The Reaction of 3, 5-Dibromo-4-hydroxybenzenesulfonyl Chloride with Weak Bases (The Question of the "Quinoid Sulfene" Intermediate*)

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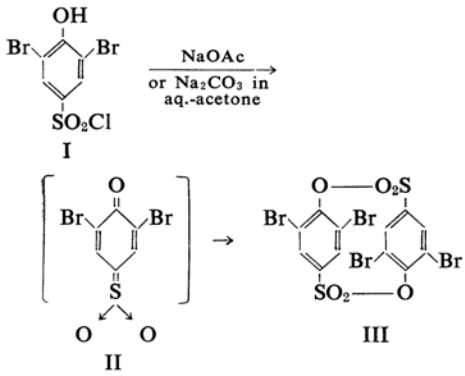
(Received February 22, 1965)

Many decades ago, Zincke[1] and his coworkers suggested the formation of the "sulfene" intermediate (II) in the reaction of 3, 5-dibromo-4-hydroxybenzenesulfonyl chloride (I) with either sodium acetate or carbonate in an aqueous acetone solution; they made this suggestion on the basis of their observations that a bright yellow color is formed and then gradually disappears during the reaction, finally giving a colorless precipitate which was presumed to have structure (III).



I II III

The possibility of this "quinoid sulfene" intermediate is rather fascinating in view of the recent interest in aliphatic "sulfene."[2] However, there has been no legitimate evidence to substantiate the formation of the intermediate during the reaction, nor has the product ever been proved to have structure III.

We have investigated this reaction, first by following the change in the ultraviolet absorption and then by determining the structure of the product. When an acetone solution of 3, 5-dibromo-4-hydroxybenzenesulfonyl chloride was mixed with a 20% aqueous solution containing an equimolar amount of potassium acetate, a bright yellow color developed immediately. Meanwhile, colorless precipitates started to form gradually and the yellow color faded away. Then the ultraviolet absorption was swept at several time intervals. The results are shown in Fig. 1. At an early stage of the reaction, when the yellow color was still strong, one saw a clear maximum at 310 mμ, but this maximum gradually faded away as time passed. The strong absorption around 310 mμ might be due to the quinoid structure of the intermediate "sulfene."

However, Cannell[3] has recently shown that the quinoid intermediate (IV) formed during the bromination of sodium 3, 5-dibromo-4-hydroxybenzenesulfonate has a strong absorption around 280 mμ ($\varepsilon = 11400$).

IV

The process was also followed by the sweeping of the infrared spectrum around 1500—2000 cm^{-1}, in order to detect the presence of a conjugated carbonyl group. However, as Fig. 2 shows, there was no detectable absorption of any carbonyl function in the spectrum.

Since quinoid compounds are known to undergo electron transfer with phenolic compounds, thus forming fairly stable radicals, usually detectable by means of ESR spectroscopy,[4] the color which appeared in this reaction was suspected of being associated with the formation of an radical. The ESR spectrum was taken during the process of color formation. However, no detectable signal was observed.

Therefore, we have at present no concrete evidence to support the formation of the "quinoid sulfene" intermediate, nor can we offer any alternative suggestion as to the nature of the yellow color or of the incipient ultraviolet absorption perk at 310 mμ.

When triethylamine was used in place of sodium acetate, it was found to effect the same reaction. In fact, with the tertiary amine one

* Presented at the 14th Annual Meeting of the Chemical Society of Japan, April, 1961. Paper V of "Reactions of Phenols and Phenolic Esters."

1) a) T. Zincke and W. Glahn, *Ber.*, **40**, 3039 (1907); b) T. Zincke and R. Brune, ibid., **41**, 902 (1908).

2) a) W. E. Truce, J. J. Breiter, D. J. Abraham and J. R. Norell, *J. Am. Chem. Soc.*, **84**, 3030 (1962); b) G. Optiz and H. Adalph, *Angew. Chem.*, **74**, 77 (1962); c) G. Optiz and K. Fischer, *Z. Naturforsch*, **186**, 775 (1963).

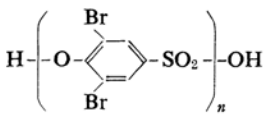
3) L. G. Cannell, *J. Am. Chem. Soc.*, **79**, 2927 (1957).

4) Private communication from Dr. R. Konaka.

can use anhydrous conditions and usually get better results. However, in this case the product appeared to be slightly more soluble in benzene, nitrobenzene or dioxane, possibly because of the lower molecular weight. Several attempts were made to freeze the intermediate for physical measurement by running the reaction in a dry-ice acetone bath. However, as soon as the solvent was evaporated, only a colorless precipitate remained.

