J. Phys. Chem. **1992**, *96*, 238–244

$= 1.777,^{42}$ $\partial(\epsilon_{\mathrm{op}}^{-1} - \epsilon^{-1})_T/\partial P = -1.17 \times 10^{-4}$ MPa^{-1},[42] $C = 1.174$ M$^{-1/2}$,[54] and $B = 3.29$ M$^{-1/2}$ nm^{-1}.[54] The distance of closest approach $\dot{a}$ of the reacting cations to their counteranions was estimated in this study to be 790 pm.[55] From these and the above given data it can be calculated that $\Delta V^{\ddagger}{}_{\mathrm{SR}} = -8.0$, $\Delta V^{\ddagger}{}_{\mathrm{COUL}} = -4.0$, $\Delta V^{\ddagger}{}_{\mathrm{DH}} = +4.6$, and $\lambda^{\ddagger}\Delta\bar{V} = (0.41)\,(22.8) = 9.3$ cm^3 mol^{-1}, such that $\Delta V^{\ddagger}{}_{\mathrm{ET}} = 1.9$ cm^3 mol^{-1}. Combining this value with $\Delta\bar{V}_{\mathrm{os}}$ results in $\Delta V^{\ddagger} = \Delta\bar{V}_{\mathrm{os}} + \Delta V^{\ddagger}{}_{\mathrm{ET}} = -2.6 + 1.9 = -0.7$ cm^3 mol^{-1} which is close to the experimental values quoted in Table I.

We conclude that the studied reaction can be well described theoretically on the basis of an adiabatic OSET process. The theoretically predicted values of k, $\Delta G^{\ddagger}$, and $\Delta V^{\ddagger}$ obtained by applying the theories of Fuoss and Marcus–Hush–Stranks are indeed in good agreement with the experimental data and encourage further detailed analysis of such ET processes.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and Universidad Autónoma (Madrid) for sabbatical leave to P.M. Informative discussions during the initial phase of this project with Professor K. E. Wieghardt and Dr. P. Chaudhuri (Ruhr-Universität Bochum) are appreciated.

Registry No. Co(terpy)$_2^{3+}$, 19137-07-6; V(H$_2$O)$_6^{2+}$, 15696-18-1.

---

(54) Kortüm, G. *Lehrbuch der Elektrochemie*; Verlag Chemie: Weinheim, FRG, 1962; Chapter 5.

(55) The distance of closest approach $\dot{a}$ should be determined experimentally by measuring k at various ionic strengths. Alternatively, it has been recommended to adopt an averaging procedure[54] in which $\dot{a}$ is taken as the mean diameter of the reacting ions and their counterions. Therefore $\dot{a} = (d(\mathrm{V^{II}}) + d(\mathrm{Co^{III}}) + d(\mathrm{ClO_4^-}))/3 = (710 + 1100 + 550)/3 = 790$ pm. Frequently $\dot{a}$ is simply set equal to σ, i.e., the sum of the radii of the reacting ions. The selected value of $\dot{a}$ is not that critical since a value of for instance 860 pm ($=\sigma$) results in $\Delta V^{\ddagger}{}_{\mathrm{DH}} = 4.3$ cm^3 mol^{-1}, that is, only slightly smaller than calculated above.

Photoinduced Intramolecular Electron Transfer Mechanism for Photochemical Dissociation of Para-Substituted Benzyl 9,10-Dimethoxyanthracene-2-sulfonates

Kazuhiko Naitoh,* Koh Yoneyama, and Tsuguo Yamaoka

Department of Image Science and Technology, Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Chiba 260, Japan *(Received: June 5, 1991)*

The photochemical behavior of para-substituted benzyl 9,10-dimethoxyanthracene-2-sulfonates with varying electron-withdrawing ability of substituents has been investigated by both steady-state and laser flash photolysis techniques. *p*-Nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate is photochemically dissociated to give 9,10-dimethoxyanthracene-2-sulfonic acid, 9,10-dimethoxy-2-(*p*-nitrobenzyl)anthracene, and *p,p'*-dinitrobibenzyl which were assigned on the basis of mass spectroscopic data and ^{1}H NMR spectroscopy. Quantum yields for the photodissociation of *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate and for the formation of 9,10-dimethoxyanthracene-2-sulfonic acid with excitation at 436 nm in degassed acetonitrile solution are 0.12 ± 0.03 and 0.10 ± 0.03, respectively. Photodissociation of *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate is considered to proceed via an intramolecular electron transfer from the excited singlet state of 9,10-dimethoxyanthracene moiety to *p*-nitrobenzyl moiety followed by the heterolytic bond cleavage at oxygen–carbon bond of the sulfonyl ester from the fact that the transient absorptions at 310 and 425 nm due to 9,10-dimethoxyanthracene-2-sulfonate radical cation and around 340 nm due to *p*-nitrobenzyl radical anion are detected in laser spectroscopy. The rate constant for dissociation of *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate was determined to be (1.1 ± 0.5) × 10^5 s^{-1} by kinetic analyses. Possible mechanisms for the photodissociation are discussed and it is concluded that the three factors which control the rate of photodissociation are intramolecular electron transfer, feasibility of oxygen–carbon bond scission, and stability of benzyl-type radical formed by the photodissociation.

Introduction

Photoinduced electron transfer reactions play an important role in organic photochemistry.[1] One of our interests in these areas is concentrated on electron-transfer systems which can lead to the formation of light-induced reactive species.

It is well-known that *o*-nitrobenzyl esters of carboxylic acids[2] and sulfonic acids photochemically dissociate to generate the parent acid and *o*-nitrosobenzaldehyde via an intramolecular rearrangement. Much attention has been paid to photochemical generation of acids from *o*-nitrobenzyl esters in terms of photoremovable protecting groups for sugar and nucleic acid syntheses[2a,3] because of their ability to provide regioselective protection of functional groups, and recently as a photochemical acid-generating agent in the field of cationic polymerization as well as lithographic resist materials.[4-6]

The tosyl group is also an unique protecting group in synthetic chemistry.[2b] However, the drastic conditions that have been employed for the detosylation step reduce the utility of this group.[7] As a mild and selective method for this step, direct photolysis of

---

(1) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401; In *Photoinduced Electron Transfer. Part C: Organic Substrates. D: Application*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; p 241; *Topics in Current Chemistry 156. Photoinduced Electron Transfer I*; Springer-Verlag: Berlin, 1990.

(2) (a) Mayo, P. De. *Adv. Org. Chem.* **1960**, *2*, 367. (b) Binkley, R. W.; Flechtner, T. W. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, 1984; p 375.

(3) Pillai, V. N. R. *Synthesis* **1980**, 1.

(4) Reichmanis, E.; Wilkins, Jr., C. W.; Chandross, E. A. *J. Vac. Sci. Technol.* **1981**, *19*, 1388. Wilkins, Jr., C. W.; Reichmanis, E.; Chandross, E. A. *J. Electrochem. Soc.* **1982**, *129*, 2553. Reichmanis, E.; Wilkins, Jr., C. W.; Price, D. A.; Chandross, W. A. *J. Electrochem. Soc.* **1983**, *130*, 1433. Reichmanis, E.; Gooden, R.; Wilikins, Jr., C. W.; Schonhorn, H. *J. Polym. Sci., Polm. Chem. Ed.* **1983**, *21*, 1075.

