# Photolysis of Methyl Benzenesulfonate in Methanol

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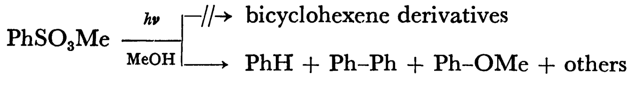
The irradiation of methyl benzenesulfonate (**1**) in methanol undergoes a photolysis ($\Phi_{disapp}=0.07\pm0.005$) leading to benzene (5—34%), biphenyl (9—15%), and anisole (trace), in place of a photo-addition of methanol to give bicyclohexene derivatives. The rate of desulfonation of **1** is only 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.



$$\mathrm{PhSO_3Me}\ \xrightarrow[\mathrm{MeOH}]{h\nu}\ \begin{cases}\not\to \text{bicyclohexene derivatives}\\ \to \mathrm{PhH} + \mathrm{Ph\text{-}Ph} + \mathrm{Ph\text{-}OMe} + \text{others}\end{cases}$$

**1** **2** **3** **4** **5**

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 $N_2$ 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 photochemically 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 $0.07\pm0.005$ at 254 nm at room temperature, using a ferrioxalate actinometer.

Table 1. Photolysis of methyl benzenesulfonate (**1**) in methanol using 300W high pressure Hg lamp

| [1] M | Conv. (%) | Yield (%)[a] | | | Product ratio |
|---|---|---|---|---|---|
| | | **2** | **3** | **4** | [3]/[2] |
| 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.

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 $\tau$, 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 $1.06\times10^{10}\ M^{-1}\ s^{-1}$ on the basis of the Debye expression, the value of $\tau$ is calculated to be $1.8\times10^{-9}$ s. On the other hand, the fluorescence of **1** in methanol is quenched by 1,3-pentadienes[7] 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 $\tau_f$ is estimated to be $1.1\times10^{-9}$ s, which is in agreement with the value of $\tau$. Thus, it seems that the photolysis proceeds *via* a singlet state rather than a triplet state of **1**.

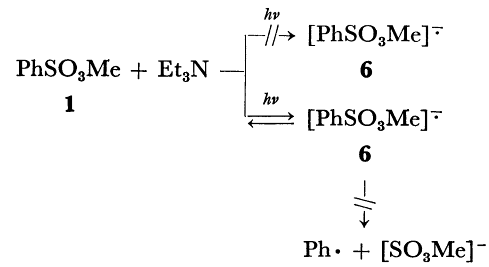
In order to examine whether the present desulfonation is induced by a photochemical electron transfer (ETR)[8] from methanol to **1**, the photolysis was carried out in the presence of triethylamine, which is an efficient electron domor.[9] If ETR takes place, the relative rates of disappearance of **1** 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 2. Effect of $NEt_3$ on the photo-desulfonation of **1**

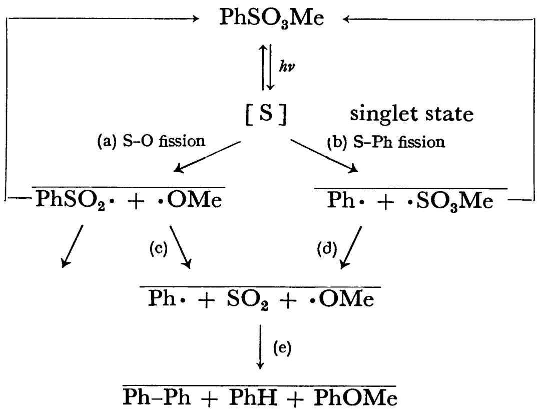
| | | | | |
|---|---|---|---|---|
| $[NEt_3]/[1]$ (Molar ratio) | 0 | 0.5 | 1.0 | 2.0 |
| Relative rate[a] ($k/k_0$) | 1.00 | 1.00 | 0.98 | 1.07 |

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

leave as an anion from **6**. This result implies that a similar ETR does not occur for methanol, since the $I_p$ (10.85 eV[10]) of methanol is higher than that (7.50 eV[10a]) of the amine.



On the basis of these facts, the possible reaction pathways of photo-desulfonation of **1** to give benzene, biphenyl, and anisole can be postulated as follows:



Scheme 1.

Step (c), however, may be less probable, since a desulfonation of $PhSO_2\cdot$ radical to give $Ph\cdot$ radical may be significantly endothermic,[11] and it is known that two arylsulfonyl radicals react with each other to produce a sulfonic anhydride and thiosulfonate *via* a mixed sulfonic sulfinic anhydride.[12] Accordingly, the reaction pathway (b→d→e) beginning with the homolysis of Ph-S bond appears to play an important role in the photolysis of **1** leading to benzene, biphenyl, and anisole.

