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Photolysis of Benzenesulfonic Acid[1)]

Yoshiro OGATA,* Katsuhiko TAKAGI, and Shin YAMADA
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Nagoya 464

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Synopsis. Photolysis of benzenesulfonic acid(**1**) in an aqueous solution gave sulfurous acid, SO_2, and/or sulfuric acid as inorganic products in a total yield of 38.6% based on the consumed **1** along with organic products. The organic products are mainly acidic tarry material containing sulfur(8.7%) together with a small amount of biphenyl (1%). Photolysis of an alkaline solution of **1** afforded a considerable amount of benzene (16%) and biphenyl(<1%). The photolysis is started by the C–S bond fission of **1** to give Ph· and ·SO_3H radicals. The quantum yield for decomposition of **1** in acidic conditions is 0.26.

Sodium alkylbenzenesulfonate is known to be an environmental pollutant. The studies on the photochemical decomposition of the sulfonate have recently been increasing,[2)] but little is known about the mechanism and intermediates of the photolysis except for photolysis of sulfonate ester[3)] and sulfonanilide.[4)] The present paper deals with the attempts to obtain on the subject, in particular, the mechanism for photolysis of benzene sulfonic acid as a model of the surfactant.

Results and Discussion

Irradiation of Alkaline Aqueous Sodium Benzenesulfonate. The photolysis of an aqueous mixture of benzenesulfonic acid (**1**) and two equivalents of NaOH was carried out by bubbling N_2 gas in order to introduce volatile materials into a trapping tube containing ethyl ether cooled at −50 °C. After irradiation for 24 h, GLC analysis of the ether solution showed formation of benzene in a 16% yield on the basis of starting **1**. The irradiated reaction mixture was found to contain a trace amount of biphenyl (<1%) by GLC up to 250 °C.

Irradiation of Aqueous Benzenesulfonic Acid (1). Aqueous benzenesulfonic acid (**1**) was irradiated with a high-pressure mercury lamp under N_2. Evolved gas was identified to be SO_2 by the fuchsine test. The photolysis of **1** was carried out by bubbling N_2 in order to introduce the evolved gas into a trapping tube containing 10% H_2O_2. The evolved SO_2 was converted into H_2SO_4 by aqueous H_2O_2 and titrated with standard aqueous alkali. The yield of resulting SO_2 was 9.6% based on the consumed **1**. The irradiated solution was extracted with ether. The aqueous layer, containing unreacted **1** and other acidic materials, was concentrated *in vacuo*, esterified by CH_2N_2, and then analyzed by GLC. Only a peak of methyl benzenesulfonate was observed (35% recovery). The aqueous layer contains H_2SO_3 and/or H_2SO_4 in a total yield of 29.0%.

On the other hand, the organic layer of the ether extract contains biphenyl (1%, mp and mixture mp 69—70 °C). No formation of benzene was observed even under conditions similar to those for sodium benzenesulfonate. In contrast to sodium benzenesulfonate, the resulting phenyl radical formed by homolysis of the C–S bond may form complex products; the H_2SO_3 (and probably H_2SO_4) may attack the phenyl radical, inhibiting the formation of benzene.

Addition of 6-fold excess H_2O_2 to the system markedly increased the consumption of **1**. About 97% of **1** disappeared after 11 h to afford CO_2 (8%), H_2SO_4 (34%), phenol (<1%) *etc.*

No reaction occurred in the dark with the same system. Hence the acceleration by H_2O_2 may be due to the oxidation induced by ·OH radical from H_2O_2. The quantum yield for decomposition of **1** in water was 0.26 with 254 nm light.

Attempt to Characterize Tarry Material. Irradiation of **1** under acidic conditions yielded only a small amount of volatile product, biphenyl (1%), most part of the product being a black tarry material (95 wt % based on the consumed **1**). The structure of the substance is still obscure on account of its contaminant and experimental difficulties. After elimination of **1** and H_2SO_4, the tarry substance was found to contain 8.7 wt % of sulfur atom, the total amount of sulfur in recovered and isolated materials reaching 91%.