(5) Houlihan, F. M.; Shugard, A.; Gooden, R.; Reichmanis, E. *Macromolecules* **1988**, *21*, 2001. Neenan, T. X.; Houlihan, F. M.; Reichmanis, E.; Kometani, J. M.; Bachman, B. J.; Thompson, L. F. *Macromolecules* **1990**, *23*, 145. Houlihan, F. M.; Neenan, T. X.; Reichmanis, E.; Kometani, J. M.; Thompson, L. F.; Chin, T.; Nalamasu, O. *J. Photopolym. Sci. Technol.* **1990**, *3*, 259.

(6) *Polymers in Microlithography*; *Materials and Processes*; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; ACS Symposium Series No. 412; American Chemical Society: Washington, DC, 1989.

(7) Detosylation of 2'-*O*-tosyladenosine derivative using sodium amalgam has been reported: Ranganathan, R.; Larwood, F. *Tetrahedron Lett.* **1978**, 4341. However, this reaction is only applicable to purine nucleosides.

0022-3654/92/2096-238$03.00/0

tosyl esters in the presence of sodium methoxide has been reported.[8] Recently, Masnovi[9] showed that the mechanism of this type of reaction involves an electron-transfer process. Yonemitsu et al. reported that photohydrolysis of tosylamides[10] and some esters of sulfonic acids[11] proceeds smoothly via an electron transfer in the excited state in the presence of electron-donating sensitizers such as 1,5-dimethoxynaphthalene.

Although extensive studies have been reported on the photodissociation of *o*-nitrobenzyl esters and the photosensitized dissociation of *p*-nitrobenzyl esters, reports of the direct photodissociation of *p*-nitrobenzyl esters are limited. Busman et al. reported[12] that *p*-nitrobenzyl esters of alkanesulfonic acids dissociate by the aid of a photosensitizer such as 9,10-dimethoxy-2-ethylanthracene and that an electron-transfer mechanism is involved in this photodissociation process.

Our earlier paper reported[13] that *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate (abbreviated hereafter as NAS) photodissociates to generate 9,10-dimethoxyanthracene-2-sulfonic acid and that quantum yield for photodissociation of NAS in acetonitrile is 0.11 using UV–visible spectrophotometry. In the present study, we have extended our previous work to further detailed study to elucidate the mechanism of photochemical reactions of para-substituted benzyl 9,10-dimethoxyanthracene-2-sulfonates by means of both steady-state and laser flash photolysis techniques. We will discuss the effects of substituents on the photochemical behavior of the title compounds. Further, the photodecomposition products of NAS in degassed acetonitrile solution were analyzed by electron impact mass spectroscopy (EIMS) and ^{1}H NMR spectroscopy. Herein we report unique photochemical reactivity associated with photoinduced intramolecular electron transfer in para-substituted benzyl 9,10-dimethoxyanthracene-2-sulfonates.

Experimental Section

Materials. Where possible, commercially available materials were used in this study. 3,4-Dinitrotoluene (Aldrich, abbreviated hereafter to DNT), *p*-nitrotoluene (Wako, PNT), and *p*-cyanotoluene (Wako, PCT) were recrystallized from benzene, ethanol, and benzene, respectively. *p*-Chlorotoluene (Wako, PClT) and toluene (Cica-Merck, Uvasol) were used as received. Acetonitrile was refluxed over diphosphorus pentaoxide and then distilled. The distillate was refluxed over calcium hydride and redistilled prior to use for photoreaction and cyclic voltammetry experiments as solvent. The syntheses of compounds not commercially available are described below. No attempts were made to maximize product yields.

Preparation. The synthesis of 9,10-dimethoxyanthracene-2-sulfonyl chloride (DASC) has been described previously.[13]

Ethyl 9,10-Dimethoxyanthracene-2-sulfonate (EAS). An amount of 5.00 g (0.015 mol) of DASC, 0.83 g (0.018 mol) of ethanol, and 2.32 g (0.023 mol) of triethylamine (Wako) was dissolved in dried THF. Stirring at room temperature was continued for 24 h, and water was added to wash the reaction mixture and then evaporated to remove THF under reduced pressure to obtain ethyl 9,10-dimethoxyanthracene-2-sulfonate. EAS was recrystallized from cyclohexane three times; yield 2.43 g (45.0%). Mp 107 °C. Anal. Calcd for $C_{18}H_{18}O_5S$: C, 62.43; H, 5.20. Found: C, 62.60; H, 5.22. ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.96 (s, 1 H), 8.43 (d, 2 H), 8.35 (d, 2 H), 7.80 (d, 1 H), 7.61 (t, 2 H), 4.20 (q, 2 H, SO_3–CH_2–), 4.17 (s, 3 H, –OCH_3), 4.13 (s, 3 H, –OCH_3), 1.34 (t, 3 H, –CH_3); IR (KBr pellet) 3000, 2800, 1100 cm^{-1}.

3′,4′-Dinitrobenzyl 9,10-Dimethoxyanthracene-2-sulfonate (DNAS). The DASC (5 g, 0.015 mol), 3,4-dinitrobenzyl alcohol (Aldrich 3.52 g, 0.018 mol), and triethylamine (2.32 g, 0.023 mol) were dissolved in dried THF and the solution was stirred for 24 h at room temperature, washed with water, and then evaporated to remove solvent to obtain 3′,4′-dinitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate. DNAS was purified by recrystallization from cyclohexane three times; yield 4.53 g (60.6%). Mp 139.5–140.5 °C. Anal. Calcd for $C_{23}H_{18}N_2O_9S$: C, 55.43; H, 3.61; N, 5.62. Found: C, 55.43; H, 3.71; N, 5.52. ^{1}H NMR (500 MHz chloroform-*d*) δ 8.94 (s, 1 H), 8.44 (d, 1 H), 8.35 (d, 2 H), 7.84 (d, 2 H), 7.80 (s, 1 H), 7.75 (d, 1 H), 7.63 (t, 2 H), 5.26 (s, 2 H, SO_3–CH_2–), 4.17 (s, 3 H, –OCH_3), 4.14 (s, 3 H, –OCH_3); IR (KBr pellet) 3200, 2900, 1550, 1460, 1380, 1180 cm^{-1}.

***p*-Nitrobenzyl 9,10-Dimethoxyanthracene-2-sulfonate (NAS).** NAS was synthesized for previous work and its preparation is described elsewhere.[13] Mp 147 °C. Anal. Calcd for $C_{23}H_{19}NO_7S$: C, 60.93; H, 4.19; N, 3.09. Found: C, 60.81; H, 4.18; N, 2.91. ^{1}H NMR (500 MHz chloroform-*d*) δ 8.95 (s, 1 H), 8.43 (d, 1 H), 8.35 (d, 2 H), 8.14 (d, 2 H), 7.76 (d, 1 H), 7.65 (t, 2 H), 7.48 (d, 2 H), 5.23 (s, 2 H, SO_3–CH_2–), 4.17 (s, 3 H, –OCH_3), 4.12 (s, 3 H, –OCH_3); IR (KBr pellet) 3200, 2900, 1460, 1360, 1180 cm^{-1}.