The colorless precipitate, which was presumed to have structure III, is insoluble in most common solvents but only sparingly soluble in benzene and a little more soluble in nitrobenzene. It has no melting or decomposition points below 350°C. Since the amorphous precipitate is sparingly soluble in benzene and nitrobenzene, the molecular weight determination in these solvents was not successful, despite repeated careful attempts.

When this material was refluxed in a 6 N sodium hydroxide solution for an hour, the precipitate dissolved completely to give a clear solution. From the clear solution 3, 5-dibromo-4-hydroxybenzenesulfonic acid was recovered almost quantitatively as its *S*-benzylthiuronium salt. The mode of the facile hydrolysis was very similar to that with phenyl benzenesulfonate.[5] The acid hydrolysis was very sluggish and was found to take place only above 160°C in a sealed tube using 10 N hydrochloric acid, similar to the case of phenyl benzenesulfonate.[6] When it was hydrolyzed at 180°C for 24 hr., 3, 5-dibromo-4-hydroxybenzenesulfonic acid was recovered in an almost quantitative yield as its *S*-benzylthiuronium salt. These observations on the hydrolyses, together with the analytical data, seem to suggest that the precipitate has a structure similar to phenyl benzenesulfonate, possibly a linear oligomer such as V.



V

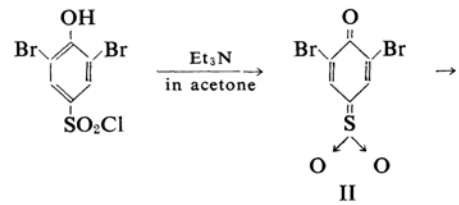
Both the infrared and the ultraviolet spectra of the material is almost identical with those of 3, 5-dibromo-4-hydroxybenzenesulfonic acid. Zincke's cyclic structure will not give similar ultraviolet and infrared spectra, because the molecule of the structure would be terribly strained and might be expected to change the nature of the electronic behavior considerably.

A rough determination of the terminal hydroxy group was carried out by reacting with phenyl isocyanate the precipitate obtained in the reaction with triethylamine. The product, presumably the urethan of the oligomer V, obtained in this reaction did not melt below 350°C, but its analytical composition is that of the phenyl urethan of either tetramer or pentamer of V, or a mixture of both.

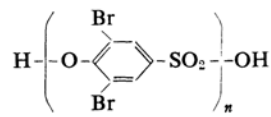
It is interesting to note that the oligomer can be crystallized from benzene, but that the crystals become amorphous powder when benzene is completely evaporated. A preliminary X-ray analysis[7] revealed the same phenomena.

Since the crystals were rather short-lived outside of the benzene solution, no further attempt was made to determine the structure. However, they are most likely a kind of clathrate complex, the oligomer and benzene being the host and the guest molecules respectively.

In conclusion, the reaction of 3, 5-dibromo-4-hydroxybenzenesulfonyl chloride (I) with a base such as triethylamine produces an quasi-stable intermediate, possibly the "quinoid sulfene" intermediate (II), which is sufficiently long-lived to find a few similar partner with which to oligomerize to the oligomer V, as is shown below:



II



V

Experimental

3, 5-Dibromo-4-hydroxybenzenesulfonyl Chloride. — Sodium 3, 5-dibromo-4-hydroxybenzenesulfonate was obtained by the methods reported by Huston and Neeley,[8] and by Oshima[9] (yield 88%). The product was recrystallized from water and identified as 3, 5-dibromo-4-hydroxybenzenesulfonic acid *S*-benzylthiuronium salt; m. p. 192—193°C.

Found: C, 33.23; H, 2.81. Calcd. for $[C_6H_3Br_2O_4S]^-[C_6H_5CH_2SC(NH_2)_2]^+$: C, 33.05; H, 2.60%.

When the product was then allowed to react with a mixture of phosphorus oxychloride and

5) D. R. Christman and S. Oae, *Chem. & Ind.*, **1959**, 1251.
6) S. Oae, T. Fukumoto and R. Kiritani, ibid., **36**, 346 (1963).
7) We are indebted to Professor M. Kakudo for his generous collaboration.
8) R. C. Huston and A. H. Neeley, *J. Am. Chem. Soc.*, **57**, 2177 (1935).
9) See "Benzenesulfonic Acid" in "Yukikagaku Goseiho," Vol. I, Gihodo, Inc., Tokyo (1953), p. 31.

phosphorous pentachloride,[1a] 3,5-dibromo-4-hydroxybenzenesulfonyl chloride was obtained (66% yield from sodium salt). The sulfonyl chloride thus obtained was recrystallized from benzene; m. p. 128—129°C (Found: C, 20.2; H, 0.82%).

