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Photolysis of Sodium Arenesulfonates in Alkaline Dimethyl Sulfoxide Solutions[1,2]

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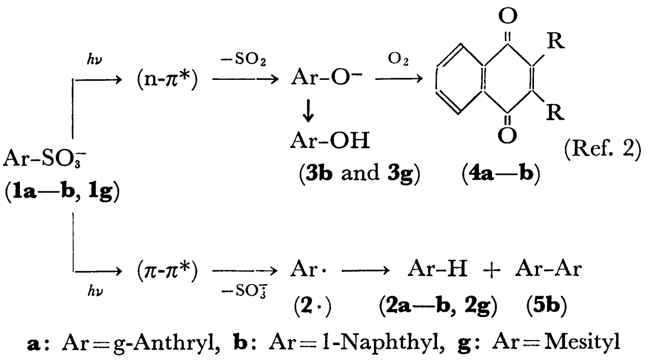
Synopsis. Photolysis of arenesulfonates in alkaline DMSO under air gave the corresponding desulfonation products, arenes, presumably *via* the π-π* excited triplet state.

With respect to the relationship between the photochemical behavior and electronic configuration (n-π* or π-π*) of the excited states of the arenesulfonates, a report was given on a new photoelimination of SO_2 (desulfonylation) of sodium 9-anthracene-, 1-naphthalene-, and mesitylene-sulfonates (**1a**—**b** and **1g**) *via* n-π* excited states, along with photoelimination of SO_3 (desulfonation) *via* π-π* excited states.[2] This seems to be the first example of the photodesulfonylation of sulfonic acids. Ogata *et al.*[3] reported on a photochemical reaction of benzenesulfonic acid in an aqueous alkaline solution, giving benzene (16%) and biphenyl (1%) and assumed to involve an initial radical fission of C–S bond giving Ph· and $\cdot SO_3H$ radicals. In this report we describe the photolysis of arenesulfonates (**1a**—**f**) in alkaline DMSO to give the corresponding arenes (**2**) by desulfonation almost as the sole product, presumably *via* the π-π* excited state.



a: Ar=g-Anthryl, **b**: Ar=1-Naphthyl, **g**: Ar=Mesityl

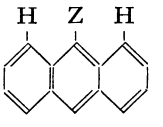
Solutions of the sulfonic acids (**1a**—**f**: *ca.* 5 mmol/l) in DMSO with aqueous 1 mol/l NaOH were irradiated with a low-pressure mercury lamp (30W) in quartz cells at tap-water temperature. The photoreactions were monitored by GLC. The results are summarized in Table 1. It was found that the photolysis of **1d**—**f** gives the parent hydrocarbons (**2**), photodesulfonation products, whereas **1a**—**c** yielded traces of a quinone (**4a**), or 1- or 2-naphthol (**3b** or **3c**) besides the parent hydrocarbons (**2a**—**b**) as main products. The results significantly differ from those obtained by the experiments in aqueous medium. In aqueous solutions, photodesulfonylation was distinctly observed for **1a**—**b**.[2]

$$\underset{\textbf{1a—f}}{\text{Ar-SO}_3^-} \xrightarrow[\text{DMSO/H}_2\text{O}]{h\nu} (\pi\text{-}\pi^*) \longrightarrow \underset{\textbf{2a—f}}{\text{Ar-H}}$$

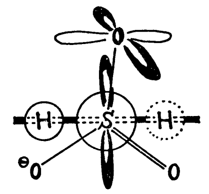
a: Ar=9-anthryl; **b**: Ar=1-naphthyl;
c: Ar=2-naphthyl; **d**: Ar=*o*-tolyl;
e: Ar=*p*-tolyl; and **f**: Ar=phenyl

DMSO accelerates reactions of anions in contrast with the reduced activity of hydrogen-bonded anions in protic solvents of comparative dielectric constants.[4] A (π-π*) excited state is more ionic than an appropriate (n-π*) excited state considered to be biradical. Hence, in DMSO, preference of the desulfonation ($-SO_3$) to the desulfonylation ($-SO_2$) can be expected.