***p*-Cyanobenzyl 9,10-Dimethoxyanthracene-2-sulfonate (CAS).** The DASC (5 g, 0.015 mol), *p*-cyanobenzyl alcohol (prepared by $NaBH_4$ reduction of *p*-cyanobenzaldehyde (Aldrich) 2.39 g, 0.018 mol), and triethylamine (2.32 g, 0.023 mol) were dissolved in dried THF and the solution was stirred for 24 h at ambient temperature, washed with water, and then evaporated to obtain *p*-cyanobenzyl 9,10-dimethoxyanthracene-2-sulfonate. Repeated recrystallizations from cyclohexane gave yellow needles of CAS; yield 3.89 g (59.8%). Mp 93–94 °C. Anal. Calcd for $C_{24}H_{19}NO_5S$: C, 67.68; H, 4.99; N, 3.04. Found: C, 67.47; H, 4.98; N, 2.92. ^{1}H NMR (500 MHz chloroform-*d*) δ 8.95 (s, 1 H), 8.42 (d, 1 H), 8.33 (d, 2 H), 7.74 (d, 1 H), 7.65 (t, 2 H), 7.60 (d, 2 H), 7.41 (d, 2 H), 5.18 (s, 2 H), SO_3–CH_2–), 4.17 (s, 3 H, –OCH_3) 4.13 (s, 3 H, –OCH_3); IR (KBr pellet) 3200, 3000, 2210, 1380, 1180 cm^{-1}.

***p*-Chlorobenzyl 9,10-Dimethoxyanthracene-2-sulfonate (ClAS).** The DASC (5 g, 0.015 mol), *p*-chlorobenzyl alcohol (Wako 2.29 g, 0.018 mol), and triethylamine (2.32 g, 0.023 mol) were dissolved in dried THF and the solution was stirred for 24 h at room temperature and filtered. The solvent was evaporated and the residue was recrystallized from cyclohexane to give yellow crystals of ClAS; yield 3.04 g (45.8%). Mp 113 °C. Anal. Calcd for $C_{23}H_{20}O_5SCl$: C, 62.44; H, 4.30. Found: C, 62.18; H, 4.27. ^{1}H NMR (500 MHz chloroform-*d*) δ 8.95 (s, 1 H), 8.41 (d, 1 H), 8.37 (d, 2 H), 7.74 (d, 1 H), 7.66 (t, 2 H), 7.26 (d, 2 H), 7.23 (d, 2 H), 5.12 (s, 2 H, SO_3–CH_2–), 4.16 (s, 3 H, –OCH_3) 4.13 (s, 3 H, –OCH_3); IR (KBr pellet) 3000, 2800, 1380, 1180, 810 cm^{-1}.

Benzyl 9,10-Dimethoxyanthracene-2-sulfonate (BAS). BAS was synthesized from benzyl alcohol (Wako) by similar procedure to those employed for preparation of ClAS. The product was recrystallized from *n*-hexane three times; yield 2.13 g (34.8%). Mp 105–6 °C. Anal. Calcd for $C_{22}H_{17}NO_7S$: C, 60.14; H, 3.87; N, 3.19. Found: C, 60.40; H, 3.99; N, 3.10. ^{1}H NMR (400 MHz chloroform-*d*) δ 8.83 (s, 1 H), 8.46 (d, 1 H), 8.34 (d, 2 H), 8.16 (d, 2 H), 7.78 (d, 1 H), 7.63 (t, 2 H), 7.23 (t, 3 H), 5.10 (s, 2 H, –SO_3–CH_2–), 4.14 (s, 3 H, –OCH_3), 4.06 (s, 3 H, –OCH_3); IR (KBr pellet) 3200, 3000, 1360, 1180, 760, 680 cm^{-1}.

***p*-Nitrophenyl 9,10-Dimethoxyanthracene-2-sulfonate (NAS0).** NAS0 was synthesized in a manner similar to that described above for the preparation of DNAS with using *p*-nitrophenol (Wako). The product was purified by repeated recrystallization from cyclohexane; yield 4.82 g (73.2%). Mp 133–4 °C. Anal. Calcd for $C_{22}H_{17}NO_7S$: C, 60.14; H, 3.87; N, 3.19. Found: C, 60.44; H, 3.99; N, 3.10. ^{1}H NMR (500 MHz chloroform-*d*) δ 8.84 (s, 1 H), 8.46 (d, 1 H), 8.33 (d, 2 H), 8.18 (d, 2 H), 7.79 (d, 1 H), 7.65 (t, 2 H), 7.26 (d, 2 H), 4.15 (s, 3 H, –OCH_3), 4.07 (s, 3 H,

---

[8] Zen, S.; Tashima, S.; Koto, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 3025. Izawa, Y.; Kuromiya, N. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3197. Pete, J. P.; Portella, C. *Bull. Soc. Chim. Fr.* **1980**, 275.

[9] Masnovi, J.; Koholic, D. J.; Binkley, R. *J. Am. Chem. Soc.* **1987**, *109*, 2851.

[10] Hamada, T.; Nishida, A.; Matsumoto, Y.; Yonemitsu, O. *J. Am. Chem. Soc.* **1980**, *102*, 3979. Hamada, T.; Nishida, A.; Matsumoto, Y.; Yonemitsu, O. *Tetrahedron Lett.* **1989**, 4241. Hamada, T.; Nishida, A.; Yonemitsu, O. *J. Am. Chem. Soc.* **1986**, *108*, 140.

[11] Nishida, A.; Hamada, T.; Yonemitsu, O. *J. Org. Chem.* **1988**, *53*, 3386.

[12] Busman, S. C.; Trend, J. E. *J. Image Technol.* **1985**, *11*, 191.

[13] Yamaoka, T.; Adachi, H.; Matsumoto, K.; Watanabe, H.; Shirosaki, T. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1709.

–OCH$_3$); IR (KBr pellet) 3200, 2800, 1480, 1380, 1180 cm^{-1}.

p-Nitrophenethyl 9,10-Dimethoxyanthracene-2-sulfonate (NAS2). NAS2 was prepared according to DNAS preparation procedure with using p-nitrophenethyl alcohol (Aldrich). Recrystallization from n-hexane gave the desired ester; yield 5.23 g (74.6%). Mp 112–3 °C. Anal. Calcd for $C_{24}H_{21}NO_7S$: C, 61.67; H, 4.50; N, 3.00. Found: C, 61.67; H, 4.55; N, 2.93. ^{1}H NMR (500 MHz chloroform-d) δ 8.84 (s, 1 H), 8.35 (d, 1 H), 8.34 (d, 2 H), 8.04 (d, 2 H), 7.65 (d, 1 H), 7.62 (t, 2 H), 7.26 (d, 2 H), 4.38 (t, 2 H, SO_3–CH_2–), 4.13 (s, 3 H, –OCH$_3$) 41.2 (s, 3 H, –OCH$_3$), 3.09 (t, 2 H, –CH_2–$PhNO_2$–p); IR (KBr pellet) 3200, 2800, 1460, 1380, 1180 cm^{-1}.

