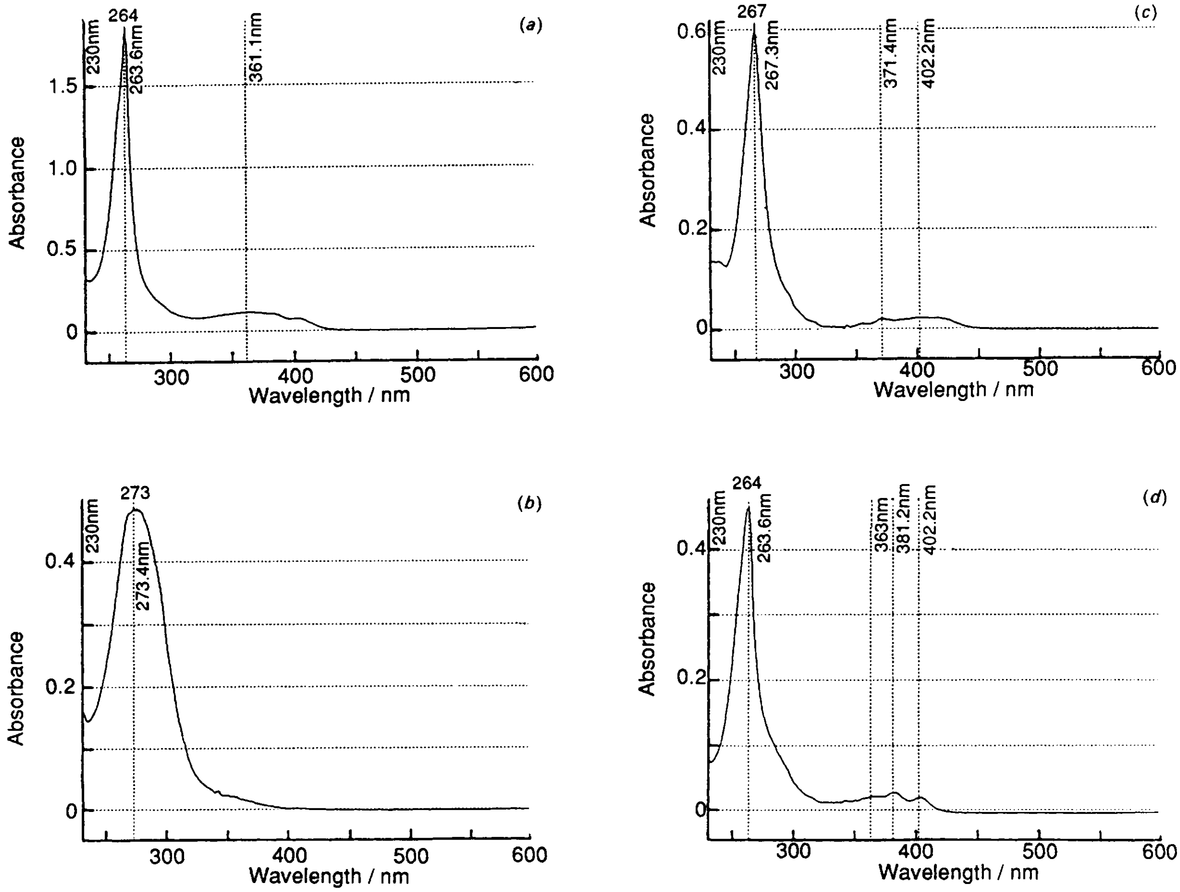


Figure 4. The electronic spectra of photodissociation products. (*a*)–(*d*) are the spectra for peaks 1–4 of the high-pressure chromatogram in Figure 3.

However, unlike *o*-nitrobenzyl esters, *p*-nitrobenzyl tosyl ester is unable to dissociate by direct excitation since a nitro group at the *para*-position is too far from the methylene group to interact with it. Busman reported[7] that *p*-nitrobenzyl sulphonates dissociate by the aid of an electron-donating photosensitizer to release the corresponding sulphonic acid, and the photodissociation proceeds *via* electron transfer from the sensitizer to the sulphonate. We have found that the *p*-nitrobenzyl ester of poly(vinylbenzene-4-sulphonic acid) is converted into poly(vinylbenzene-4-sulphonic acid) in the presence of 9,10-dimethoxy-2-ethylanthracene, while it is not dissociated in the absence of this sensitizer.[10] Nishida *et al.* have proposed an electron-transfer mechanism for the photosensitized hydrolysis of sulphonic acid esters and sulfonamides.[8]