## Experimental

The glpc analysis was carried out on a Yanagimoto GC-1800 apparatus equipped with hydrogen-flame detectors. The IR spectra were measured with a JASCO IR-G grating instrument and the UV spectra were recorded with a Shimadzu UV-200 spectrophotometer. The NMR data were obtained with a JEOL JNM MH-100 spectrometer. Monochromatic irradiation (254 nm) was performed with a monochrometer of the Hitachi MPF-2A type fluorescence spectrophotometer (150 W Xe lamp).

*Materials.* Methyl benzenesulfonate (**1**) was prepared from benzenesulfonyl chloride and methanol according to the known procedure,[13] bp 110—114 °C/1.5—3 mmHg, $\lambda_{\max}^{\mathrm{MeOH}}$ ($\varepsilon$): 252.5 (390), 257.5 (680), 264.8 (980), and 272 (85) nm; $\delta$ ($CCl_4$): 3.70 (s, $-CH_3$) and 7.42—8.00 (m, -Ph); 1365 and 1189 cm$^{-1}$ (liq. film, $-SO_2-$). Methanol was dried over Mg metal and distilled. Triethylamine was dried over Na metal and distilled. Silica gel Woelm containing an inorganic fluorescent indicator was used for column chromatography and silica gel $PF_{254}$ containing $CaSO_4$ (Merk) was used for tlc. Piperylene (a mixture of isomers) of a g.r. grade supplied by the Nakarai Chemicals, Ltd. was distilled ,bp 41.8—42.0 °C. Other reagents were of the first grade commercial materials.

*Preparative Scale Irradiation.* The irradiation was carried out using an immersion type Halos 300W high pressure Hg lamp without filter. A solution of **1** (1.7 g) in methanol (250 ml) was placed in a reaction vessel, which was immersed in a water-bath, equipped with a $N_2$ gas inlet, thermometer, and a condensor. The solution was irradiated under $N_2$ at about 10 °C for 17 hr. After irradiation, the reaction mixture was carefully neutralized with aqueous sodium hydroxide solution and then evaporated under reduced pressure below 30 °C. Separation of photo-products was carried out by liquid chromatography with silica gel column (Nylon column, diameter: 3 cm, height: 35 cm), using a mixed solution of hexane and acetone (50: 1) as a eluent, to give **3** (0.2 g), brownish viscous liquid **5** (44 mg), and **1**. Furthermore, in order to detect the presence or absence of bicyclohexene derivatives, the viscous liquid (**5**) was then subjected to silica gel tlc using 50: 1 hexane–acetone solution as a developer. Three products were isolated and subjected to IR and NMR analyses. However, the existence of bicyclohexene derivatives could not be demonstrated.

*Irradiation for Analtyical Purposes.* The solutions (5 ml) of 0.05—0.5 M **1** in methanol were placed in 12-mm o.d. quartz tubes, and these were capped with polyethylene-stopples after flushing with $N_2$ gas at 0 °C for 5 min. A Halos 300 W high pressure Hg lamp with a water cooling quartz jacket was used without filter. The tubes and lamp were placed in a water-bath and irradiation was carried out at about 10 °C for 20 hr. After irradiation, the analysis of the reaction mixtures was done by means of glpc. The agreement of the retention times of the peaks with those of authentic samples established their identity. The conditions for glpc were as follows: 2 m×3 mm column of 13% Apiezon L on 60—80 mesh Diasolid L at 50 °C for benzene (**2**) and at 100 °C for anisole (**4**); 1 m×3 mm column of 5% PEG 20 M on 60—80 mesh Diasolid L at 130 °C for methyl benzenesulfonate (**1**) and biphenyl (**3**). The yields were estimated by glpc on the basis of **1** consumed.

*Quantum Yield.* These experiments were performed with 254 nm radiation from the monochrometer at room temperature and the quantum yields were determined by means of a liquid phase actinometer using potassium ferrioxalate. Cylindrical ($\phi$=2 cm) fused-quartz cells with optically flat windows were used for the photolysis (path length 2 cm, 5 ml) and actinometer (path length 5 cm, 15 ml) cells. A solution of 0.4 mM **1** in methanol was placed in the photolysis cell; irradiation was started by opening a shutter and continued for 1 hr. The actinometer was photolyzed simultaneously. Photolysis was carried to 5% or less conversion and the number of molecules of consumed **1** in the cell was determined spectrophotometrically. The quantum yield was the average of the two analyses.

*Effect of Added Triethylamine on the Photolysis.* The solutions of 0.7 mM **1** and 0—1.4 mM triethylamine in methanol were flushed with $N_2$ gas at 0 °C for 5 min and sealed in 12 mm o.d. quartz tubes. The tubes were then irradiated on a merry-go-round apparatus using 30 W Halos low pressure Hg lamp without filter at room temperature for 10 min. The amount of consumed **1** in the tubes was determined spectrophotometrically. The relative rates ($k/k_0$) of disappearance of **1** were determined by comparison with the rate ($k_0$) without amine.

*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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