Absorption and Fluorescence Measurements. Absorption spectra were recorded in 1.00-cm-path quartz cells by a Shimadzu UV-2100S UV–visible recording spectrophotometer. Steady-state fluorescence spectra were recorded with samples in 1.00 × 1.00 cm quartz cells in a Hitachi MPF-2A or a Hitachi F-4010 fluorescence spectrophotometer. Fluorescence quantum yield (ϕ_f) of EAS (2.0 × 10^{-5} M; absorbance at 365 nm 0.089) in oxygen-free acetonitrile was estimated by comparing emission intensities integrated between 410 and 700 nm with that of quinine bisulfate in 1 N H_2SO_4 for which ϕ_f is 0.55 as a standard. Fluorescence lifetimes τ were determined at room temperature by means of time-correlated single-photon counting with a Horiba NAES-1100, with NFL-111 hydrogen flash lamp (~2 ns fwhm) as the excitation source.

Redox Potentials. Redox potentials were measured by cyclic voltammetry with a Hokuto-Denko Function Generator HB-104 and a potentiostat/galvanostat HA-301. Electrochemical measurements were 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. The electrolyte was 0.1 M tetra-n-butylammonium perchlorate in acetonitrile. The voltammograms were scanned at 50 mV s^{-1}. All potentials are calculated vs SCE as $E_{1/2}$ values, where $E_{1/2} = 0.5(E_P{}^a + E_P{}^c)$; $E_P{}^a$ and $E_P{}^c$ are the anodic and cathodic peak potentials, respectively. Calibration was vs ferrocene.

Irradiation. For irradiation at 436 nm a 450-W high-pressure mercury lamp with a sharp cut filter L-42, a band-pass interference filter KL-43 (Toshiba Co.), and heat absorbing filter HA-30 (Hoya Co.) were used. Irradiations at 365 nm were made with the above mercury lamp with a glass filter UV-33, UV-D2 (Toshiba Co.), and HA-30 filter. A Hoya ND filter was used as an attenuation filter when necessary. The light filters were collimated to the sample cell. The intensity of the incident light was measured with an Eppley Model E-6 thermopile. Sample solutions for the irradiation were deaerated by five freeze–pump–thaw cycles.

Sample Analysis. Samples were analyzed by reverse-phase 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 RP-18 endcapped column (250 × $\phi 4$ mm) eluting a 9:1 mixture of MeCN and H_2O at ambient temperature. All samples were HPLC analyzed immediately after irradiation using 9,10-dimethoxyanthracene-2-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 analyzed 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 analyzer (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 analyzed with a personal computer (NEC PC9801VM). Sample solutions were deaerated by bubbling argon for 30 min. A control laser experiment was carried out with using pyrene in benzene solution.[14]

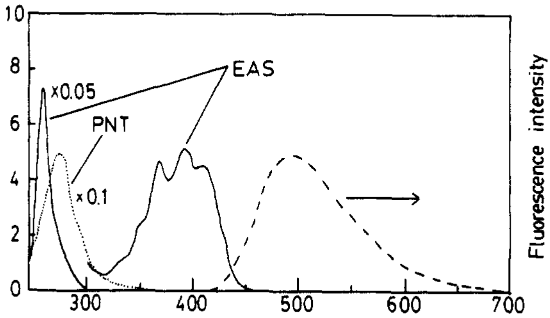


Figure 1. Electronic absorption spectra of ethyl 9,10-dimethoxyanthracene-2-sulfonate (EAS) and p-nitrotoluene (PNT) in CH_3CN solutions at room temperature, and the fluorescence spectrum of EAS in oxygen-free acetonitrile solution.

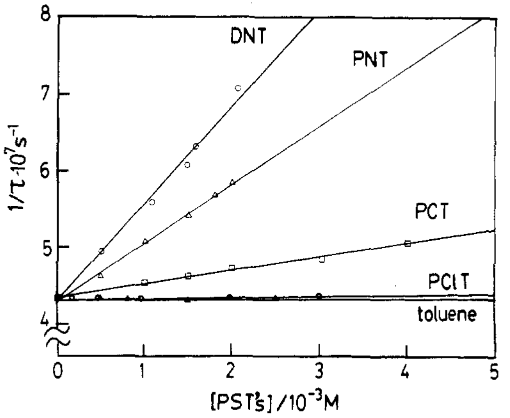


Figure 2. Stern–Volmer plots of fluorescence quenching of EAS by PST's in degassed acetonitrile solution. The reciprocal of the fluorescence lifetime is plotted as the function of PST's concentration. DNT = 3,4-dinitrotoluene; PNT = p-nitrotoluene; PCT = p-cyanotoluene; PClT = p-chlorotoluene.

Results and Discussion

From the viewpoint of π-electron system, para-substituted benzyl 9,10-dimethoxyanthracene-2-sulfonates are considered to be comprised of two molecules since the conjugation of π-electrons is separated by the sulfonyl ester group. Prior to the study on para-substituted benzyl 9,10-dimethoxyanthracene-2-sulfonate, the intermolecular interaction of ethyl 9,10-dimethoxyanthracene-2-sulfonate with para-substituted toluenes (PST's) was studied as a model reaction.

Absorption, Fluorescence Spectra, and Fluorescence Quenching. Figure 1 shows the absorption and fluorescence spectra of EAS in oxygen-free acetonitrile together with the absorption spectrum of PNT. EAS has a strong absorption at 266 nm, a broad absorption with vibrational structures in the wavelength region 330–450 nm, and a broad and structureless fluorescence spectrum in the wavelength region from 410 to 700 nm. While the spectral response of PNT extends only to ca. 350 nm, the absorption of EAS extends to longer wavelength than that of PNT. From these spectra, the lowest excited singlet state energy of EAS is estimated to be 65.9 kcal mol^{-1}. The fluorescence quantum yield and lifetime of EAS are 0.79 and 23.0 ns, respectively.

The fluorescence quenching rate constants k_q's of EAS by PST's were determined from the relation

$$1/\tau' = 1/\tau + k_q[Q] \qquad (1)$$

where τ and τ' are the fluorescence lifetime of EAS in the absence of and presence of the PST's, respectively, and [Q] is concentration of PST's. Stern–Volmer plots of fluorescence quenching of EAS

---

(14) Charmicheal, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, No. 1, 155.

TABLE I: Reduction Potentials of the Substituted Benzyl Moiety, Calculated ΔG Values for Electron Transfer between EAS and PST's, and Fluorescence Quenching Rate Constants of EAS by PST's

	E_{red}/V vs SCE	ΔG/kcal mol^{-1}	k_q/M^{-1} s^{-1}
DNT	-0.90	-20.3	1.6×10^{10}
PNT	-1.19	-13.6	1.1×10^{10}
PCT	-1.50	-6.48	7.6×10^{9}
PClT	<-2.23	$>+10.3$	7.2×10^{7}
toluene	<-2.23	$>+10.3$	1.0×10^{7}

by PST's in Figure 2 show that the fluorescence of EAS is efficiently quenched by PST's with a strong electron-withdrawing group but is not quenched efficiently by PClT and toluene.

