Photolytic Oxidation of Alkylbenzenesulfonic Acids by Aqueous Sodium Hypochlorite[1)]

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Photolyses of alkylbenzenesulfonic acids, such as benzene-, *p*-toluene-, and *p*-ethylbenzenesulfonic acids, in aqueous solution by sodium hypochlorite have been studied. In the presence of a large excess of hypochlorite, benzenesulfonic acid is completely photolyzed to give carbon dioxide and sulfuric acid. Irradiation of an equimolar mixture of substrate and hypochlorite in an aqueous solution yields the corresponding alkylbenzene, alkylphenol, arylalkyl alcohol and arylalkylaldehyde, some of which may be produced by an attack of the oxidant on alkyl chain. In some cases, small amounts of diaryl sulfones and chlorinated compounds are also detected.

Interest has recently centered on the decontamination of surfactants, sodium alkylbenzenesulfonate in particular, from waste water. Practically, the removal of surfactants has been done by biochemical or physical (*e.g.* adsorption) methods and sometimes by irradiation of sunlight or ultraviolet light in the presence of oxygen or appropriate oxidizing agents such as alkali hypochlorite and hydrogen peroxide. However, these methods are often insufficient for certain surfactants.

Matsuura and Smith[2,3)] reported from kinetic and product analysis (GLC) studies that the photochemical autoxidation of aqueous alkali dodecylbenzenesulfonate (DBS) gives products containing formaldehyde, formic acid and acetaldehyde, which are finally oxidized to CO_2. On the other hand, a loss of surface activity of some surfactants by hypohalite on UV irradiation was observed.[4)]

Recently, an effective industrial process[5)] was developed for the photo-oxidative removal of several organic contaminants in waste water by aqueous alkali hypochlorite in excess, by which most organic materials are completely decomposed into CO_2, HCl and H_2O. Decontamination of organic compounds in waste water was accomplished by the combined use of irradiation with UV light in the presence of Cl gas or hypochlorite and activated sludge treatment.[6)]

However, there is no detailed information on the intermediary products and reaction mechanism for the hypohalite oxidation. Some products might cause secondary pollution. We have examined the intermediary products and mechanism for the UV photolyses of anionic surfactants by aqueous sodium hypochlorite. As model compounds of alkylbenzenesulfonate type surfactants, simple sulfonates such as benzene-, *p*-toluene-, and *p*-ethylbenzenesulfonic acids were chosen. They were photolyzed under conditions of short irradiation time and a nearly equivalent amount of sodium hypochlorite. Analyses were carried out by means of GLC-mass spectra along with a comparison of the retention times of products with those of authentic samples by GLC.

Experimental

Gas chromatograms were recorded with a Yanagimoto Model GCG550 chromatograph employing a flame ionization detector and a 1.5 m×3 mm copper column packed with Silicone OV17 5% on Celite. The mass spectra were measured with a Shimadzu Model GCMS-7000 mass spectrometer.

Materials. *Sodium Hypochlorite*: The aqueous solution of sodium hypochlorite was prepared as follows. Gaseous chlorine was bubbled into an aqueous 1 M-NaOH with ice-cooling, and the sodium chloride precipitated was filtered off. The solution can be stored for severl days in a refrigerator. The concentration was determined by iodometry before use.

Alkylbenzenesulfonic Acids: All the alkylbenzenesulfonic acids were commercial products of the best grade.

Irradiation of Benzenesulfomic Acid. A mixture of benzenesulfonic acid (0.099 M), aqueous sodium hypochlorite (0.103 M), and 1 M-NaOH solution (100 ml) were diluted with distilled water until the total volume became 400 ml. The solution was degassed with nitrogen and irradiated by quartz-filtered UV light employing a 300 W high pressure mercury lamp, nitrogen being bubbled at room temperature. Irradiation was stopped before complete disappearance of sodium hypochlorite. After irradiation, the excess sodium hypochlorite was removed with sodium sulfite, the aqueous solution being extracted with 100 ml ether. The aqueous layer was acidified to pH 2—3 with HCl and again extracted with 100 ml ether. The combined extracts, after being dried over anhydrous sodium sulfate, were concentrated, and then analyzed by means of GLC and GLC-mass spectrometry. The work-up for other alkylbenzenesulfonic acids is similar to that mentioned above.

Estimation of Evolved Carbon Dioxide. Carbon dioxide produced by photolysis was kept absorbed in the aqueous alkaline solution. The solution was acidified with sulfuric acid, carbon dioxide being expelled by N_2 stream from the reaction mixture. The CO_2 evolved was absorbed by aqueous 0.05 M-$Ba(OH)_2$ and determined by titration with 0.1 M-HCl.

