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The Photochemical Sulfoxidation of Alkylbenzenes[1]

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The photochemical sulfoxidation of alkylbenzenes with sulfur dioxide and oxygen in acetic anhydride to give the corresponding sulfonic acids has been studied. The sulfoxidation of the higher alkylbenzenes, such as that with a side-chain of trimerized propylene (ABTP) with a total average mol. wt. of 253 and that with a linear side-chain (ABL) with an average mol. wt. of 254, and also that of ethylbenzene give, by homolytic reaction, the corresponding sulfonic acids substituted at their side-chains. In contrast, the sulfonation of *m*-xylene occurs at the benzene ring by ionic reaction, while toluene gives a very poor yield of sulfonic acid. The surface activities of the resulting sodium alkylbenzenesulfonate with their sulfonate group at the side-chain were comparable to the corresponding ring-substituted sulfonates.

The present authors have previously postulated, for the photochemical sulfoxidation of *n*-hexane, a mechanism involving the simultaneous steps of a radical chain reaction and a molecular mechanism; the primary process seems to involve two processes, i. e., energy transfer and hydrogen abstraction with excited sulfur dioxide,[2] the ratio of reactivities of C–H bonds (primary : secondary : tertiary) being 1 : 0.8—1.3 : 3.2—6.2.[3]

It is well-known that the sulfonation of alkylbenzenes with sulfur trioxide occurs via an electrophilic attack on the benzene ring. However, little is known about the photochemical sulfoxidation of alkylbenzenes, though perhaps they are attacked at the side-chain via a radical mechanism. At the same time, the ionic sulfonation with sulfur trioxide is conceivable because of the possible photooxidation of sulfur dioxide to sulfur trioxide.[4]

The present paper will deal with the results obtained in a study of the photochemical sulfoxidation of various alkylbenzenes, such as toluene, ethylbenzene, *m*-xylene, alkylbenzene with a side-chain of trimerized propylene (ABTP) and alkylbenzene with a linear side-chain (ABL).

Experimental

Materials.—ABTP was purified by the fractionation of commercial material, b. p. 80°C/3 mmHg, n_D^{25} 1.4887, average mol. wt., 253, with an alkyl chain of 12—13 carbon atoms. ABL was of a commercial grade, prepared by the Friedel-Crafts reaction of chlorinated paraffin with benzene, b. p. 309—325°C, average mol. wt., 254, with an alkyl chain of 11—16 carbon atoms. The mol. wt. was determined cryoscopically in a benzene solution. Toluene, b. p. 109—110°C, ethylbenzene, b. p. 135—136°C; n_D^{18} 1.4971, and *m*-xylene, b. p. 138—138.5°C, were purified by the fractionation of commercial materials of an extra pure grade. Acetic anhydride, carbon tetrachloride, sulfur dioxide, oxygen, sodium *o*-toluenesulfonate and sodium *p*-toluenesulfonate were commercial materials and were used without further purification.

Sodium toluene-ω-sulfonate was prepared by the same procedure as was used by Johnson and Ambler.[5] Sodium *m*-xylene-ω-sulfonate was prepared by the reaction[5] of ω-bromo-*m*-xylene,[6] b. p. 117—120°C/60 mmHg, with anhydrous sodium sulfite. Sodium *p*-ethylbenzenesulfonate was prepared by the reaction of ethylbenzene with concentrated sulfuric acid at 136°C; the m. p. of its sulfonamide was 106—108°C (lit.[7] m. p. 109°C). Sodium 2, 4-dimethylbenzene-1-sulfonate was prepared by the reaction of *m*-xylene with concentrated sulfuric acid at 100—110°C; the m. p. of its acid was 58—59°C (lit. m. p. 59.8°C[8] and 63—64°C).[9] The sodium sulfonates with a ring-sulfonate group were prepared by the sulfonation of the corresponding ABTP and ABL with concentrated sulfuric acid.

The ultraviolet spectra were measured by a Shimadzu automatic recording spectrophotometer (Type SV-50A), and the infrared spectra, by a Perkin-Elmer grating infrared spectrophotometer (Type 337).

The Photochemical Sulfoxidation of Ethylbenzene.—Ethylbenzene (1.6 g., 0.015 mole), acetic anhydride (0.1 ml.), and carbon tetrachloride (150 ml.) were placed in a quartz reaction vessel. Sulfur dioxide (9 l./hr.) and oxygen (4.5 l./hr.) were introduced simultaneously into the ethylbenzene solution (0.01 mol./l.) at 17—22°C under the irradiation of ultraviolet light (Toshiba HSL-100 UV) for 12 hr. After the irradiation had ended, the resulting sulfonic acid was extracted with hot water (ca. 60 ml.). The extract was then neutralized with sodium carbonate and

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1) Contribution No. 85. Presented in part at the 4th Symposium on Oil Chemistry, Tokyo, October, 1965.

