Photolysis of Sodium Anthracene-9-sulphonate and Naphthalene-1-sulphonate in Aqueous Solutions[1]

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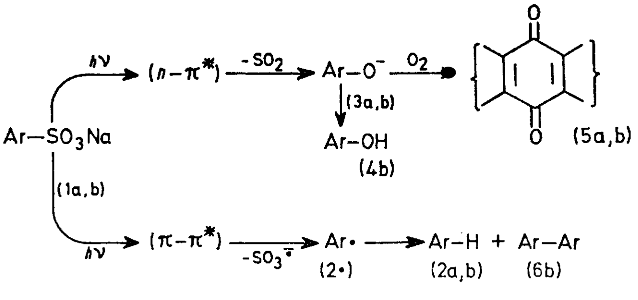
Summary Photolysis of sodium anthracene-9-sulphonate (**1a**) gave 9,10-anthraquinone (**5a**) *via* the 9-anthrol anion (**3a**) by desulphonylation ($-SO_2$; *via* the n–π^* state) and anthracene (**2a**) by desulphonation ($-SO_3$; *via* the π–π^* state) in aqueous solution; in contrast, sodium naphthalene-1-sulphonate (**1b**) gave mainly binaphthyl (**6b**) by desulphonation under similar conditions.

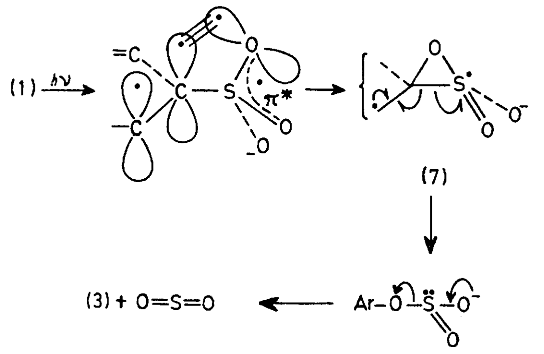
ONLY a little information is available on the relationship between the photochemical behaviour and electronic configuration (n–π^* or π–π^*) of the excited states of the arenesulphonates.[1,2] We now report the photolysis of the arenesulphonates (**1a**) and (**1b**), in which loss of SO_2 and loss of SO_3 may occur *via* n–π^* and π–π^* excited states, respectively, at the same time (Scheme).

A solution of (**1a**)[3] (2·9 mM) in water (180 ml) containing 1 ml of 1N NaOH was irradiated with an unfiltered 300 W high-pressure mercury lamp in air for 3 h at *ca.* 30 °C. After irradiation the precipitated products were filtered off and separated by preparative t.l.c. [silica gel PF_{254} (Merck), n-hexane] to give anthracene (**2a**) (54·3%) and 9,10-anthraquinone (**5a**) (36·8%). Photolysis of (**1b**) gave mainly binaphthyl (**6b**) (15·8%) together with 1-naphthol (**4b**) (trace), 1,4-naphthoquinone (**5b**) (trace), and naphthalene (**2b**) (1·5%). Most of the unchanged (**1b**) was recovered by t.l.c. (*ca.* 80%).



SCHEME. **a**; Ar = anthracen-9-yl **b**; Ar = 1-naphthyl

To gain insight into the reaction pathways of desulphonylation, an aqueous solution of (**1a**) (3·7 mM; 9 ml) containing 150 μl of 1N KOH was degassed and then irradiated at 15 °C in a quartz cell. After irradiation for 3 min the u.v. spectrum of the solution showed a maximum at 435 nm due to the 9-anthrol anion (**3a**).[4] However, when the solution was aerated this maximum disappeared readily and a new maximum appeared at 324 nm due to (**5a**). In contrast, upon irradiation in air the spectrum showed only the new maximum at 324 nm. Similar results were obtained for (**1b**).[†] These results show the presence of a phenolate anion (**3a**) or (**3b**) as an intermediate which may be generated *via* an oxathi-iran ring (**7**),[5] analogous to the oxiran and oxazirane intermediates proposed by Chapman and his co-workers in the photolyses of 9-anthroates[4] and 9-nitroanthracene.[6] In addition, the production of SO_2 was detected from each of the reaction mixtures.[7] The most important process in the desulphonylation is considered to be an intramolecular rearrangement to give (**7**) in the *n*–π* state.



Desulphonation by photolysis of the sulphonates may proceed *via* a radical pathway, which is supported by the generation of (**6b**) and (**2**).

Solvent effects on the fluorescence and phosphorescence spectra show that the electronic configurations of the S_1 and T_1 states of (**1a**) may be π–π* and *n*–π*, while, conversely, those of (**1b**) may be *n*–π* and π–π*, respectively.[‡]

It is interesting that the photoreactions of (**1a**) occurred from both S_1 (π–π*) and T_1 (*n*–π*) states with comparable rates while the photoreaction of (**1b**) occurred in the usual way, mainly from an excited state, T_1 (π–π*).

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[†] The yield of (**3b**) was calculated to be *ca.* 0·2% from the extinction coefficient, ε (7600) of (**3b**) at 332·5 nm (for ε; M. J. Kamlet, 'Organic Electronic Spectral Data', Vol. 1, Interscience, New York, 1960, p. 304).

[‡] λ_{0-0} in fluorescence and phosphorescence at 77 K of (**1a**): 406 and 459 nm (isopentane); 406 and 455 (ether); 406 and 406·5 (EtOH); 407 and 408 (Me_2SO); 416·5 and 417 (H_2O). Those of (**1b**): 330 and 430 (ether); 325·5 and 478·5 (EtOH).

[1] For previous paper in the series: Sulphonyl Compounds, see Y. Izawa and N. Kuromiya, *Bull. Chem. Soc. Japan*, 1975, **48**, 3197.

[2] For examples: O. P. Studzinskii, N. I. Yaischhev, N. N. Kravchenko, and A. V. El'tsov, *Zhur. org. Khim.*, 1975, **11**, 386; H. Inoue and M. Hida, *Yûki Gôsei Kagaku Kyôkai Shi*, 1974, **32**, 348 (*Chem. Abs.*, 1974, **81**, 129756c); J. D. Coyle, *Chem. Soc. Rev.*, 1975, **4**, 523.

[3] S. Yura and R. Oda, *Kogyo Kagaku Zasshi*, 1941, **44**, 731 (*Chem. Abs.*, 1948, **42**, 6792i).

[4] A. W. Bradshaw and O. L. Chapman, *J. Amer. Chem. Soc.*, 1967, **89**, 2372.

[5] L. Carlsen, N. Harrit, and A. Holm, *J.C.S. Perkin I*, 1976, 1404.

[6] O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thakarerry, *J. Amer. Chem. Soc.*, 1966, **88**, 5550.

[7] F. Feigl, 'Spot Tests in Inorganic Analysis', Elsevier-Maruzen, Tokyo, 5th edn., 1958, p. 307; [$ZnFe(CN)_5(NO)$] was used to detect gaseous SO_2, and [$Na_2Fe(CN)_5(NO)$] for sulphite anion.