The Reaction of 3,5-Dibromo-4-hydroxybenzenesulfonyl Chloride with Sodium Acetate.[1b]—A solution of 3,5-dibromo-4-hydroxybenzenesulfonyl chloride (2 g., 0.0058 mol.) and 5 ml. of acetone was cooled in an ice-water bath. As soon as an equimolar amount of a 20% aqueous sodium acetate solution (3.5 ml.) was slowly added to the solution, the mixture turned a bright yellow; this color gradually disappeared during the reaction, and white precipitates were formed. The mixture was heated to reflux gently for a few minutes and then allowed to stand. The colorless solid product was obtained in a 30—35% yield based on the starting sulfonyl chloride. It could be recrystallized from nitrobenzene (no m. p. below 350°C). Together with the water-insoluble solid, the hydrolysis product, 3,5-dibromo-4-hydroxybenzenesulfonic acid, was also obtained from the filtrate; it was identified as a *S*-benzylthiuronium salt. The unchanged reactant was also recovered.

The Reaction of 3,5-Dibromo-4-hydroxybenzenesulfonyl Chloride with Triethylamine.—An acetone solution of 3,5-dibromo-4-hydroxybenzenesulfonyl chloride (2 g. in 5 ml. of acetone) was cooled and added to an equimolar amount of triethylamine. The reaction was nearly identical with that in an aqueous acetone solution with sodium acetate. The water-insoluble colorless product (yield 30—35%) was slightly soluble in hot benzene (no m. p. below 350°C). Recrystallization from benzene gave colorless shiny prismatic crystals in the bottom of the benzene layer; however, when the crystals were collected on filter paper, they gradually pulverized to an amorphous white powder. The analytical values of the colorless precipitate are as follows:

	C%	H%	Br%	S%
Calcd. for III	22.92	0.64	50.93	10.21
Calcd. for $V_{n=5}$	22.69	0.76	50.33	10.10
Found (by Zincke et al.)	23.36	0.40	50.75	10.07
Present investigation	22.59	0.77	50.83	9.99

The Alkaline Hydrolysis of the Colorless Precipitate.—The colorless precipitate (1 g.) was added to a 20% aqueous sodium hydroxide solution (25 ml.); the mixture was refluxed for 1.5 hr., neutralized with hydrochloric acid, and finally evaporated down to 2 ml. When a few drops of hydrochloric acid and *S*-benzylthiuronium chloride (0.7 g.) were added to this solution, the *S*-benzylthiuronium salt of 3,5-dibromo-4-hydroxybenzenesulfonic acid (1.5 g.) was obtained (in a nearly quantitative yield).

The Acid Hydrolysis of the Colorless Precipitate.—The colorless precipitate (1 g.) and 10 N hydrochloric acid (20 ml.) were sealed in a tube and heated at 180°C for 24 hr. The resultant mixture was filtered, and the filtrate was treated with *S*-benzylthiuronium chloride as described above; the *S*-benzylthiuronium salt of 3,5-dibromo-4-hydroxybenzenesulfonic acid (1.3 g.) was obtained. The precipitate was found to be the unchanged polymer (0.1 g., 10%).

The Reaction of the Colorless Precipitate with Phenyl Isocyanate.[10]—Phenyl isocyanate (0.3 g., 0.0025 mol.) was added to a solution of the colorless precipitate (1.6 g., 0.0025 mol. as the linear dimer) in 20 ml. of dioxane, and then a few drops of anhydrous pyridine were added to the mixture. After the mixture has been refluxed for one hour, the solvent was removed. The residual precipitate was washed thoroughly with a large quantity of ice-water. Thus, a light brown precipitate partially soluble in benzene was obtained (1.6 g.) (no m. p. below 350°C). The analytical values of the product recrystallized from benzene, shown below, indicate that the urethan derivative of the oligomer was a mixture of the tetramer and the pentamer.

Found: C, 26.43; H, 1.15; Br, 46.46; S. 9.31; N, 0.88. Calcd. for $C_{37}H_{17}O_{17}Br_{10}S_5N$ (pentamer): C, 26.03; H, 1.00; Br, 46.82; S, 9.39; N, 0.82, for $C_{31}H_{15}O_{14}Br_8S_4N$ (tetramer): C, 26.73; H, 1.09; Br, 45.90; S, 9.21; N, 1.01%.

Ultraviolet Spectra.—The ultraviolt spectra of the "quinoid sulfene" intermediate, the colorless precipitate and 3,5-dibromo-4-hydroxybenzenesulfonyl chloride are shown in Fig. 1.