2) Y. Ogata, Y. Izawa and T. Tsuda, *Tetrahedron*, **21**, 1349 (1965).

3) Y. Ogata, Y. Izawa and T. Tsuda, This Bulletin, **38**, 1984 (1965).

4) A. Coehn, *Z. Elektrochem.*, **13**, 545 (1907).

5) T. B. Johnson and J. A. Ambler, *J. Am. Chem. Soc.*, **36**, 381 (1914).

6) E. F. G. Atkinson, *J. Chem. Soc.*, **91**, 1696 (1907).

evaporated to dryness on a water bath, and the residue was further dried under a vacuum. The residue was then extracted with ethanol to give sodium ethylbenzenesulfonate as a light yellow solid (0.06 g.; 2.2%).

The Photochemical Sulfoxidation of Toluene.—Toluene (21.8 g., 0.24 mol.) and acetic anhydride (1.3 ml.) were placed in a quartz vessel. Sulfur dioxide (2 l./hr.) and oxygen (0.7 l./hr.) were then introduced simultaneously into the solution at 18—20°C under the irradiation of ultraviolet light for 12 hr. After the irradiation had ended, a work-up similar to the sulfoxidation of ethylbenzene gave a trace of a product; its infrared spectrum showed absorptions at 1135, 1015 and 650 cm^{-1} due to characteristic absorption bands of sulfonate.

The Photochemical Sulfoxidation of Alkylbenzenes.—A solution of ABTP (10 g., 0.04 mol.) and acetic anhydride (0.3 ml.) in carbon tetrachloride (100 ml.), after being dried with Drierite, was placed in a quartz vessel. Sulfur dioxide (7 l./hr.) and oxygen (3.5 l./hr.) were introduced simultaneously into the solution at 17—20°C under the irradiation of ultraviolet light (Toshiba H-400PUV) for 12 hr. After the irradiation had ended, water (ca. 1 ml.) was added to the reaction mixture and it was stirred at 40—50°C for 1 hr. in order to complete the decomposition of the acetyl phenylalkanesulfonyl peroxide. The resulting sulfonic acid was extracted with hot water (ca. 60 ml.), and isopropanol (ca. 60 ml.) was added to the extract. The solution was then neutralized with sodium carbonate, and further sodium carbonate added to the solution until the separated aqueous layer was saturated at 40°C. The separated isopropanol layer was dried with anhydrous sodium sulfate and evaporated to dryness on a water bath, and the residue was further dried under a vacuum. The yield of sodium sulfonate was about 0.4 g. (3%). The crude sulfonate was extracted with ethanol to give sodium sulfonate of ABTP (0.16 g.).

The sulfoxidation of ABL was carried out similarly. The yield was 2.9%.

The Photochemical Sulfoxidation of *m*-Xylene.—*m*-Xylene (21.5 g., 0.2 mol.), acetic anhydride (1.3 ml.) and carbon tetrachloride (75 ml.) were placed in a quartz vessel. Sulfur dioxide (7.0 l./hr.) and oxygen (3.5 l./hr.) were introduced simulatneously into the solution at room temperature under the irradiation of ultraviolet light for 9 hr. After the irradiation had ended, a work-up similar to that used for ethylbenzene gave the sodium sulfonate (yield 1.0%).