Steric effect of the sulfonyl group on the peri H atom(s) (**1a**—**b**) or the *o*-methyl group (**1d**) can be expected for the present reactions by the analogy of a similar photoelimination of 9-nitro- and 9-carboxyanthracene (**6** and **7**),[5] whose nitro and carboxyl functional groups are not coplanar, not being able to resonate with aromatic rings[5] due to the steric hindrance with the peri H atoms. In contrast to **6** and **7**, the sulfonyl group is tetrahedral and the hindrance with the peri H atoms would not inhibit the coplanarity between one of the three S–O bonds and the aromatic nucleus as shown in formula **8**.



6: $Z=NO_2$
7: $Z=CO_2H$



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The data showing absence or presence of a trace of desulfonylation, obtained by changing the arene moieties attached to the sulfonyl groups for the purpose of differentiating the effect of peri H atom on the sulfonyl groups (*i.e.*, **1a**, **1b**, **1d**, and **1f**: also **1c** and **1e** were employed) supported the above interpretation on the steric effect.

It seems that the arene moieties determine the electronic configurations (n-π* or π-π*) of the S_1 and T_1 excited states of the arenesulfonates and also the reaction course. In contrast to the results in aqueous solution where desulfonylation and desulfonation of **1a** proceed *via* T_1 (n-π*) and T_2 (π-π*), respectively,[2] quenching experiments of **1a**—**c** in DMSO with 1,3-pentadiene on the fluorescence (not quenched), desulfonation (quenched), and desulfonylation (not quenched) revealed that desulfonation occurs *via* T and not S_1, and that desulfonylation might proceed *via* S_1 in DMSO. The results could be explained if the desulfonation and desulfonylation in DMSO proceed *via* T_1 (π-π*) and S_1 (n-π*), respectively. The relative stability of n-π* and π-π* excited states of **1a** might be inverted in water and in DMSO. Stern-Volmer plots of the other sulfonates with 1,3-pentadiene to the reaction products suggest that the desulfonation proceeds *via* T_1 excited states. Large viscosity of DMSO might cause relatively small rates of diffusion of 1,3-pentadiene, and no quenching of the fluorescence and desulfonylation. Measurement of viscosity of DMSO, however, eliminated the possibility, the observed diffusion constant, $k_{\text{dif.}}$ being 3.80×10^9 l/mol, which is in the range of that of the other organic solvents ($k^{25}_{\text{dif.}}=10^9$—$10^{10}$).[6]

Experimental

Fluorescence and phosphorescence spectra were recorded on a Hitachi MPF-2A spectrometer and GLC on a Yanagimoto Yanaco G-1800F gas chromatograph.

Materials. Sodium anthracene-9-sulfonate (**1a**) was prepared according to the method worked out by Yura and Oda.[7] Commercial sodium naphthalene-1- and -2-, *o*- and *p*-toluene-, and benzene-sulfonates (**1b**—**1f**), and commercial authenitic samples (**2a**—**f**, **3b**—**f**, **4a**—**b**, **4f**, and **5b**) were used. DMSO was distilled *in vacuo* from CaH_2. 1,3-Pentadiene was distilled before use in quenching experiments.

General Method for Photolyses of 1a—f. A solution of compound **1** (*ca.* 5 mmol/l) in DMSO (3 ml) and aqueous 1 mol/l NaOH (100 μl) was irradiated with a low pressure mercury lamp (30 W, Eikosha; P1L-30) in a quartz cell (*ϕ* 10 mm) at tap-water temperature (*ca.* 15 °C). The reaction was monitored at intervals by GLC. The product(s) was identified and the yields were determined by comparison with the corresponding authentic sample(s) on GLC (Table 1). GLC were afforded on 10% Silicone SE-GE-31 on Diasolid L (60—80 mesh) for **1a**, **1d**—**e**, and **1f**, and on Apiezon L on Diasolid L, 2.2 m for **1b**—**c**.