The electrochemical behavior has been studied in acetonitrile solution with tetra-*n*-butylammonium perchlorate as the supporting electrolyte. EAS shows a reversible oxidation wave at 1.08 eV vs SCE and the reduction potentials ($E_{1/2}^{red}$) of DNT, PNT, PCT, PClT, and toluene are -0.90, -1.19, -1.50, <-2.23, and <-2.23 V vs SCE, respectively. From the $E_{1/2}^{red}$ value and k_q, the higher the $E_{1/2}^{red}$ value for PST's, the more efficent the fluorescence quenching is.

Based on these values of redox potentials, the free-energy changes (ΔG's) accompanying the electron transfer from the lowest excited singlet state of EAS to PST's can be calculated according to the Rehm–Weller equation[15] (2) (listed in Table I), where

$$\Delta G = 23.06\{E(D/D^+) - E(A^-/A) - C\} - E_{0,0} \qquad (2)$$

$E(D/D^+)$ is the oxidation potential of the donor, $E(A^-/A)$ is the reduction potential of the acceptor, $E_{0,0}$ is the electronic energy corresponding to the excited singlet state of the donor, and C is the Coulombic interaction between the radical ions. The Coulombic interaction energy is generally 1–2 kcal mol^{-1} in the polar solvent. This value was neglected in the present study. The experimental facts that the k_q values are well related to ΔG's for EAS and PST's suggest that the quenching of the fluorescence of EAS is due to an electron transfer from EAS to PST's via the interaction of excited singlet state of EAS with DNT, PNT, and PCT.

On the other hand, the absorption spectrum of NAS in acetonitrile is similar to the overlap of the spectra of PNT and EAS. No broadening or red-shifting due to ground-state interactions between EAS and PNT was observed, providing evidence for the absence of ground-state interactions between the 9,10-dimethoxyanthracene moiety and *p*-nitrobenzyl moiety for NAS. This observation also applies to the other para-substituted derivatives. Moreover, the redox potentials of DNAS, NAS, CAS, ClAS, and BAS are of similar values to those of the corresponding intermolecular model compounds.

No fluorescence of DNAS, NAS, and CAS was detected with excitation at 436 and 365 nm in deaerated acetonitrile solution. Similarly, no fluorescence was observed with NAS0 and NAS2. In contrast with these results, ClAS and BAS emit fluorescence, the spectra of which are similar to that of EAS. These results demonstrate that the fluorescence of 9,10-dimethoxyanthracene moiety is intramolecularly quenched by the benzyl moiety having an electron-withdrawing group, while it is not quenched by benzyl or chlorobenzyl moiety. Judging from the results with the fluorescence quenching experiments in the intermolecular model systems, intramolecular quenching rate constants for the 3′,4′-dinitro, *p*-nitro, and *p*-cyanobenzyl esters may be higher than those estimated by the corresponding intermolecular model compounds.

Photochemical Reaction and Assignment of Photoproducts. Exposure of NAS to 436-nm light results in the shift of absorption peak to shorter wavelength as well as the decrease in intensity. Figure 3 shows the absorption spectrum of NAS in the region 300–450 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 is analogous to that of 9,10-dimethoxyanthracene-2-sulfonic acid (AS). Similar photochemical behavior was observed for DNAS and CAS. However, the spectra of ClAS and BAS in degassed acetonitrile showed no change upon irradiation with 436- and 365-nm light, suggesting that ClAS and BAS are insensitive to the light. Taking into consideration the fluorescence quenching data for intermolecular model compounds and electron affinity of the benzyl moiety, we infer that the intramolecular electron transfer mechanism is involved for the photochemical reactions of DNAS, NAS, and CAS. The electron transfer from the excited 9,10-dimethoxyanthracene moiety to the *p*-chlorobenzyl or benzyl moiety may not proceed efficiently due to the lower electron affinity of the benzyl group. This implies that the electron-transfer process is one of the rate-determining steps in these photochemical dissociations.

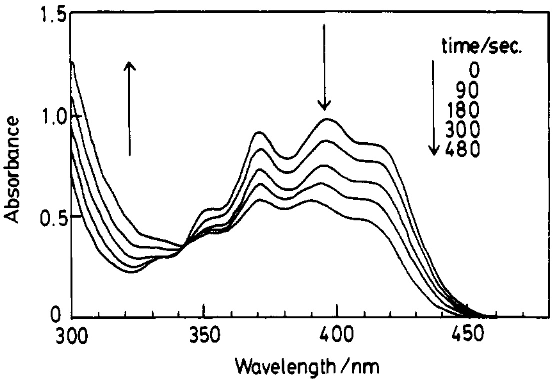


Figure 3. Change of the absorption spectrum of NAS (2.0×10^{-4} M) in degassed acetonitrile due to irradiation by 436-nm light.

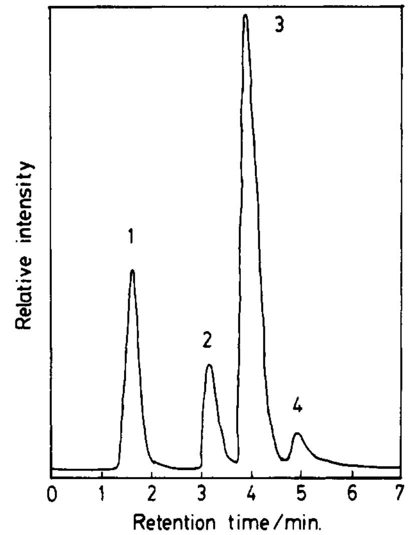


Figure 4. A typical high-pressure liquid chromatogram of photodissociation products of NAS. Analysis at 264 nm. Eluent: CH_3CN:H_2O = 9:1, 1 mL/min.

A solution of NAS in degassed acetonitrile was irradiated with 436-nm light and the photoproducts were characterized. The HPLC of the products shows four peaks at different retention times as shown in Figure 4. Among these peaks, peaks 1 and 3 agree with those of AS and unreacted NAS in the retention time. All the photoproducts were identified by separating with a preparative GPC column followed by EIMS or ^{1}H NMR spectroscopy. Based on the strong peaks at *m*/*z* 318 and 453 in EIMS spectra, the products for peaks 1 and 3 were concluded to be AS and NAS, respectively. EIMS spectrum of the product for peak 2 shows a peak at *m*/*z* 136 which corresponds to the mass of nitrobenzyl radical. In addition, the ^{1}H NMR spectrum for peak 2 provided further information for the chemical structure of this product.[16]

---

(15) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(16) In previous work in ref 13, the photoproduct for peak 2 gave the electronic absorption which has no absorption due to the 9,10-dimethoxyanthracene moiety. ^{1}H NMR (500 MHz chloroform-*d*) spectrum for peak 2 in the liquid chromatogram; δ 8.14 (d, 4 H), 7.28 (d, 4 H), 3.08 (s, 4 H).