Estimation of Sulfate Ion. Analysis of sulfate ion in the products was achieved gravimetrically by adding excess aqueous barium chloride to the acidified reaction mixture, barium sulfate precipitated being weighed.

Results and Discussion

Irradiation of an aqueous solution of benzenesulfonic acid in the presence of a 20-fold equivalent of sodium hypochlorite gives, after complete disappearance of hypochlorite, carbon dioxide and sulfate, their yields by photolysis being 95.7 and 83.5%, respectively. Benzenesulfonic acid is decomposed almost completely to give CO_2 and inorganic materials.

In the photolysis of an equimolar mixture of benzene-

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sulfonate and hypochlorite by means of quartz-filtered UV light (>180 nm) for a short time, the yield of CO_2 was only *ca.* 3%. The organic products extracted with ether are given in Table 1. The products were identified by direct comparison of the GLC peaks with those of the authentic samples and also the parent ion peak and its pattern of fragmentation in mass spectra. Crystals of mp 128.5—129° C (lit, mp 128—129 °C) were isolated by condensation of the ether extract, and identified by GLC using three different columns (Silicone OV17 5% on Celite, Apiezon grease L 3% on Celite and PEG 20M 10% on Chromosorb) as diphenyl sulfone.

Table 1. Partial mass spectra of photo-oxidation products of benzensulfonic acid[a]

Parent ion peak *m/e*	Fragment ion peak	Compound	Relative mole ratio
94	66 65 55 39	Phenol	1
154	153 152 115 77 76 64 51	Biphenyl	0.01
218	152 125 97 77 51	Diphenyl sulfone	0.06

a) Initial concentration: $PhSO_3H$ 247.5 mM, NaOCl 257.5 mM; pH≈11; room temperature. Conversion of $PhSO_3H$ into products was *ca.* 8%.

Table 2. Partial mass spectra of photo-oxidation products of *p*-toluenesulfonic acid[a]

Parent ion peak *m/e*	Fragment ion peak	Compound	Relative mole ratio
92	91 65 63 51 50 39	Toluene	1
106	105 78 77 51	Benzaldehyde	0.16
108	107 91 79 77	Benzyl alcohol	2.18
108	107 91 90 79 77 53 51	*p*-Cresol	0.42

a) Initial concentration: *p*-toluenesulfonic acid 25.0 mM, NaOCl 31.2 mM; pH≈11; room temperature. Conversion of toluenesulfonic acid into products was *ca.* 10%.

Table 3. Partial mass spectra of photo-oxidation products of *p*-ethylbenesulfonic acid[a]

Parent ion peak *m/e*	Fragment ion peak	Compound	Relative mole ratio
106	91 79 78 77 65 51	Ethyl-bennzene	1
94	66 65 55 39	Phenol	0.18
122	107 91 79 77 51 43	1-Phenyl-ethanol	0.41
120	105 91 77 51 43	Acetophenone	3.26
122	107 91 79 77 51 39	2-Phenyl-ethanol	5.97
122	107 94 91 77 39	*p*-Ethylphenol	2.15

a) Initial concentration: *p*-ethylbenzenesulfonic acid 23.0 mM, NaOCl 22.5 mM; pH≈11; room temperature. Conversion of ethylbenzenesulfonic acid into products was *ca.* 7%.

The results of photolysis of *p*-toluene- and *p*-ethylbenzenesulfonate, with equimolar hypochlorite by quartz-filtered light, are given in Tables 2 and 3, respectively. Reports[7] on mass spectrometry are cited for identification of the products.

The photolytic oxidation of alkylbenzenesulfonic acid with hypochlorite gives rise mainly to alkylbenzene, alkylphenol, arylakyl alcohol, and arylalkyl aldehyde. Small amounts of chlorinated compounds such as monochlorophenols were also detected.

Typical conversion curves for the photodecomposition of aqueous sodium hypochlorite in the presence and absence of benzenesulfonic acid are shown in Fig. 1. Decomposition is rather fast with light of over 180 nm, and is accelerated by the addition of benzenesulfonic acid which probably acts as a sensitizer.

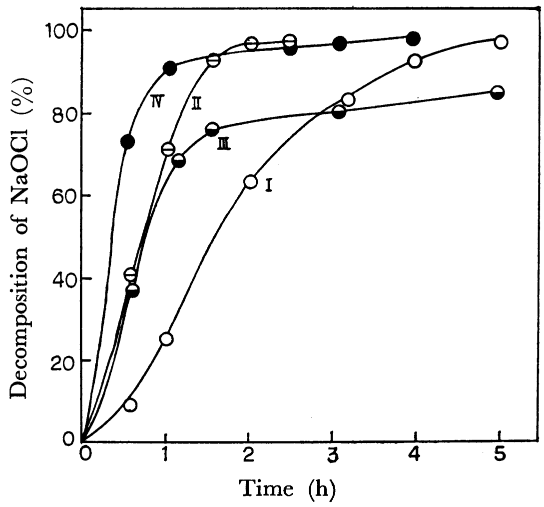

Fig. 1. Photodecomposition of aqueous sodium hypochlorite at room temperature and pH≈11 in the presence and absence of $PhSO_3H$.