$$\mathrm{D} \xrightarrow{h\nu} \mathrm{D^*} \qquad (2)$$

$$\mathrm{D^*} + \mathrm{Tos{-}OR} \longrightarrow \mathrm{D^{+\bullet}} + \mathrm{Tos^{-\bullet}OR} \qquad (3)$$

$$\mathrm{Tos^{-\bullet}OR} \xrightarrow{\mathrm{H_2O}} \mathrm{Tos^{\bullet}} + \mathrm{ROH} + \mathrm{OH^-} \qquad (4)$$

$$\mathrm{OH^-} + \mathrm{Tos^{\bullet}} \longrightarrow \mathrm{Tos^{-\bullet}OH} \qquad (5)$$

$$\mathrm{Tos^{-\bullet}OH} + \mathrm{D^{+\bullet}} \longrightarrow \mathrm{Tos{-}OH} + \mathrm{D} \qquad (6)$$

NBAS incorporates an electron-donating sensitizer within its structure and the photodissociation may proceed spontaneously *via* an intramolecular electron transfer from the 9,10-dimethoxyanthracene moiety to the *p*-nitrobenzyl moiety.

Figure 5 shows the absorption spectrum of benzyl 9,10-dimethoxyanthracene-2-sulphonate (abbreviated hereafter to BAS). While BAS has exactly the same molecular structure as NBAS, except that it has no nitro group substituted on the benzyl group, its photochemical behaviour is quite different from that of NBAS. The electron affinity of the benzyl group in BAS should be lower than that in NBAS due to the absence of the electron-withdrawing nitro group. The spectrum of BAS in degassed acetonitrile showed no change on irradiation of the solution with 365 nm light, suggesting that BAS is insensitive to light. This result supports the intramolecular electron-transfer mechanism for the photodissociation of NBAS. The electron transfer from the excited 9,10-dimethoxyanthracene moiety to the benzyl group may not proceed effectively due to the lower electron affinity of the benzyl group.

From the viewpoint of a π-electronic system, NBAS is considered to consist of two molecules since the conjugation of π-electrons is separated by the sulphonyl ester group. Therefore, the interaction of ethyl 9,10-dimethoxyanthracene-2-sulphonate (abbreviated hereafter to EAS) with *p*-nitrotoluene or toluene was studied, where EAS, *p*-nitrotoluene, and toluene correspond to 9,10-dimethoxyanthracene-2-sulphonyl moiety, *p*-nitrobenzyl moiety, and benzyl moiety, respectively. Figure 6 shows the fluorescence spectrum of EAS in degassed acetonitrile. The lifetime of the fluorescence is 8.12 ± 0.015 ns. Stern–Volmer plots of the fluorescence quenching by *p*-nitrotoluene and toluene in Figure 7 show that the fluorescence of EAS is efficiently quenched by *p*-nitrotoluene but is not quenched by toluene. Measurement of the fluorescence lifetime

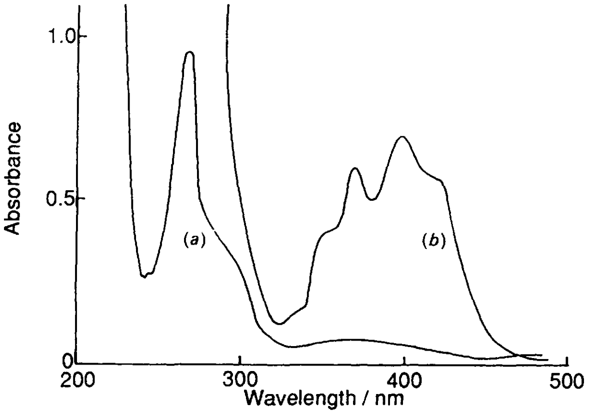


Figure 5. The electronic spectrum of BAS in acetonitrile. (*a*) 2.10 × 10^{-6} mol dm^{-3}, (*b*) 1.06 × 10^{-4} mol dm^{-3}.