TABLE II: Assignment of Peaks in the Mass Spectrum of the Photoproduct for Peak 4 in the Liquid Chromatogram

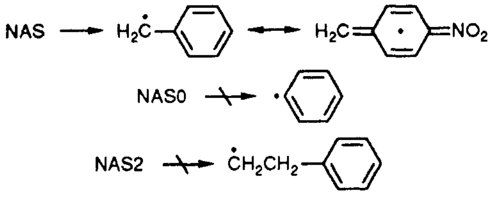
m/z	fragment
373	parent peak of DNBA:M
358	M-CH_3
343	M-(CH_3 × 2)
327	M-NO_2
312	M-(CH_3 + NO_2)
297	M-(CH_3 × 2 + NO_2)
251	M-$PhNO_2$
237	M-CH_2PhNO_2
222	M-(CH_3 + CH_2PhNO_2)
207	M-(CH_3 × 2 + CH_2PhNO_2)

From these results, the photoproducts for peak 2 was concluded to be *p,p'*-dinitrobibenzyl. EIMS spectra of the product for peak 4 shows a strong peak at *m/z* 373 in EIMS spectrum. The peaks of the fragments are summarized in Table II. These results indicate that the product for peak 4 is 9,10-dimethoxy-2-(*p*-nitrobenzyl)anthracene (DNBA). A similar photofragmentation has been observed for DNAS and CAS.

The mechanism of the photoreaction of *o*-nitrobenzyl esters involves insertion of an excited nitro group oxygen into a benzylic carbon-hydrogen bond. Subsequent rearrangment and cleavage generate *o*-nitrosobenzaldehyde and the corresponding organic acid from *o*-nitrobenzyl carboxylates[4] and sulfonates,[5] respectively. These photorearrangements contain a benzylic 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 the benzylic carbon-hydrogen bond to interact with it. As mentioned above, Busman et al. have reported[12] that *p*-nitrobenzyl sulfonates dissociate by the aid of an electron-donating photosensitizer to release the corresponding sulfonic acid, and the photodissociation proceeds via an electron transfer from the sensitizer to the sulfonate. NAS 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.

In contrast with the result obtained with NAS, no photolysis in degassed acetonitrile solution was observed for NAS0 and NAS2 under similar conditions. The different photochemical behavior of *p*-nitro-substituted derivatives may be due to the stability of the resulting radical by delocalizing through benzene ring. The large stabilization of the radical formed by the C-O bond cleavage probably favors the observed fragmentation. The absence of photodissociation of NAS0 and NAS2 indicates the importance of the stability of resulting *p*-nitrobenzyl radical.



Quantum Yields for Photodissociation (ϕ_{dis}) and for Photo-Acid Generation (ϕ_{acid}). Quantum yields for photodissociation and photo-acid generation of DNAS, NAS, and CAS were determined by irradiating the degassed acetonitrile solution at 436 and 365 nm at low conversion (less than 10%). The concentrations of the starting materials and AS were measured using HPLC. Quantum yields were estimated based on the absorbed dose. A typical plot of conversion of NAS vs absorbed dose is shown in Figure 5. As is shown in Figure 5 the photodissociation rate as the function of the absorbed dose are plotted as a single straight line. In addition, the quantum yield for photodissociation is independent of the concentration of NAS, suggesting that the photodissociation of NAS proceeds via an unimolecular reaction. In other words, the possibility of the intermolecular electron transfer from the excited 9,10-dimethoxyanthracene moiety to *p*-nitrobenzyl moiety of other NAS molecules may be eliminated. Furthermore, the results listed in Table III show that ϕ_{dis} and ϕ_{acid} are independent of the excitation wavelength.

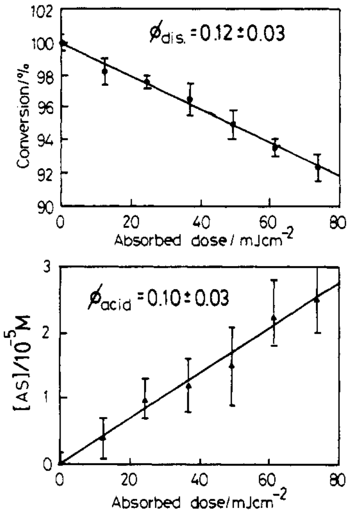


Figure 5. A plot of conversion of NAS (above) and concentration of acid generation (below) vs absorbed dose with excitation at 436 nm in degassed acetonitrile solution.

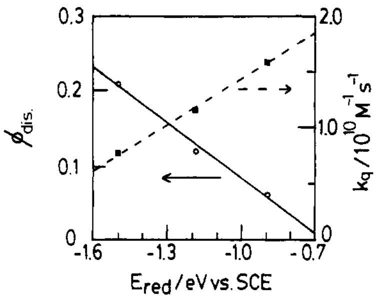


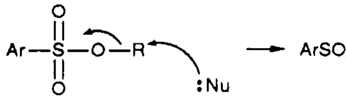
Figure 6. Dependence of ϕ_{dis} (circles, values obtained with excitation at 436 nm) and k_q (squares) on $E_{1/2}{}^{red}$ of PST's.

TABLE III: Quantum Yields for Photodissociation and Photo-Acid Generation of DNAS, NAS, and CAS with Excitation at 436 and 365 nm

	436-nm irradiation		365-nm irradiation	
	ϕ_{dis}	ϕ_{acid}	ϕ_{dis}	ϕ_{acid}
DNAS	0.06 ± 0.01	0.04 ± 0.01	0.06 ± 0.01	0.05 ± 0.01
NAS	0.12 ± 0.03	0.10 ± 0.03	0.14 ± 0.04	0.11 ± 0.02
CAS	0.21 ± 0.04	0.19 ± 0.03	0.20 ± 0.02	0.18 ± 0.03

The relationships of k_q and ϕ_{dis} with $E_{1/2}{}^{red}$ in Figure 6 indicate that the fluorescence quenching rate constant (k_q) increases with increase in the reduction potential, while the quantum yield (ϕ_{dis}) of photodissociation is decreased with increase in the reduction potential. A comparison of these data shows that the dependence of k_q and ϕ_{dis} on $E_{1/2}{}^{red}$ is the reverse. The rate constant for quenching is governed by the substituents on the para position of benzyl group. The order (CN < NO_2 < di-NO_2) found for the fluorescence quenching is different from that (CN > NO_2 > di-NO_2) obtained for quantum yield of photodissociation.

In view of electron-transfer mechanism, the higher the $E_{1/2}{}^{red}$ value is, the more efficiently electron transfer occurs. On the other hand, in the cleavage of sulfonic esters, for example, alkyl arenesulfonates undergo nucleophilic attack at alkyl carbon because the weak basicity of sulfonate anions, $ArSO_3^-$, makes them good leaving groups:



R = alkyl group; :Nu = nucleophile

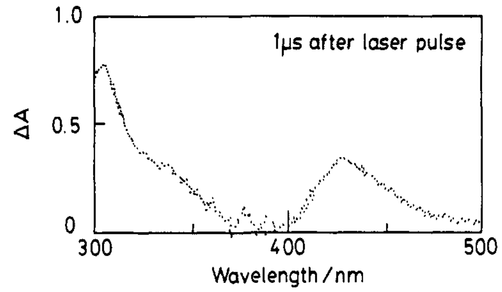


Figure 7. Transient absorption spectrum of EAS (5.0×10^{-4} M) in the presence of PNT (1.0×10^{-2} M) in oxygen-free acetonitrile solution at 1 μs after a 355-nm laser pulse excitation.