Curve	Initial concentration (mM)		Light
	NaOCl	$C_6H_5SO_3H$	
I	89.5	0	>300 nm
II	89.5	0	>180 nm
III	83.4	84.2	>300 nm
IV	102.7	98.8	>180 nm

The photodecomposition of aqueous hypochlorite has been studied, but the overall mechanism of photochemical decomposition does not seem to have been clarified. Earlier workers[8] showed that the products of the photolysis of aqueous hypochlorite are oxygen, chloride and chlorate ions and that the amount of decomposed hypohalite is proportional to the light energy absorbed. Recently, Buxton and Subhani[9] demonstrated with flash photolysis technique that the primary products of the photolysis of hypochlorite ion at 365 nm are O (triplet oxygen atom), O^-, Cl, and Cl^- and that, at 313 and 253.7 nm, O (singlet oxygen atom) and Cl^- are also produced. The stoichiometry is expressed as follows.

$$\mathrm{ClO^-} \left| \begin{array}{lr} \xrightarrow{h\nu} \mathrm{Cl^-} + \mathrm{O}\ (^3\mathrm{P}) & \text{(1a)} \\ \xrightarrow{h\nu} \mathrm{Cl} + \mathrm{O^-} & \text{(1b)} \\ \xrightarrow{h\nu} \mathrm{Cl^-} + \mathrm{O}\ (^1\mathrm{D}). & \text{(1c)} \end{array} \right.$$

We employed quartz-filtered light (>180 nm) for *p*-ethylbenzenesulfonic acid in which non-selective oxidation on α- and β-carbon atoms of alkyl chain with little chlorination was observed (Table 3). Thus, the photo-oxidation should proceed mostly by an attack of oxygen atom produced from hypochlorite by the above mechanism (1a and 1c) to give the observed products.

A probable mechanism for an initial stage in the photolysis is as follows (R: H, *p*-Me, *p*-Et).

$$RC_6H_4SO_3H \xrightarrow{h\nu} RC_6H_4\cdot + \cdot SO_3H, \quad (1)$$

$$\cdot SO_3H \xrightarrow{h\nu} SO_2 + \cdot OH, \quad (2)$$

$$SO_2 + O + H_2O \xrightarrow{h\nu} H_2SO_4. \quad (3)$$

Formation of sulfur dioxide from benzenesulfonic acid (Eqs. 1 and 2) was confirmed by the Fuchsine test for the photolysis of aqueous benzenesulfonic acid alone. As regards Eq. 3, we have reported on the photo-oxidation of aqueous sulfur dioxide to sulfuric acid with H_2O_2 and O_2.[10] There are other reports[11] which support this kind of photo-oxidation.

The aryl and hydroxyl radicals produced might undergo reactions as follows in view of the observed products.

1) Phenyl radical:

$$Ph\cdot + \cdot OH \longrightarrow PhOH, \quad (4)$$

$$2Ph\cdot \longrightarrow Ph\text{-}Ph. \quad (5)$$

2) *p*-Tolyl radical:

$$\cdot C_6H_4CH_3 \longrightarrow C_6H_5CH_2\cdot, \quad (6)$$

$$C_6H_5CH_2\cdot + \cdot OH \longrightarrow C_6H_5CH_2OH, \quad (7)$$

$$\cdot C_6H_4CH_3 \text{ (or } C_6H_5CH_2\cdot \text{ or another radical)} + C_6H_5CH_2OH \longrightarrow C_6H_5CH_3 \text{ (}etc.\text{)} + C_6H_6\dot{C}HOH, \quad (8)$$

$$C_6H_5\dot{C}HOH + O \longrightarrow C_6H_5CHO + \cdot OH, \quad (9)$$

$$\cdot C_6H_4CH_3 + \cdot OH \longrightarrow HOC_6H_4CH_3. \quad (10)$$

3) *p*-Ethylphenyl radical:

$$\cdot C_6H_4CH_2CH_3 \longrightarrow C_6H_5\dot{C}HCH_3, \quad (11)$$

$$\cdot C_6H_4CH_2CH_3 \longrightarrow C_6H_5CH_2CH_2\cdot, \quad (12)$$

$$C_6H_5\dot{C}HCH_3 + \cdot OH \longrightarrow C_6H_5CH(OH)CH_3, \quad (13)$$

$$C_6H_5CH_2CH_2\cdot + \cdot OH \longrightarrow C_6H_5CH_2CH_2OH, \quad (14)$$

$$\cdot C_6H_4CH_2CH_3 + SH \longrightarrow C_6H_5CH_2CH_3 + S\cdot, \quad (15)$$