Attempts were made to isolate organic substance from the residue. Chromatography of the tarry material with a SiO_2 column yielded an yellow oil (5 wt %), giving two GLC peaks. However, the two components were too small in quantity for further purification. They were thus analyzed by GLC-MS, the results of which indicated their molecular weight to exceed 300 with no aromatic fragment ions (*e.g.*, *m/e* 77 and 91). The structure has not been identified yet. A remaining solid was obtained by the column chromatography.

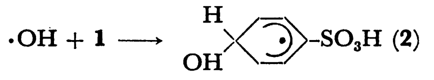
Mechanism. The photoproducts, *e.g.*, benzene and biphenyl, indicate that the primary process may be the fission of C–S bond. The sum of yields of fission products (SO_2+H_2SO_4) in Eq. 1 reaches 38.6% based on the consumed **1**; thus Eq. 1 should be the main primary path for the decomposition. The fate of the resulting Ph· and ·SO_3H radicals may be as follows:

$$PhSO_3H\ (\mathbf{1}) \xrightarrow{h\nu} Ph\cdot + \cdot SO_3H \qquad (1)$$

$$Ph\cdot + \mathbf{1} \longrightarrow Ph_2 + \cdot SO_3H \qquad (2)$$

$$Ph\cdot + RH \longrightarrow PhH + \cdot R \qquad (3)$$

$$\cdot SO_3H \longrightarrow SO_2 + \cdot OH \qquad (4)$$



(5)

$$\mathbf{2} \longrightarrow Ph\cdot + H_2SO_4 \qquad (6)$$

$$\mathbf{2} \longrightarrow \text{further reaction (tarry materials)} \qquad (7)$$

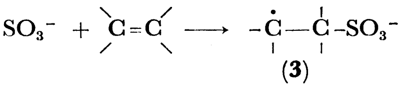
$$2\ \cdot OH \longrightarrow H_2O_2 \qquad (8)$$

$$H_2O_2 + SO_2 \longrightarrow H_2SO_4 \qquad (9)$$

(RH: Hydrogen sources)

It may be concluded that the homolysis of excited **1** to (Ph·+·SO_3H) is more plausible than the heterolysis into phenyl cation because of the formation of biphenyl but not phenol in both acidic and basic media. Water cannot be a hydrogen source for phenyl radical to benzene in Eq. 3, since the bond energy of C–H for benzene (112 kcal/mol) is lower than that of O–H for H_2O (120 kcal/mol).[5] Intermediary products such as **2** may play the role of hydrogen donor in Eq. 3.

It is of interest to note that the formation of benzene is favored in alkaline media. A plausible reason is as follows. In acidic media, ·SO_3H collapses into SO_2 and ·OH which subsequently oxidizes **1**, whereas in alkaline media, ·SO_3H exists as metastable ·SO_3^- species[6] which expels only slowly ·OH radical. The anion radical ·SO_3^- is known to add to unsaturated bonds, *e.g.*, aromatic ring according to Eq. 10.[7] Species **3** in Eq. 10 as well as **2** in Eq. 5 can be H· source for benzene formation.



$$\cdot\mathrm{SO_3^-} + \mathrm{>C{=}C<} \longrightarrow -\overset{\bullet}{\mathrm{C}}-\mathrm{C}-\mathrm{SO_3^-} \qquad (10)$$

(3)

Intermediacy of phenyl radical was also confirmed by the formation of benzene in the photolysis of **1** in the presence of a hydrogen donor such as 2-PrOH even under acidic conditions. The observed biphenyl may be formed either by the coupling of two Ph· or by an attack of Ph· on a phenyl ring of the starting **1** followed by a collapse to biphenyl and ·SO_3H radical (Eq. 2).

