

Photooxidation of Some Aromatic Sulfonic Acids with Alkaline Hypochlorite¹⁾

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Photochemical oxidation of aromatic sulfonic acids such as *p*-cumenesulfonic, 2-mesitylenesulfonic, 1- and 2-naphthalenesulfonic acids with aqueous sodium hypochlorite has been studied. Addition of a large excess of alkali enhances the decomposition of sulfonic acids remarkably. *p*-Cumenesulfonic and 2-mesitylenesulfonic acids are oxidized faster than 1- and 2-naphthalenesulfonic acids. The photooxidation of sulfonic acids with an equimolar amount of hypochlorite gives intermediary oxidation products involving desulfonation to parent hydrocarbons, aromatic hydroxylation, side-chain oxidation, and ring cleavage; *e.g.*, *p*-cumenesulfonic acid gives cumene, 2- and 4-isopropylphenol and 2-phenyl-2-propanol; 1- and 2-naphthalenesulfonic acids give phthalic anhydride. Light-absorbing aromatic sulfonic acids sensitize the decomposition of hypochlorite ion leading to hydroxyl radical, which reacts mainly with ground state sulfonic acid to give radical intermediates. The photooxidation may also involve direct C–S bond fission of sulfonic acids.

Alkyl-substituted aromatic sulfonic acids which are important for surfactants and dyestuffs are often present in waste water causing environmental pollution, being difficultly decomposed by the biochemical method involving microbes. UV-irradiation decomposes aromatic sulfonic acids to their parent hydrocarbons as exemplified by benzenesulfonic acid,²⁾ 1-naphthalenesulfonic acid, *etc.*³⁾ Suitable oxidizing agents are further needed to decompose sulfonic acids into harmless substances such as carbon dioxide and water.

Sodium hypochlorite which oxidizes various organic compounds in the dark⁴⁾ exhibits much higher oxidation power under UV-irradiation because of the formation of atomic oxygen.⁵⁾ Thus, alkylbenzenesulfonic acids,⁶⁾ some ethers⁷⁾ and carboxylic acids⁸⁾ are effectively oxidized by irradiation in the presence of a large excess of hypochlorite to carbon dioxide and water, *etc.*

We wish to report here the photochemical hypochlorite oxidation of other aromatic sulfonic acids such as *p*-cumene-, 2-mesitylene-, 1- and 2-naphthalenesulfonic acids to clarify their intermediary oxidation products and mechanism. Effects of alkali added on sulfonic acid decomposition and relative reactivity of the above sulfonic acids are also examined to elucidate the oxidation pathways.

Results and Discussion

Photodecomposition of Sodium Hypochlorite and Aromatic Sulfonic Acids. Aqueous *p*-cumene-, 2-mesitylene-, 1- and 2-naphthalenesulfonic acids were stable toward alkaline sodium hypochlorite (NaClO) in the dark at room temperature for several days. Short time irradiation of the sulfonic acids and NaClO with UV-light ($\lambda > 290$ nm) brought about rapid decomposition of NaClO (iodometry) and partial decomposition of sulfonic acids (HPLC analysis). Though the extent of decomposition of sulfonic acid increased with increasing amount of NaClO added, the time for $>90\%$ decomposition of NaClO was unaffected (40–60 min) in spite of 1–20 fold change in relative amount of NaClO added. When NaClO equimolar to sulfonic acid was used, the decomposition time of NaClO was apparently independent of the kind of sulfonic acid (the decomposition extent of each sulfonic acid was

ca. 5%). The above results indicate that the decomposition of NaClO is sensitized by excited sulfonic acids. The excitation energy of aromatic sulfonic acids (>400 kJ/mol), which is much higher than the bond-breaking energy of ClO[–] (*ca.* 200 kJ/mol), would cause the effective sensitized decomposition of ClO[–] irrespective of the kind of sulfonic acids.

The decomposition of sulfonic acid was found to be increased by addition of a large amount of alkali. Table 1 exemplifies the effect of alkali on the decomposition of *p*-cumenesulfonic acid. Likewise, other sulfonic acids were much more effectively decomposed by the addition of a mixture of NaOH and NaClO than by independent addition of NaOH or NaClO alone.