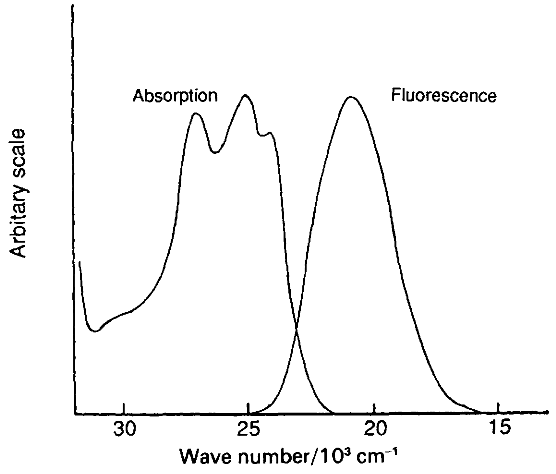


Figure 6. The absorption and fluorescence spectra of EAS in degassed acetonitrile.

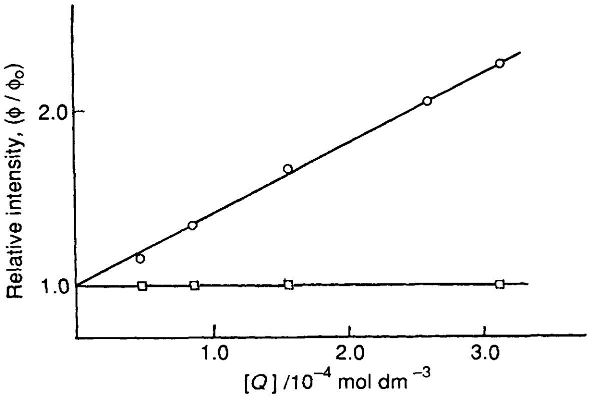


Figure 7. Stern–Volmer plots for fluorescence quenching of EAS by toluene (—□—) and *p*-nitrotoluene (—○—) in degassed acetonitrile (concentration of EAS 4.0 × 10^{-5} mol dm^{-3}, excitation light 365 nm).

indicates that the quenching rates (K_qs) of the fluorescence by *p*-nitrotoluene and toluene are 1.17 × 10^{10} dm^3 mol^{-1} s^{-1} and 1.01 × 10^7 dm^3 mol^{-1} s^{-1}, respectively. The former value is close to the diffusion-controlled rate in acetonitrile.

On the other hand, the oxidation potential of EAS is 0.68 V and the reduction potentials of *p*-nitrotoluene and toluene are -1.14 V and < -1.9 V, respectively. Based on these values of redox potentials, the free-energy changes (ΔG) accompanying the electron transfer from the lowest excited singlet state of EAS to *p*-nitrotoluene and toluene are calculated as -22.1 kcal mol^{-1}* and > -4.6 kcal mol^{-1},* respectively. These values for ΔG suggest that the quenching of the fluorescence of EAS is due to electron transfer from EAS to *p*-nitrotoluene or toluene *via* the interaction of the excited singlet state of EAS with *p*-nitrotoluene or toluene.

These experimental results with model compounds indicate that the photodissociation of NBAS proceeds *via* intramolecular electron transfer from the excited state of the 9,10-dimethoxyanthracene moiety to the *p*-nitrobenzyl moiety. Further, the fact that BAS is not photodissociated is reasonably explained by considering the much smaller value of K_q for toluene (a model compound for the benzyl moiety) and the fluorescence lifetime of EAS.

Figure 8 shows the concentration dependence of the photodissociation rate of NBAS in solution based on equation (10). The photodissociation rate of NBAS was measured with acetonitrile solutions of different concentrations of NBAS from 4.4 × 10^{-5} to 1.6 × 10^{-3} mol dm^{-3}. As is shown in Figure 8, the relationships between the photodissociation rate and the exposure time plot as a single line regardless of the concentration of NBAS in solution. This result means that the photodissociation rate is independent of the concentration of NBAS in solution and that the photodissociation of NBAS proceeds *via* a unimolecular reaction if the relatively long lifetime of the lowest excited singlet state of 9,10-dimethoxyanthracene moiety (EAS) is taken into account. In other words, the possibility of intermolecular electron transfer from an excited 9,10-dimethoxyanthracene moiety to the *p*-nitrobenzyl moiety of other NBAS molecules may be discounted.

Consequently, the Scheme (facing page) is proposed for the photolysis of NBAS.