Another fragment, ·SO_3H, can be succesively decomposed to SO_2 and hydroxyl radical (Eq. 4). Hydration of SO_2 gives H_2SO_3, which is easily converted by H_2O_2 into H_2SO_4. Formation of H_2SO_4 from SO_2 and H_2O_2 was actually observed (Eq. 9). The resulting ·OH radical may couple to form H_2O_2 and also may attack **1** and other materials to give derivatives of **2** and oxidized tarry materials.[8]

It is less probable that $PhSO_3H$ is cleaved to ·OH and $PhSO_2$·, and then collapses to Ph· and SO_2, since the fission of $PhSO_2$· to Ph· and SO_2 is endothermic.[9]

The following results suggest that the reactive state is a singlet: (i) No quenching by a triplet quencher, *i.e.*, molecular oxygen, and (ii) no heavy atom effect by *n*-BuBr as a solvent.

Experimental

Melting points were measured on a hot plate with a Ynagimoto micro melting point apparatus and were corrected. IR spectra were measured with a Perkin-Elmer Model 337 spectrophotometer. A Yanagimoto GCG 550F gas chromatograph was used with two 2 m×2.5 mm columns, one packed with 2.5% PEG 20 M on a Chamelite CS and the other with Bentone 34+DIDP on a Chromosorb. A Shimadzu GC-MS 7000 was used for GLC-MS spectra.

A Typical Photolysis of Sodium Benzenesulfonate in Alkali. An aqueous solution (500 ml, 2.2×10^{-2} M) of **1**(2 g) with two equivalents of NaOH was irradiated with a 300 w Halos high pressure Hg lamp. Volatile materials evolved were introduced with N_2 gas as a carrier into a trapping tube containing ethyl ether at −50 °C. After irradiation for 24 h, GLC analysis of the ether solution indicated the formation of benzene (16% based on the starting **1** used). Biphenyl(<1%) was detected by GLC of the irradiated aqueous solution.

A Typical Photolysis of Benzenesulfonic Acid(1). An aqueous solution (200 ml, 5×10^{-2} M) of **1**(1.65 g) was irradiated under N_2 for 16 h using a 100 w Halos high pressure Hg lamp. Evolved SO_2 was identified by the color change of a fuchsine solution. The yield of evolved SO_2 was 9.6% based on the consumed **1** using titrimetry with a 0.01 M NaOH after its conversion into H_2SO_4 with aqueous H_2O_2. After the completion of irradiation, the solution was extracted with ether (200 ml). Biphenyl was obtained after evaporation of ether (20 mg, mp and mixture mp 69—70 °C).

The aqueous layer was subdivided into three equal portions. The first portion was used for the measurement of the conversion of **1**. After concentration under reduced pressure, it was esterified with CH_2N_2. The conversion of **1** was found to be 65% by GLC. The data were checked by a blank experiment in the dark.

The yield of H_2SO_3 and/or H_2SO_4 in the second portion (29.0%) was determined as $BaSO_4$ (0.13 g) by addition of $BaCl_2$ after treatment of excess H_2O_2.

The third portion was condensed *in vacuo* to give a black tarry material (0.5 g) contamintated with **1** (0.17 g). The yield of this was 95 wt% based on the consumed **1**.

Column Chromatography. The tarry material (0.5 g) was passed through a column of 50 cm×2.0 cm packed with SiO_2. A mixture of benzene and methanol was used as an eluant. The eluate, a mixture of two components not separable, showed the following spectra: IR(cm^{-1}) 1725(C=O); NMR(CCl_4) δ 0.7—1.8, 4.0—4.3, and 7.2—7.6; *m/e* 362, 265, 247, 176, 149, 121, 99, 70, 69, and 43. The elemental analysis of the black solid. Found; C, 59.00; H, 3.83; O, 27.68; S, 9.49%.

Quantum Yield. An aqueous 5×10^{-6} M solution of **1** in a 10 mm thick quartz cell(10 ml) was irradiated with a 30 w low-pressure Hg lamp (254 nm). A ferrioxalate actinometer was used.[10]

Quenching Study. A 4.6×10^{-2} M solution of **1** saturated with a quencher, molecular oxygen, was irradiated with a 300 w high-pressure Hg lamp for 8 h. The conversion of **1** was 54%, which was similar to that(50% for 8 h) in the experiment in the absence of the quencher.

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