$$C_6H_5\dot{C}HCH_3 + SH \longrightarrow C_6H_5CH_2CH_3 + S\cdot, \quad (16)$$

$$C_6H_5CH_2CH_2\cdot + SH \longrightarrow C_6H_5CH_2CH_3 + S\cdot, \quad (17)$$

$$\text{(SH: } C_6H_5CH(OH)CH_3,\ C_6H_5CH_2CH_2OH\text{)}$$

$$S\cdot + O \longrightarrow C_6H_5COCH_3 \text{ or } C_6H_5CH_2CHO, \quad (18)$$

$$\cdot C_6H_4CH_2CH_3 + \cdot OH \longrightarrow HOC_6H_4CH_2CH_3. \quad (19)$$

The aryl radical, $RC_6H_4\cdot$, produced might abstract a hydrogen atom from its own alkyl chain to give arylalkyl radical *via* successive internal *o*- and *m*-H atom shifts (Eqs. 6, 11, and 12), giving alcohols and carbonyl compounds. Aryl radical can also abstract a hydrogen atom from another molecule to give alkylbenzene (Eqs. 8 and 15), but the yield is very low and the contribution of intermolecular H-atom abstraction seems to be small. Polymerization of aryl radical might be impossible in consideration of the absence of $(-C_6H_4-R)_2$ except biphenyl. The product distribution shows that the H-abstraction is preferable to coupling of $RC_6H_4\cdot$ with hydroxyl radical to form alkylphenol. The absence of products formed by chlorine addition to radicals or by chlorination of the side chain suggests that the hydrogen abstraction by Cl· is unimportant. Higher yields of *p*-alkylphenol than *o*- and *m*-substituted phenols may be due to the greater resonance stability of *p*-$RC_6H_4\cdot$ radical. The higher yield of $PhCH_2CH_2OH$ than $PhCH(OH)CH_3$ is of interest, since the radical stability in the latter is greater. This suggests that the attack of ·OH on these arylalkyl radicals is very fast, giving a statistical distribution of the OH position of alcohols. The unsubstituted phenol formation, though small, from ethylbenzenesulfonate but not from toluenesulfonate implies easier elimination of the larger alkyl chain to give the phenyl radical.

There are reports stating that (i) benzyl phenyl sulfone can be formed by coupling of benzyl and phenylsulfonyl radicals produced from phenyl radical and SO_2[12] and (ii) the ESR evidence of methylsulfonyl radical photochemically formed from methyl radical and SO_2.[13] The results suggest the following mechanism for this diaryl sulfone formation.

$$Ph\cdot + SO_2 \xrightarrow{h\nu} PhSO_2\cdot, \quad (20)^{14)}$$

$$\text{(or } PhSO_3H \xrightarrow{h\nu} \cdot PhSO_2\cdot + \cdot OH\text{)}, \quad (21)$$

$$PhSO_2\cdot + \cdot Ph \longrightarrow PhSO_2Ph, \quad (22)$$

$$Ph\cdot + PhSO_3H \longrightarrow PhSO_2Ph + \cdot OH, \quad (23)$$

$$PhSO_2\cdot + PhSO_3H \longrightarrow PhSO_2Ph + \cdot SO_3H. \quad (24)$$

The phenol produced might subsequently be chlorinated to give mono- and di-chlorinated phenols. In fact, mono- and di-chlorophenols were formed on irradiation of a mixture of phenol and aqueous sodium hypochlorite (Table 4). However, the poor yield of chlorinated phenol in the photo-oxidation of alkylbenzenesulfonate shows that an attack of Cl species is not important.

We found that the photo-oxidation by aqueous hypochlorite proceeds even by Pyrex-filtered light (>300

TABLE 4. PARTIAL MASS SPECTRA OF PHOTO-OXIDATION PRODUCTS OF PHENOL[a]

Parent ion peak *m/e*	Fragment ion peak	Compound	Relative mole ratio
128	130 95 94 66 65 55 39	Monochlorophenols	1
162	166 164 94 66 65	Dichlorophenols	0.08

a) Initial concentration: phenol 49.6 mM, NaOCl 46.0 mM; pH≈11; room temperature.

nm), where a grater variety of products were observed, since the substrate cannot be excited and thus only a random attack of oxygen atom predominates. In photo-oxidation employing a Pyrex filter, slightly larger amounts of various chlorinated compounds were also detected. An attack of Cl· on the unexcited substrate might become significant in this case.

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