Quantum Yield of Photodissociation.—Based on equations (7)—(9), the rate of photodissociation and the quantum yield of NBAS (Φ) is expressed by equations (10) and (11), respectively, where k_1 and k_2 are rate constants of dissociation and

$$\text{NBAS} \xrightarrow{h\nu} \text{NBAS*} \qquad (7)$$

$$\text{NBAS*} \xrightarrow{k_1} \text{Dissociation} \qquad (8)$$

$$\text{NBAS*} \xrightarrow{k_2} \text{NBAS} \qquad (9)$$

$$\ln \frac{\exp(2.303\, D_{0\lambda}) - 1}{\exp(2.303\, D_{t\lambda}) - 1} = I_{0\lambda'} \varepsilon_{\lambda'} l \Phi t \qquad (10)$$

$$\Phi = \frac{k_1}{k_1 + k_2} \qquad (11)$$

deactivation; $D_{0\lambda}$ and $D_{t\lambda}$ are absorbance of NBAS at wavelength λ nm before and after *t* seconds of photoirradiation; $I_{0\lambda'}$ is intensity of the monochromatic exposure light with wavelength λ′ (einstein cm^{-2}); ε_{χ} is molar extinction coefficient of NBAS at wavelength λ′; *l* is length of the optical path. The photodissociation rate of NBAS in degassed acetonitrile was measured by exposure to 254 or 436 nm monochromatic light.

As can be seen in Figure 9 the plot gives straight lines, indicating that the photodissociation of NBAS can be expressed by equation (10).

---

* 1 cal = 4.184 J.

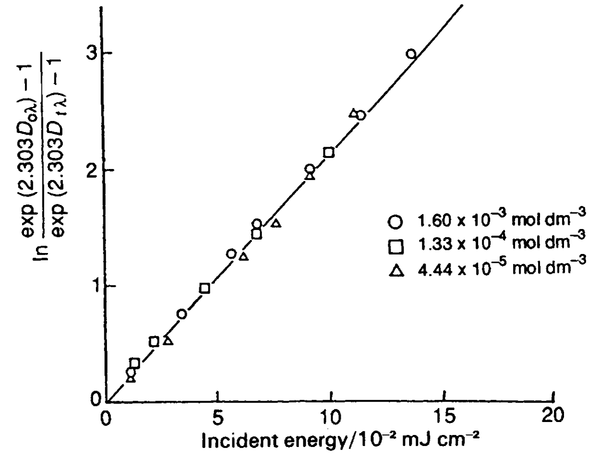


Figure 8. Concentration dependence of the rate of photodissociation of NBAS in degassed acetonitrile. The wavelength of the irradiation light was 436 nm.

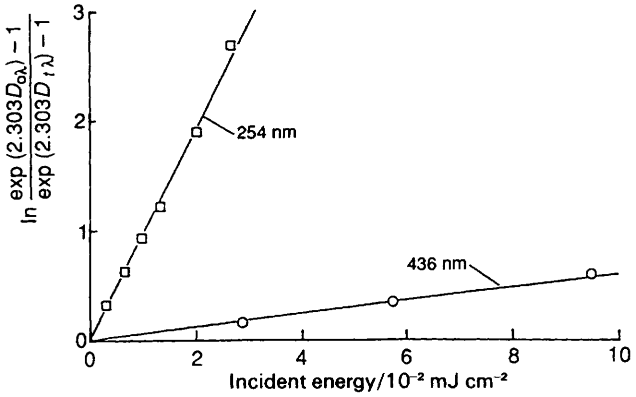
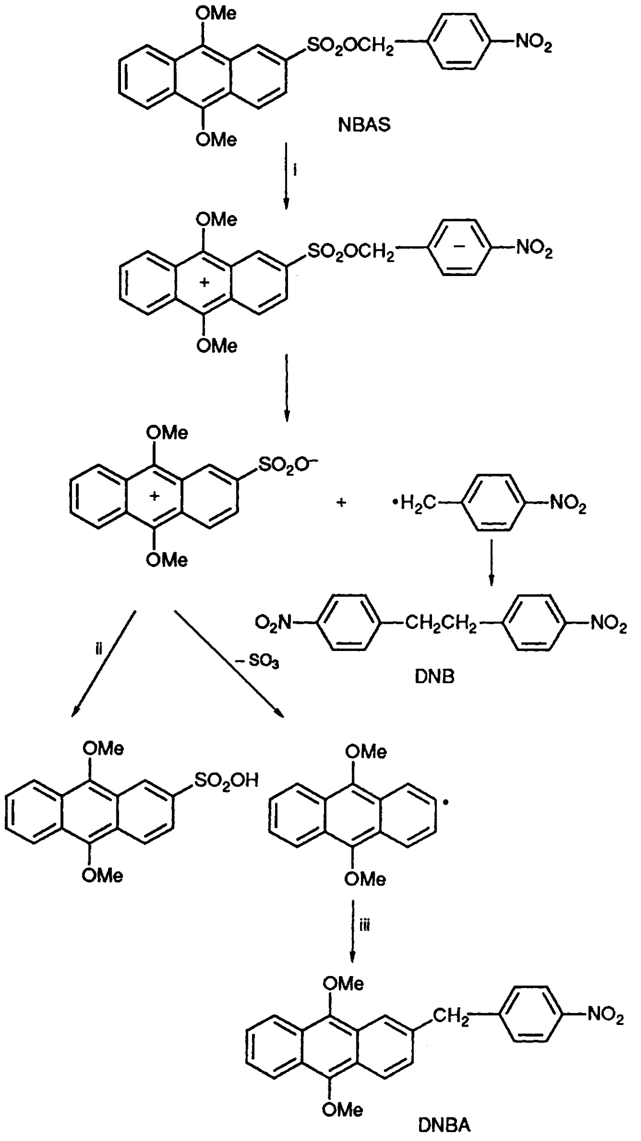