Results and Discussion

The photochemical sulfoxidation of various alkylbenzenes gave the corresponding sulfonic acids in yields lower than those for *n*-hexane and *n*-decane[2] (see Table I). The lowering of the yields may be due to an inner-filter effect of alkylbenzenes as a substrate, although the λ_{max} value of sulfur dioxide (290 mμ) is longer than those of the substrates. Table II summarizes the ultraviolet and the infrared spectral data on the sodium sulfonates obtained from the sulfoxidized ethylbenzene, ABTP, with an average mol. wt. of 253 (with a side-chain consisting of 12—13 carbon atoms), and ABL, with an average mol. wt. of 254 (with a side-chain of 11—16 carbon atoms). The sulfonate from ethylbenzene showed a λ_{max} value at 256 mμ in water and characteristic infrared absorption bands at 1168 and 1048 cm^{-1} (assigned to the S–O stretching vibrations), at 650 cm^{-1} (assigned to the C–S stretching vibration) and at 734 and 696 cm^{-1} (assigned to the out-of-plane C–H deformation vibrations of five adjacent hydrogen atoms in the benzene ring). Similarly, the sodium sulfonate from ABTP showed a λ_{max} value at 250 mμ in dilute aqueous ethanol and characteristic infrared absorption bands at 1180 and 1045 cm^{-1} (assigned to the S=O stretching vibrations), at 648 cm^{-1} (assigned to the C–S stretching vibration) and at 758 and 695 cm.$^{-1}$ (assigned to the out-of-plane C–H deformation of five adjacent hydrogen atoms in the benzene ring). The sodium sulfonate from ABL showed a λ_{max} value at 258 mμ in ethanol and similar characteristic infrared absorption bands.

As Table III shows, however, the absorption peaks of all authentic alkylbenzenesulfonates with a sulfonate group at the benzene ring are observed above 260 mμ, while those with a sulfonate group at the side-chain shift to below 258 mμ.

On the other hand, the photochemical sulfoxidation of *m*-xylene was found to give a product with a sulfonate group in the benzene ring, i. e., 2, 4-dimethylbenzene-1-sulfonate, which was identified by ultraviolet and infrared spectroscopy (Tables II and III). Although the sulfoxidation of toluene gave a trace of a product which showed the infrared characteristic absorption bands associated with the sulfonate group, attempts to detect the position of the sulfonate group were unsuccessful.

On the basis of these facts, the sulfoxidation of the alkylbenzenes with secondary and/or tertiary hydrogen atoms in the side-chain, such as ethylbenzene, ABTP and ABL, may be described as follows:

$$\underset{}{SO_2} \xrightarrow{h\nu} \underset{\text{(Singlet state)}}{SO_2^{*}} \longrightarrow \underset{\text{(Triplet state)}}{SO_2^{**}} \qquad (1)^{10)}$$

$$Ph(CH_2)_nCH_3 + SO_2^{**} \longrightarrow Ph\dot{C}H(CH_2)_{n-1}CH_3 + \cdot H + SO_2 \qquad (2)$$

$$Ph\dot{C}H(CH_2)_{n-1}CH_3 + SO_2 \longrightarrow PhCH\dot{S}O_2(CH_2)_{n-1}CH_3 \xrightarrow{O_2} \cdots \qquad (3)$$

In contrast, *m*-xylene gave ring-substituted products via an ionic mechanism with sulfur trioxide as an attacking species, since another probable

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7) L. Sempotowski, *Ber.*, **22**, 2663 (1889).

8) J. M. Craft, ibid., **34**, 1352 (1901).

9) F. A. H. Schreinemakers, *Rec, trav. chim.*, **16**, 420 (1898).

10) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

TABLE I. PHOTOCHEMICAL SULFOXIDATION OF ALKYLBENZENES

Alkylbenzene	(mol.)	Ac_2O ml.	Solvent	(ml.)	Irrad. time hr.	Yield[a)] %
Toluene	(0.24)	1.3	None		12	Trace
			CCl_4	(75)	4	Trace
Ethylbenzene	(0.015)	0.1	CCl_4	(150)	12	2.2
ABTP	(0.04)	0.3	CCl_4	(100)	12	3.0
ABL	(0.04)	0.3	CCl_4	(100)	12	2.9
m-Xylene	(0.2)	1.3	CCl_4	(75)	9	1.0

a) The yield of the sodium sulfonate based on the used alkylbenzenes.

TABLE II. UV AND IR SPECTRAL DATA OF THE RESULTING SULFONATES IN THE SULFOXIDATION

Sodium sulfonate	UV λ_{max} (mμ)	IR (KBr disk) Out-of-plane C–H deformation of adjacent hydrogen in benzene ring (cm^{-1})				
		1-H	2-H	3-H	4-H	5-H
Toluene	—	—	—	—	—	—
Ethylbenzene	256[a)]	None	None	None	None	734, 696
ABTP	250[b)]	None	None	None	None	758, 695
ABL	258[c)]	None	None	None	None	751, 699
2,4-Dimethyl-benzene-1-	275.7[d)]	874 (?)	832	None	None	None

a) In water.
b) In aqueous ethanol.
c) In ethanol.
d) In methanol.

