

Photolysis of Methyl Benzenesulfonate in Methanol

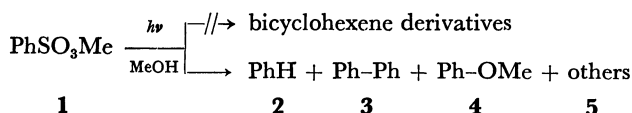
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The irradiation of methyl benzenesulfonate (**1**) in methanol undergoes a photolysis ($\Phi_{\text{disapp}} = 0.07 \pm 0.005$) leading to benzene (5—34%), biphenyl (9—15%), and anisole (trace), in place of a photo-addition of methanol to give bicyclohexene derivatives. The rate of desulfonation of **1** is only slightly affected by triethylamine. Stern-Volmer quenching by piperylene occurs and the results suggest a significant singlet participation in this photolysis.

It has been reported that irradiation of benzene and alkylbenzenes in alcohols gives alkoxybicyclo[3.1.0]hexenes by 1,3-addition of alcohols.¹⁻⁵⁾ During the course of studies of the photochemical behavior of various monosubstituted benzenes, *e.g.*, anisole, *N,N*-dimethylaniline, benzoates, and phenylacetates, in protic solvents, it was discovered that, upon irradiation in methanol, methyl benzenesulfonate readily undergoes a photolysis to give benzene, biphenyl, and anisole, in place of a photo-addition of methanol; the results will be reported in this paper.



Although photochemical reactions beginning with an initial Ph-S bond cleavage have been reported for diaryl sulfone, sulfoxide, and sulfide in benzene,⁶⁾ little information is available on the photochemical reactions of benzenesulfonates.

Results and Discussion

A solution of **1** (1.7 g, 0.04 M) in methanol was irradiated with an unfiltered 300 W high pressure Hg lamp for 17 hr at about 10 °C, with N₂ gas being bubbled into the mixture during irradiation. After irradiation the photoproducts were separated by column chromatography on silica gel, giving colorless crystals (0.2 g), mp 69—70 °C, and other products (**5**) (44 mg) containing solid and polymeric materials. On the basis of mp and spectroscopic properties, the crystal was identified to be biphenyl (**3**). No bicyclohexene derivatives were detected in the other photoproducts. On the other hand, the formation of benzene and anisole was evident from glc on Carbowax 20 M of the reaction mixture. Thus, it has been shown that the benzene sulfonate (**1**) is photo-

chemically desulfonated to give benzene, biphenyl, and anisole in methanol. Table 1 shows the relation between the yields of photoproducts and the initial concentration of **1**. As shown in Table 1, the relative yields of biphenyl to benzene decrease as the concentration of **1** is lowered. Furthermore, when a methanol solution of 0.7 mM of **1** was irradiated in a sealed quartz cell, after 30 min irradiation the spectrum of the solution became identical with that of benzene. That is, no biphenyl was detected in a dilute solution of **1**. These results suggest undoubtedly that benzene and biphenyl are derived from phenyl radicals produced by Ph-S bond cleavage. The quantum yield for disappearance of **1** was estimated to be 0.07 ± 0.005 at 254 nm at room temperature, using a ferrioxalate actinometer.

Quenching by 1,3-pentadienes was carried out in order to obtain information about an excited state of **1**. The photolysis of **1** is quenched by 1,3-pentadienes to give a linear Stern-Volmer plot, whose slope ($k_q\tau$) is 18.6 M⁻¹. Assuming that the quenching is diffusion-controlled, the value of τ , the mean life time of an excited state of **1**, may be estimated. Hence, assuming again the bimolecular diffusion-controlled rate constant for neat methanol at 20 °C to be 1.06×10^{10} M⁻¹ s⁻¹ on the basis of the Debye expression, the value of τ is calculated to be 1.8×10^{-9} s. On the other hand, the fluorescence of **1** in methanol is quenched by 1,3-pentadienes⁷⁾ to give a linear Stern-Volmer plot, whose slope ($k_q\tau_f$, fluorescence quenching constant) is 14.0 M⁻¹ at 30 °C. From the slope τ_f is estimated to be 1.1×10^{-9} s, which is in agreement with the value of τ . Thus, it seems that the photolysis proceeds *via* a singlet state rather than a triplet state of **1**.

In order to examine whether the present desulfonation is induced by a photochemical electron transfer (ETR)⁸⁾ from methanol to **1**, the photolysis was carried out in the presence of triethylamine, which is an efficient electron donor.⁹⁾ If ETR takes place, the relative rates of disappearance of **1** would increase with addition of triethylamine. As shown in Table 2, however, the relative rates are about unity. These facts suggest that an electron transfer from amine to **1** to give a radical anion (**6**) does not occur and/or that the sulfonate group is less able to

TABLE 1. PHOTOLYSIS OF METHYL BENZENESULFONATE (**1**) IN METHANOL USING 300W HIGH PRESSURE Hg LAMP

[1] M	Conv. (%)	Yield (%) ^{a)}			Product ratio [3]/[2]
		2	3	4	
0.5	14	5.1	9.9	trace	1.9
0.1 ^{b)}	38	8.0	9.1	trace	1.1
0.2	30	21.9	15.3	trace	0.7
0.1	46	34.4	10.1	trace	0.3
0.05	43	24.0	12.0	trace	0.5

a) Determined by glpc after 20 hr, based on **1** consumed. b) 30W Low pressure Hg lamp.

TABLE 2. EFFECT OF NEt₃ ON THE PHOTO-DESULFONATION OF **1**

[NEt ₃]/[1] (Molar ratio)	0	0.5	1.0	2.0
Relative rate ^{a)} (k/k_0)	1.00	1.00	0.98	1.07

a) Relative rates (k/k_0) of disappearance of **1** were determined by comparison with the rate (k_0) without triethylamine.

Quenching of Photolysis. The solutions of 7.1 mM **1** in

methanol with or without piperylenes were placed in closed 12 mm o.d. quartz tubes. The tubes were then irradiated on a merry-go-round apparatus using 300 W high pressure Hg lamp without filter at about 20 °C for 5 hr. Five concentrations (0.7—5.6 mM) of piperylenes, in addition to blanks containing no piperylenes, were used for the Stern-Volmer plot. The amount of consumed **1** in the tubes was determined spectrophotometrically.

Fluorescence Quenching of 1. A methanol solution of **1** showed a structureless fluorescence spectrum with a maximum at 289 nm. A stock solution of **1** in methanol (35.8 mM) was prepared and varying amounts of 1,3-pentadienes were added to aliquots of the stock; [dienes]=6.9—34.5 mM. Six solutions were used for the quenching experiment. The fluorescence spectra were recorded at room temperature (about 30 °C) and the relative intensities at 289 nm in the absence and presence of the dienes (I_0/I) were plotted with concentration of the dienes. A linear Stern-Volmer plot was obtained.

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