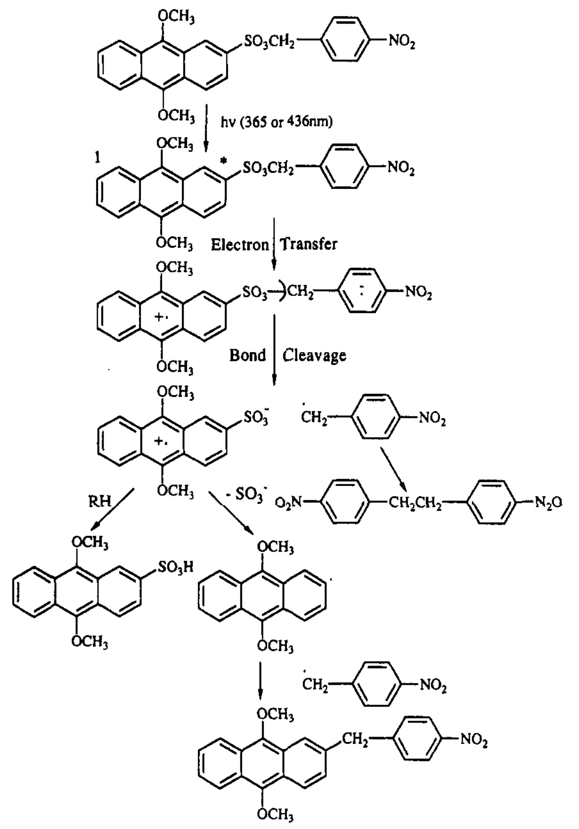
In contrast to carboxylic esters, it is well-known that sulfonate ester cleavage occurs between the alkyl group carbon and oxygen and not between sulfur and oxygen. From the analogy to this fact, the difference of photochemical reactivity of para-substituted derivatives might reflect the feasibility of C–O bond cleavage in contrast to the reported fact that the heterolytic cleavage of the sulfonate S–O bond of the tosylate ester radical anion produces a *p*-toluenesulfonyl radical and alkoxide ion in solution.[9]

The efficiency of the fragmentation of the sulfonate esters is dependent upon the electron affinity of benzyl moiety. With increase in the electron-withdrawing ability of substituents, the quantum yields for photodissociation and photo-acid generation decrease. Cleavage of substituted benzyl C–O bond following electron transfer presumably takes place more easily with benzyl moiety having moderately weak electron affinity.

Laser Flash Photolysis. Laser flash photolyses were performed in deaerated acetonitrile solution by irradiating with 355-nm laser pulse at ambient temperature. No transient absorption spectrum was observed with direct excitation of EAS (5.0×10^{-4} M), indicating that intersystem crossing of ^{1}EAS* to its triplet state may not proceed with measurable yield. The transient absorption spectrum of EAS (5.0×10^{-4} M) in the presence of PNT (1.0×10^{-2} M) in acetonitrile at 1 μs after the laser flash is shown in Figure 7. The absorption band at 340 nm is assigned to PNT radical anion by identification with the spectrum independently generated by radiolysis.[17] The bands at 310 and 425 nm are assigned to the absorption by EAS radical cation. This interpretation is supported by the fact that electron transfer leads to formation of radical anion and cation. This assignment is also supported by the fact that the excitation of EAS (5.0×10^{-4} M) in the presence of *p*-dicyanobenzene (1.0×10^{-2} M) as an electron acceptor gave the transient absorption bands at 310 and 425 nm and the absorption of *p*-dicyanobenzene radical anion whose spectrum has already been assigned (λ_{max} = 340 and 430 nm).[18]

Time-resolved absorption spectra of NAS exhibit both a strong absorption at 310 and 425 nm and a broad absorption around 340 nm (Figure 8). The former species are assigned to 9,10-dimethoxyanthracene-2-sulfonate radical cation and the latter are assigned to *p*-nitrobenzyl radical anion on the basis of above results. Both of these bands appear instantaneously after the laser pulse and then the absorption bands at 310 and 425 nm decay following a first-order rate law with a lifetime of 3.6 ± 0.7 μs. It was difficult to analyze the decay kinetics of the absorption band around 340 nm accurately because of the small signal changes. However, these experiments show that intramolecular electron transfer from the 9,10-dimethoxyanthracene moiety to the *p*-nitrobenzyl moiety leads to formation of 9,10-dimethoxyanthracene-2-sulfonate radical cation and *p*-nitrobenzyl radical anion.

SCHEME I



The time-resolved spectroscopic behaviors of DNAS, CAS, NAS0, and NAS2 are analogous to those of NAS. Transient absorption monitored at 425 nm in DNAS, CAS, NAS0, and NAS2 decay completely with first-order kinetics to afford a lifetime of 4.8 ± 0.5, 2.7 ± 0.5, 5.8 ± 0.6, and 6.0 ± 0.6 μs, respectively. Laser flash photolysis of ClAS and BAS in acetonitrile fails to produce the transient intermediates, suggesting that these compounds may not undergo intramolecular electron transfer and the results of the transient spectrum are consistent with those of the fluorescence quenching.

Considering both the steady-state and the transient results, the rate of bond cleavage may be competitive with that of back electron transfer, and the 9,10-dimethoxyanthracene-2-sulfonate radical cation lifetime (τ) for DNAS, NAS, and CAS depends on the rates of back electron transfer (k_{-et}) and dissociation (k_{dis}) and is given by eq 3. According to the fact that NAS0 and NAS2

$$\tau = 1/(k_{-et} + k_{dis}) \qquad (3)$$

are not photochemically dissociated, i.e., $k_{dis} = 0$, the lifetime of these intermediates corresponds to reciprocal of rate constant for back electron transfer. With the assumption that back-electron-transfer rate constant is of similar value for NAS, NAS0, and NAS2,[19] the rate constant k_{dis} in NAS is given by eq 4, where

$$k_{dis} = 1/\tau_{NAS} - 1/\tau_{NAS0} \qquad (4)$$

τ_{NAS} and τ_{NAS0} are the lifetime of NAS and NAS0, respectively.

---

(17) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988; p 329.

(18) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988; p 240.