Figure 9. The first-order plots of the photodissociation rate of NBAS by irradiation with 254 and 436 nm light.

Figure 9 also shows that the apparent rate of photodissociation is much higher with excitation by 254 nm light than with excitation by 435 nm light. This may be because the molar extinction coefficient, $\varepsilon_{\lambda'}$, of NBAS is larger at 254 nm than at 436 nm. Following calibration of the slope of the straight line with the molar extinction coefficients, the quantum yield of photodissociation was determined as 0.08 for excitation with 254 nm light and 0.11 for excitation with 436 nm light. The discrepancy of the quantum yields at 254 nm and 436 nm shows that the π-electronic systems in NBAS consist of two localized, conjugated systems separated by the sulphonic ester group. Figure 10 compares the absorption spectra of NBAS, AS, and *p*-nitrobenzyl alcohol. While AS has absorptions in the vicinity of 380 and 260 nm, *p*-nitrobenzyl alcohol absorbs only at wavelengths shorter than 350 nm. Judging from these spectra, the spectrum of NBAS is similar to the overlap of the spectrum of 9,10-dimethoxyanthracene-2-sulphonic acid with that of *p*-nitrobenzyl alcohol. Irradiation of NBAS with 436 nm light excites only the 9,10-dimethoxyanthracene moiety, and 254 nm light excites both the 9,10-dimethoxyanthracene moiety and the *p*-nitrobenzyl moiety. Excitation by 436 nm light causes dissociation of NBAS. If NBAS is irradiated with 254 nm light, part of the incident light will be absorbed by the *p*-nitrobenzyl moiety. The reason why the quantum yield at 254 nm is smaller than that at 436 nm may be that the incident light absorbed by the *p*-nitrobenzyl moiety does not contribute to dissociation of NBAS.

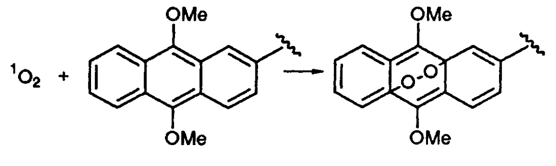
Figure 11 shows the absorption spectrum of NBAS in acetonitrile and its change due to irradiation by 254 nm or 436 nm in the presence of oxygen. The change of the spectrum due to photoirradiation is obviously different from that in degassed acetonitrile and both absorption peaks, at 269 and 330–450 nm, decrease in intensity. The drastic change of the spectrum caused by photoirradiation may be due to addition of singlet



Scheme. *Reagents and conditions:* i, *h*ν (436 nm); ii, RH; iii, *p*-$O_2NC_6H_4CH_2^{\bullet}$.

$$S \xrightarrow{h\nu} {}^1S^* \longrightarrow {}^3S^* \qquad (12)$$

$${}^3S^* + {}^3O_2 \longrightarrow S + {}^1O_2 \qquad (13)$$



(14)

(S: NBAS or AS)