In order to compare the relative reactivities of sulfonic acids, a mixture of sulfonic acid, an equimolar amount of NaClO and 10-fold mol of NaOH was irradiated for 30 min by an external irradiation to measure the decomposition extents of NaClO and sulfonic acid (Table 2). The consumption of NaClO relates to the total reactivity of sulfonic acid including subsequent reactions between initial products and NaClO, while the consumption of sulfonic acid expresses the disappearance of sulfonic acid itself. The difference in two consumptions may be a measure of the subsequent reactions. Based on the consumption of NaClO, the relative reactivity of sulfonic acid is in the order of *p*-cumene- $>$ 2-mesitylene- $>$ 1-naphthalene- \approx 2-naphthalenesulfonic acid (though the former three sulfonic acids shows a similar initial reactivity on the basis of the consumption of sulfonic acid). Hence, aromatic sulfonic acids possessing side-chain alkyl substituents are relatively more susceptible to the photooxidation leading to carbon dioxide.

Intermediary Products. As observed previously with alkylbenzenesulfonic acids,⁸⁾ the present sulfonic acids can be oxidized to carbon dioxide and water by a large excess of NaClO under irradiation. The necessary amount of NaClO for the complete oxidation was several times as much as the theoretical (25 fold mol). Use of an equimolar amount of NaClO in the photooxidation results in the formation of various intermediates. The photolysis products from a mixture of aqueous sulfonic acid, equimolar NaClO and 10 fold mol of NaOH were analyzed by GLC and GC-MS

TABLE 1. EFFECT OF ALKALI ON THE PHOTO-DECOMPOSITION OF AQUEOUS SODIUM *p*-CUMENESULFONATE^{a)}

Additive (rel mol)	Decomposition (%)
None	7.5
NaClO (1)	6.8
NaClO (1) + NaOH (10)	38.0
NaOH (10)	6.4

a) Initial concentration of the sulfonate was 33.3 mM. Internal irradiation ($\lambda > 290$ nm) was carried out for 45 min at room temperature.

TABLE 2. RELATIVE REACTIVITY IN THE PHOTOOXIDATION OF SODIUM ARENESULFONATE WITH AQUEOUS ALKALINE NaClO^{a)}

Sulfonic acid	Consumption (%)	
	NaClO	ArSO ₃ ⁻
<i>p</i> -Cumene-	74	23
2-Mesitylene-	58	20
1-Naphthalene-	50	23
2-Naphthalene-	49	14

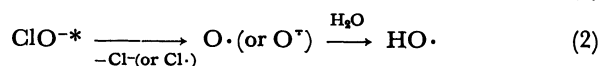
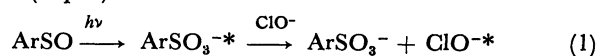
a) Initial concentration of each sulfonic acid was 33.3 mM. The mol ratio of ArSO₃⁻: NaClO: NaOH was 1 : 1 : 10. External irradiation was conducted for 30 min at room temperature.

techniques, being identified by comparison with the corresponding authentic samples (Table 3).

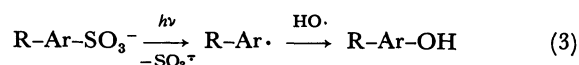
Alkyl-substituted sulfonic acids such as *p*-cumene- and 2-mesitylenesulfonic acids gave their parent hydrocarbons (*i.e.*, cumene and mesitylene, respectively) in accord with our previous report on *p*-toluene- and *p*-ethylbenzenesulfonic acids.⁶⁾ Though naphthalene was obtained in the simple photolysis of aqueous sodium 1-naphthalenesulfonate alone,³⁾ no naphthalene was detectable in the photooxidation of 1- and 2-naphthalenesulfonic acids. Also no benzene was formed in the photooxidation of benzenesulfonic acid with NaClO, while it was formed in 16% yield in the photolysis of benzenesulfonic acid alone. Hence, alkyl substituents in sulfonic acids are hydrogen sources for the conversion of aromatic radicals to aromatic hydrocarbons.