(19) The free energy change for the back electron transfer was calculated by $\Delta G_{-et} = E_{red} - E_{ox}$ (eq 5) in which E_{red} and E_{ox} are reduction potential of acceptor and oxidation potential of donor, respectively. In NAS, NAS0, and NAS2 molecules, ΔG_{-et} values should be the same because of having the same redox potentials in these three molecules. From these considerations, the back-electron-transfer rate constant may be also the same value for these molecules. With the assumption that the lifetime of the NAS0 and NAS2 intermediates corresponds to reciprocal of back-electron-transfer rate constant, we found a remarkably slow rate constant for back electron transfer (1.7×10^5 s^{-1}). This slow rate constant may be due to activation barriers and configuration requirements, although this is not conclusive. As for slow electron transfer, it was reported that the intramolecular electron transfer rate constant for linked viologen–quinone molecules in water or SDS micellar solution is surprisingly low (1.4×10^3 s^{-1}) by means of the electron pulse radiolysis technique. Burn, A. M.; Hubig, S. M.; Rogers, M. A. J.; Wade, W. H. *J. Phys. Chem.* **1990**, *94*, 3869. Since the mechanism for the slow back electron transfer is still a matter of controversy, we are continuing our investigation.

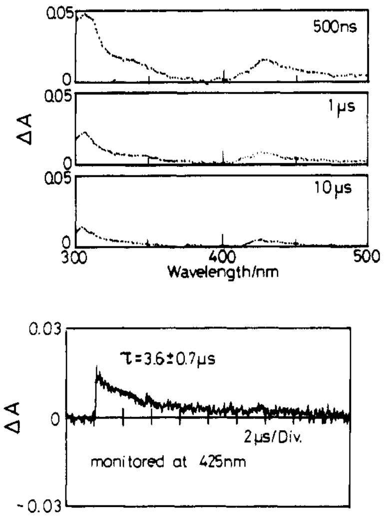


Figure 8. Time-resolved absorption spectra of NAS after 355-nm laser excitation in degassed acetonitrile solution (above). Time dependence of absorbance change (ΔA) monitored at 425 nm for NAS in acetonitrile.

Using eq 4[20] and the lifetime given above, we obtain $k_{dis} = (1.1 \pm 0.5) \times 10^5$ s^{-1}.[21]

Scheme I is proposed for the photodissociation of NAS, based on the steady-state and transient results.

NAS undergoes an intramolecular electron transfer from the excited singlet state of 9,10-dimethoxyanthracene moiety to the *p*-nitrobenzyl moiety to generate the radical ions which can either revert to starting material or undergo carbon–oxygen bond cleavage to ultimately give 9,10-dimethoxyanthracene-2-sulfonic acid, *p,p'*-dinitrobibenzyl, and 9,10-dimethoxy-2-(*p*-nitrobenzyl)anthracene after extrusion of SO_3^-.[22,23]

Conclusions

The work reported here showed that 3',4'-dinitrobenzyl, *p*-nitrobenzyl, and *p*-cyanobenzyl 9,10-dimethoxyanthracene-2-sulfonates photodissociate by the direct excitation of the 9,10-dimethoxyanthracene moiety, while *p*-chlorobenzyl, benzyl, *p*-nitrophenyl, and *p*-nitrophenethyl 9,10-dimethoxyanthracene-2-sulfonates are not photodissociated. Photodissociation proceeds via an intramolecular electron transfer from the excited singlet state of the 9,10-dimethoxyanthracene moiety to the substituted benzyl moiety. Intramolecular electron transfer induced bond cleavage was observed for 3',4'-dinitrobenzyl, *p*-nitrobenzyl, and *p*-cyanobenzyl 9,10-dimethoxyanthracene-2-sulfonates giving 9,10-dimethoxyanthracene-2-sulfonic acid.

It was found that the photochemical behavior of para-substituted benzyl 9,10-dimethoxyanthracene-2-sulfonates is governed by three factors: an intramolecular electron transfer, feasibility of sulfonate C–O bond cleavage, and stability of the resulting benzyl-type radical. The sulfonic acid formed by irradiation–electron transfer–bond cleavage sequence may be useful for the initiation of cationic polymerization.

Registry No. DNAS, 137626-72-3; NAS, 121172-98-3; CAS, 137626-73-4; ClAS, 137626-74-5; BAS, 131290-09-0; NASO, 137647-71-3; NASZ, 137626-75-6; EAS, 132246-14-1; DAS, 52212-90-5; DNBA, 132228-29-6; PNT, 99-99-0; DNT, 610-39-9; PCT, 104-85-8; PClT, 106-43-4; toluene, 108-88-3; *p,p'*-dinitrobibenzyl, 736-30-1.

Supplementary Material Available: ^1H NMR data of all para-substituted benzyl 9,10-dimethoxyanthracene-2-sulfonates and *p,p'*-dinitrobibenzyl; EIMS of AS, *p,p'*-dinitrobibenzyl, NAS, DNBA, DNAS, 9,10-dimethoxy-2-(3',4'-dinitrobenzyl)anthracene, CAS, and 9,10-dimethoxy-2-(*p*-cyanobenzyl)anthracene; a plot of conversion of CAS and DNAS and concentration of acid generation vs absorbed dose with excitation at 436 nm in degassed acetonitrile (19 pages). Ordering information is given on any current masthead page.

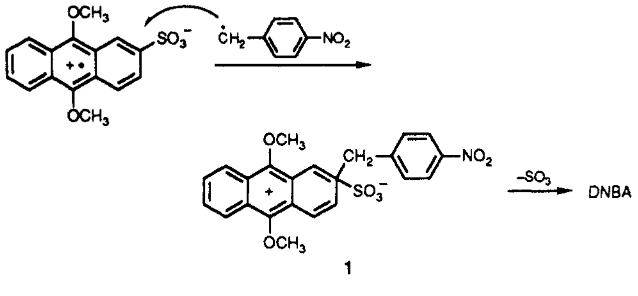
---

[20] If we calculated the rate constant for dissociation using τ_{NAS2} (intermediate lifetime for NAS2), we obtained the same value for k_{dis} (1.1×10^5 s^{-1}).

[21] The obtained values for rate constant of dissociation $k_{dis} = 1.1 \times 10^5$ s^{-1} and lifetime of radical cation $\tau = 3.6$ μs for NAS are incompatible with the quantum yield for photodissociation $\phi_{dis} \sim 0.12$ if ϕ_{dis} is expressed as $\phi_{dis} = k_{dis}\tau = 0.40$. The quantum yield obtained from steady-state irradiation experiment is not consistent with the above value estimated from transient results. This discrepancy may be due to the recombination process between 9,10-dimethoxyanthracene-2-sulfonate radical and the *p*-nitrobenzyl radical.

[22] Photorearrangement and desulfonation have been observed in α-sulfonyloxy enones. Feigenbaum, A.; Pete, J. P.; Scholler, D. *J. Org. Chem.* **1984**, *49*, 2355. Judging from photoproduct analysis, an extrusion of SO_3^- may be involved in this photodissociation process. A biphotonic process involving this extrusion may be ruled out because of the low conversional irradiation (less than 10%) and direct observation of DNBA from the initial reaction step in the liquid chromatogram.

[23] Another mechanism for the formation of DNBA, in which direct coupling of 9,10-dimethoxyanthracene-2-sulfonate radical with the *p*-nitrobenzyl radical at the 2-position of the 9,10-dimethoxyanthracene moiety to give adduct **1** followed by extrusion of SO_3 leads to the formation of DNBA, could be a possible reaction pathway.



1