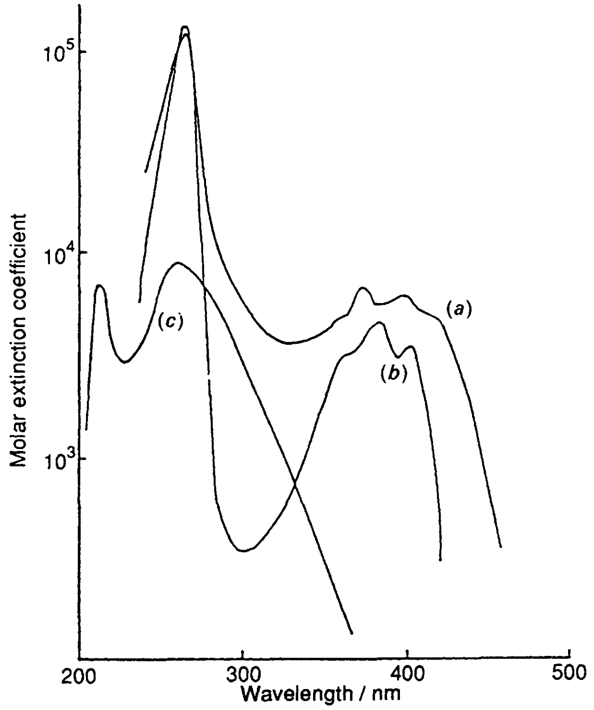


Figure 10. The electronic spectra of NBAS (*a*), AS (*b*), and *p*-nitrobenzyl alcohol (*c*) in acetonitrile.

oxygen to the anthracene structure to form an *endo*-peroxide [equations (12)–(14)].

While we have not investigated the mechanism of generation of the singlet oxygen, the triplet excited state of the anthracene moiety of NBAS or the photochemically generated AS may play the role of sensitizer.

Conclusions.—It was found that *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulphonate photodissociates by the direct excitation of the 9,10-dimethoxyanthracene moiety. This may be a novel category of photodissociation of sulphonic acid esters. The photodissociation proceeds *via* an intramolecular electron transfer from the 9,10-dimethoxyanthracene moiety to the *p*-nitrobenzyl moiety. The photodissociation is a competitive reaction between the intramolecular electron transfer and deactivation of the lowest singlet excited state of the aromatic sulphonyl moiety, and is governed by the Δ*G*-value in the electron-transfer process.

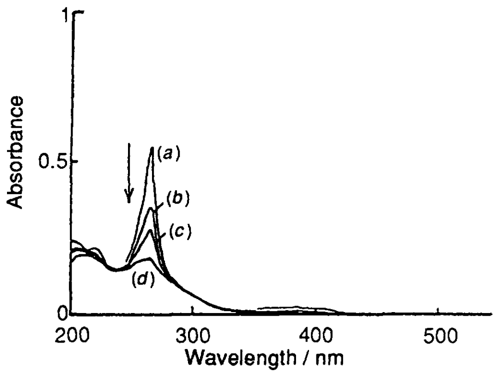


Figure 11. Change of the electronic spectrum of NBAS due to photoirradiation in the presence of oxygen (~4.9 × 10^{-6} mol dm^{-3} in acetonitrile). Photoirradiation time (*a*) 0, (*b*) 10, (*c*) 30, (*d*) 100 min. Irradiation condition is the same as that shown in Figure 2.

References

1 P. De Mayo, *Adv. Org. Chem.*, 1960, **2**, 367.
2 V. N. R. Pillai, *Synthesis*, 1980, 1.
3 E. Reichmanis, C. W. Wilkins, Jr., and E. A. Chandross, *Vac. Sci. Technol.*, 1981, **19**, 1388.
4 C. W. Wilkins, Jr., E. Reichmanis, and E. A. Chandross, *J. Electrochem. Soc.*, 1982, **129**, 2553.
5 E. Reichmanis, R. Gooden, C. W. Wilkins, Jr., and H. Schonhorn, *J. Polym. Sci., Polym. Chem. Ed.*, 1983, **21**, 1075.
6 E. Reichmanis, C. W. Wilkins, Jr., D. A. Price, and W. A. Chandross, *J. Electrochem. Soc.*, 1983, **130**, 1433.
7 S. C. Busman and J. E. Trend, *J. Imag. Technol.*, 1985, **11**, 191.
8 A. Nishida, T. Hamada, and O. Yonemitsu, *J. Org. Chem.*, 1988, **53**, 3386.
9 *Org. Synth.*, ed. N. Robjohn, John Wiley, 1963, Coll. vol. 4, p. 367.
10 N. Nakajima and T. Yamaoka, 78th Spring Meeting of the Japanese Association of Printing Science and Technology, Japan, Preprint p. 90, 1987.

Paper 0/01123A
Received 14*th March* 1990
Accepted 16*th May* 1990