Since the NaClO decomposition is sensitized by

aromatic sulfonic acid as noted above, the present photo-oxidation seems to proceed *via* excited hypochlorite ion ClO^{-*} (Eq. 1) with less probability of the direct reaction between excited sulfonate ion ArSO₃^{-*} and ground-state hypochlorite ClO⁻. Excited hypochlorite ion is known to give oxygen atoms such as O[·] and O²⁺,⁵⁾ which react with water to give hydroxyl radical HO[·] (Eq. 2).⁹⁾



Some products in Table 3 can be explained in terms of an attack of HO[·]. Phenols such as 4-isopropylphenol and 2,4,6-trimethylphenol were obtained, indicative of aromatic hydroxylation by HO[·]. Though neither 1-nor 2-naphthol was detectable, 2-naphthalenesulfonic acid gave 1-chloro-2-naphthol which is readily formed even in the dark from 2-naphthol and NaClO. These phenols may be formed by the coupling of HO[·] with aryl radical precidently cleaved from aromatic sulfonic acid by UV-light (Eq. 3).



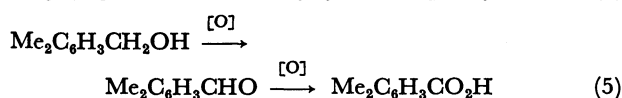
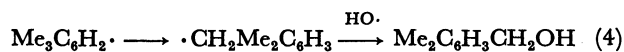
As to 2-isopropylphenol which was formed in *ca.* 5 time amounts of the 4-isomer, initial hydroxylation of *p*-cumenesulfonic acid followed by Ar-SO₃⁻ cleavage might occur.

Products oxidized at alkyl side-chain are 2-phenyl-2-propanol from *p*-cumenesulfonic acid, and 3,5-dimethylbenzyl alcohol and 3,5-dimethylbenzoic acid from 2-mesitylenesulfonic acid. Their product ratios in Table 3 suggest that alkylbenzenesulfonic acid undergoes predominantly side-chain oxidation rather than aromatic hydroxylation, in accord with the cases of *p*-toluene- and *p*-ethylbenzenesulfonic acids.⁶⁾ This may be reflected to the reactivities of *p*-cumene- and 2-mesitylenesulfonic acids toward NaClO, which are higher than those of 1- and 2-naphthalenesulfonic acids. The pathway for the side-chain oxidation is explained assuming radical isomerization of aromatic type to benzylic one (Eq. 4), leading successively to alcohol, aldehyde and carboxylic acid (Eq. 5).

TABLE 3. PRODUCTS AND MASS SPECTRA DATA IN THE PHOTOOXIDATION OF SOME AQUEOUS SODIUM ARENESULFONATES WITH ALKALINE NaClO^{a)}

Sulfonic acid	Products (rel mol)	<i>m/e</i> (rel intensity) ^{b)}
<i>p</i> -Cumene-	Cumene (1.0)	120(57, P), 105(100)
	2-Isopropylphenol (1.6)	136(67, P), 121(100)
	4-Isopropylphenol (0.3)	136(62, P), 121(100)
	2-Phenyl-2-propanol (6.8)	118(100, P-18), 94(62)
2-Mesitylene-	Mesitylene (1.0)	120(100, P), 105(48)
	2,4,6-Trimethylphenol (2.1)	136(100, P), 121(54)
	3,5-Dimethylbenzyl alcohol (0.9)	136(100, P), 134(26), 121(50)
	3,5-Dimethylbenzoic acid (0.6)	150(100, P), 105(39), 91(31)
1-Naphthalene-	Phthalic anhydride	148(20, P), 104(100)
2-Naphthalene-	Phthalic anhydride (1.0)	148(20, P), 104(100)
	1-Chloro-2-naphthol (0.1)	180(33, P+2), 178(100, P)

a) Aqueous solutions (300 ml) of sodium sulfonate (10 mmol), NaClO (10 mmol), and NaOH (0.1 mol) were irradiated at room temperature for 45–60 min. b) GC-MS spectra were measured at 20 eV.



Formation of phthalic anhydride from both 1- and 2-naphthalenesulfonic acids may involve aromatic hydroxylation by $\text{HO}\cdot$, ring cleavage and oxidation to carboxylic acid.

Experimental

Materials. An aqueous NaClO solution was prepared by introducing chlorine gas to 4.0 M (1 M = 1 mol dm⁻³) NaOH until the iodometry showed 1.85 M NaClO .