Solvent Effect of 1 on Fluorescence and Phosphorescence Spectra. The 0-0 bands of fluorescence and phosphorescence spectra of **1a**—**f** were measured in various solvents at 77 K in a quartz cell. The results showed the electronic configurations (π-π^* or n-π^*) of the S_1 and T_1 excited states of **1a**—**f** to be n-π^* for S_1 and π-π^* for T_1.

TABLE 1. PHOTOLYSIS OF $Ar{-}SO_3Na$ (**1a**—**f**) IN DMSO

1	Concn / mmol l^{-1}	Irrad. time / min	Yield/%[a] Ar-H (**2**)	Ar-OH (**3**)	Quinone (**4**)
1a	5.0	50	60	n.d.[b]	1.8
	5.0	60			2.1
	[2.9	180	54	n.d.	36.8][c]
	[5.0	180	27.9	n.d.	13.2][c]
1b	5.1	50	3.0	n.d.	n.d.
	5.1	900	16.5	trace	n.d.
1c	5.3	50	6.7	n.d.	n.d.
	5.3	60	8.4	trace	n.d.
1d	5.0	50	3.3	n.d.	n.d.
	5.0	1820	50.0	n.d.	n.d.
1e	5.0	50	2.9	n.d.	n.d.
	5.0	1820	45.0	n.d.	n.d.
1f	5.0	50	6.7	n.d.	n.d.
	5.0	360	50.0	n.d.	n.d.

a) Yields based on the starting material used. b) Not detected. c) Photolysis in aqueous solution (Ref. 2).

Quenching with 1,3-Pentadiene. (a) Quenching on fluorescence of **1** in DMSO (5.0 mmol/l) with various concentrations of 1,3-pentadiene (1.3, 2.9, 5.2, 10.3, and 20.7 mmol/l) was observed by means of the MPF-2A spectrometer at 25 °C. (b) Quenching on the products of desulfonation and/or desulfonylation from **1** in DMSO (5.0 mmol/l) with various concentrations of 1,3-pentadiene in air was observed by GLC. The $k_q\tau$ values were calculated from the slopes of the Stern-Volmer plots.[8] The fluorescence and desulfonylation of **1a**—**c** were not quenched, while desulfonation of **1a**—**c** was quenched, the $k_q\tau$ values being 2.6×10, 7.4×10, and 5.8×10, respectively.

Viscosity of DMSO. The viscosity of DMSO used was calculated from the equation

$$\begin{aligned}\eta_{\text{DMSO}} &= \eta_{H_2O}\cdot(\rho_{\text{DMSO}}\cdot t_{\text{DMSO}})/(\rho_{H_2O}\cdot t_{H_2O})\\ &= 8.004^{9)}\times1.1014^{10)}\times122.3/(0.9956756^{9)}\times61.0)\\ &= 17.751\ \text{(mpoise)},\end{aligned}$$

the values of $t^{30°}_{H_2O}$ and $t^{30°}_{\text{DMSO}}$ being measured with an Ostwald viscometer. From the results the diffusion constant $k_{\text{dif.}}$ in DMSO was estimated by

$$k_{\text{dif.}} = 8RT/3000\eta\ \text{(l/mol s)} = 3.80\times10^9\ \text{(l/mol s)},^{11)}$$

where

$$R = 8.314\times10^7\ \text{erg K}^{-1}\,\text{mol}^{-1}.$$

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11) An upper limit to the magnitude of the bimolecular quenching constant k_q of $k_q\tau$ calculated from the slope of Stern-Volmer plots is usually set by the rate of diffusion ($k_{\text{dif.}}$) of the excited state and quencher (1,3-pentadiene) into a solvent cage; see Ref. 6, p. 260.