TABLE III. UV AND IR SPECTRAL DATA OF THE AUTHENTIC SAMPLES

Sodium sulfonate	UV λ_{max} (mμ)	IR (KBr disk) Out-of-plane C–H deformation of adjacent hydrogen in benzene ring (cm^{-1})				
		1-H	2-H	3-H	4-H	5-H
o-Toluene	267[a)]	None	None	None	753	None
p-Toluene	261[a)]	None	815	None	None	None
ω-Toluene	258[a)]	None	None	None	None	731, 693
p-Ethylbenzene	261[a)] 262[b)]	None	831	None	None	None
o- or *p*-ABTP	261[c)]	None	830	None	758	None
p-ABL	268[b)]	None	828	None	None	None
2,4-Dimethylbenzene-1-	275.7[d)]	874	836	None	None	None
m-Xylene-*ω*-	273.2[d)]	892	None	771	None	None

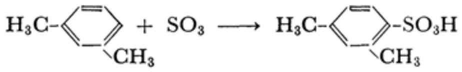
a) In water.
b) In ethanol.
c) In aqueous ethanol.
d) In methanol.

mechanism involving the excitation of a C–T complex between *m*-xylene and sulfur dioxide is unlikely because the complex has not been detected in carbon tetrachloride by ultraviolet spectroscopy. The sulfoxidation of toluene occurred only with difficulty. These facts can be explained by an equilibrium (Eq. 3′) where the benzyl radical is more stabilized than the *ω*-toluenesulfonyl radical.[11)]

$$PhCH_2\cdot + SO_2 \rightleftarrows PhCH_2\overset{\cdot}{S}O_2 \qquad (3')$$

Consequently, *m*-xylene is probably sulfonated with the sulfur trioxide obtained from the photooxidation[4)] of sulfur dioxide by the reactions of Eqs. 4 and 5:

$$SO_2 + O_2 \xrightarrow{h\nu} SO_3 \qquad (4)$$


(5)

The very poor yield of the toluenesulfonate may be due to the fact that *m*-xylene is attacked by electrophilic sulfur trioxide more rapidly than toluene.

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11) M. S. Kharasch and A. T. Reed, *J. Am. Chem. Soc.*, **61**, 3089 (1939).

A similar example of radical and ionic substitutions under irradiation has been reported in photochemical thiocyanation,[12] i. e., the reaction with thiocyanogen chloride in acetic acid occurs completely at the side-chain of ethylbenzene, but only partially at the ring of *m*-xylene, and entirely at the ring of mesitylene.

TABLE IV. THE SURFACE AND THE WATER-KEROSENE INTERFACIAL TENSIONS OF THE AQUEOUS SOLUTIONS OF SODIUM SULFONATES OF ABTP AND ABL AT 20°C

	Position of substituted sulfonate group	Surface tension[a] dyne/cm.		Interfacial tension[b] dyne/cm.	
		0.1 g.%	0.05 g.%	0.1 g.%	0.05 g.%
ABTP	Side-chain	45.9	49.3	11.5	15.1
	Benzene	29.8	33.5	2.7	—
ABL	Side-chain	40.6	43.2	2.3	5.2
	Benzene	35.0	37.1	0.7	3.3

a) By Du Nouy tensiometer. The surface tension of distilled water is 68.7 dyne/cm. at 20°C.

b) By Du Nouy tensiometer. The interfacial tension between distilled water and kerosene is 35.8 dyne/cm. at 20°C.

m-Xylyl chloride and an aromatic carboxylic acid of an unknown structure were detected by gas chromatography and infrared spectroscopy respectively as minor side-reaction products in the photosulfoxidation of *m*-xylene. The latter showed the characteristic infrared peaks of aromatic carboxylic acid at 1720, 1690 and 1277 cm^{-1}. *m*-Xylyl chloride appears to be obtained by the chlorine-atom abstraction of the *m*-xylyl radical from the solvent, carbon tetrachloride,[13] while the carboxylic acid seems to be formed by the photooxidation of *m*-xylene.

The side-chain sulfonation of ABTP and ABL is a novel reaction. The surface and the water-kerosene interfacial tensions of the aqueous solutions of sodium sulfonates of ABTP and ABL are tabulated in Table IV, together with those of the ring-sulfonated ones. The results show that the side-chain-sulfonated ABTP and ABL are also good surfactants.

The authors wish to thank the Seitetsu Chemical Co., and the Nissan Chemical Co. for their gifts of materials.

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[12] R. G. R. Bacon and R. G. Guy, *J. Chem. Soc.*, **1961**, 2428.

[13] C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **86**, 3902 (1964).