Arenesulfonic acids were used as their sodium salts. *p*-Cumenesulfonic acid¹⁰ and 2-mesitylenesulfonic acid¹¹ were obtained from sulfonation of cumene and mesitylene, respectively. Sodium 1- and 2-naphthalenesulfonates were of commercial reagents. Since these salts were often contaminated with NaCl , Na_2SO_4 and water, the salts were purified as follows. Crude sodium sulfonate was converted to its anilinium salt with aniline and hydrochloric acid as precipitate from aqueous solution. After repetition of crystallization from water, the resulting pure anilinium sulfonate was again converted to precipitate of sodium salt with an equivalent amount of sodium methoxide in methanol-ether. UV absorption maxima (molar extinction coefficient) of pure sodium sulfonate: *p*-cumesulfonate, 222 nm (1.22×10^4), 260 (400); 2-mesitylenesulfonate 222 (9.3×10^3), 271 (890), 280 (920); 1-naphthalenesulfonate, 222 (5.2×10^4), 283 (5.3×10^3), 317 (600); 2-naphthalenesulfonate, 227 (1.0×10^6), 274 (5.0×10^3), 320 (700).

Authentic 2-phenyl-2-propanol was prepared by the Grignard reaction of methylmagnesium iodide with acetophenone.¹² Authentic 3,5-dimethylbenzoic acid was prepared by the oxidation of mesitylene with dilute HNO_3 ;¹³ mp 165–166 °C (lit.¹³ 165.5–166.5 °C). 3,5-Dimethylbenzyl alcohol was prepared by LiAlH_4 reduction of 3,5-dimethylbenzoic acid;¹⁴ bp 102–103 °C/2 mm (lit.¹⁴ 115–117.5 °C/10 mm). 1-Chloro-2-naphthol was prepared by the NaClO chlorination of sodium 2-naphtholate (80%); mp 70–71 °C (aq EtOH) (lit.¹⁵ 71 °C). The other authentic samples were of commercial guaranteed grade.

Instruments. HPLC analyses for sulfonic acid determination¹⁶ were carried out on a JEOL-Twinkle model equipped with an ODS column using H_2O (0.01 M NaCl)/ MeOH = 8/1 as the eluent. GC-MS spectra were recorded on a JMS-RD 300 model with the ionization potential set at 20 eV. GLC analyses were carried out on a Yanaco G-180 using Silicone DC 550 or PEG 20M column.

Irradiation experiments were generally carried out in a 300 ml vessel equipped with a Halos 100 W high-pressure mercury lamp. Controlled irradiation (Table 2) was conducted on a merry-go-round apparatus equipped with a Halos 300 w high-pressure mercury lamp.

Photodecomposition of Sulfonic Acid with NaClO . An aqueous solution (300 ml) of sulfonic acid (10 mmol) and an appropriate amount of NaClO was irradiated internally at ambient temperature. The change in concentration of

NaClO was followed by iodometry. When consumption of NaClO reached over 90%, sulfonic acid left was determined by HPLC. Runs in Table 1 were similarly carried out by the addition of 0.10 mol of NaOH .

In the experiments for the relative reactivity of sulfonic acids (Table 2), mixtures of each 10 ml of 0.10 M aqueous sulfonic acid, 0.1 M NaOH and 0.101 M NaClO were irradiated externally for 30 min.

Products in the Photooxidation of Sulfonic Acids with NaClO .

An aqueous solution (300 ml) of a sulfonic acid (10 mmol), NaClO (10 mmol), and NaOH (0.1 mol) was irradiated internally until NaClO was consumed over 90% (45–60 min). The resulting solution was acidified with dil. HCl and extracted with ether (100 ml \times 2). The ethereal layer was dried over anhydrous sodium sulfate, concentrated by distillation and analyzed by GLC and GC-MS. Products in Table 3 were identified on the basis of accordance with the authentic samples in their GLC retention times and mass fragment patterns. All products were in low yields. In the case of 2-mesitylenesulfonic acid, formation of 2- and 4-chloro-3,5-dimethylbenzoic acids was indicated by GC-MS (rel mol ca. 1.0). Attempts to separate two isomers failed.

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