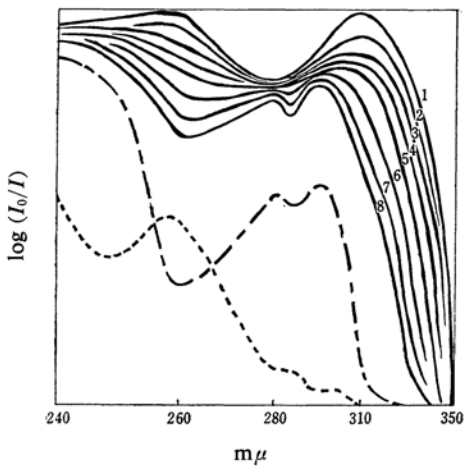


Fig. 1

—— UV spectra of quinoid sulfene intermediate: 1, 2, 3, ···, 8, after mixing the 3,5-dibromo-4-hydroxybenzenesulfonyl chloride in dioxane with an aqueous equimolar amount solution of potassium acetate, 30 sec., 5, 10, 20, 30, 40, 50, and 60 min.

– – – The oligomer V

---- 3,5-Dibromo-4-hydroxybenzenesulfonyl chloride (4×10^{-7} mol./ml.) in *n*-hexane

A known amount of 3,5-dibromo-hydroxybenzenesulfonyl chloride was dissolved in pure dioxane (1×10^{-5} mol./10 ml.), and also an aqueous solution in which has been dissolved an equimolar amount of potassium acetate solution (1×10^{-5}

10) See "Urethans" in "The Systematic Identification of Organic Compounds," by R. L. Shriner and R. C. Fuson, John Wiley & Sons, New York, N. Y. (1956), p. 211.

mol./10 ml.) was prepared. The two solutions were separately cooled in an ice-salt bath before mixing. As soon as the cooled dioxane solution was mixed with the aqueous solution, the ultaviolet spectra of the mixed solution were followed from time to time by a ultraviolet photospectrometer, with special attention paid to the absorption band at 310 mμ.

Infrared.—The infrared spectrum of the "quinoid sulfene" intermediate, sweeping at around 1500—2000 cm^{-1}, is shown in Fig. 2.

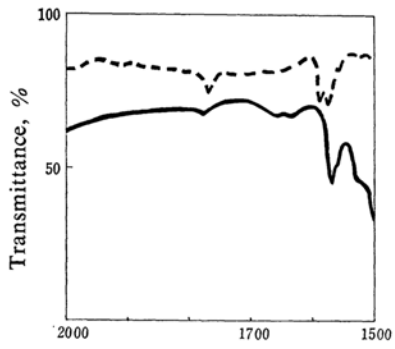


Fig. 2

—— Infrared spectra of quinoid sulfene intermediate: after mixing the 3,5-dibromo-4-hydroxybenzenesulfonyl chloride in dioxane with triethylamine, 1 min.

---- 3,5-Dibromo-4-hydroxybenzenesulfonyl chloride in dioxane

A triethylamine-dioxane solution (1 mol. soln.) was put into a liquid cell (0.5 mm. thick) containing the same amount of a solution of 3,5-dibromo-4-hydroxybenzenesulfonyl chloride in dioxane (1 mol. soln.). After the mixture has been sufficiently shaken, the absorption of the carbonyl group was followed as soon as possible. The infrared spectrum of the solid precipitate, the oligomer V, is shown in Fig. 3.

At 3450 cm^{-1}, the absorption of the hydroxy group is clearly observed, while at 1210—1150, 1060—1030 and near 650 cm^{-1} the absorption of the $-SO_3H$ and $-SO_3-$ groups are observed in contrast with that of the reactant. The figure is simple and resembles the combined infrared absorption spectra of 3,5-dibromo-4-hydroxybenzenesulfonic acid phenyl benzenesulfonate.

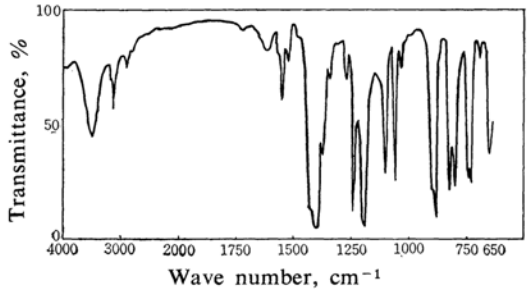


Fig. 3. Infrared spectrum of polymer in KBr disk.

Electron Spin Resonance.—All the ESR measurements were performed at X band frequencies, using a spectrometer equipped with a 100 Kc. modulation unit. A solution of 3,5-dibromo-4-hydroxybenzenesulfonyl chloride in dioxane (1.43 mol. soln.) was put into a quartz cell, and then a few drops of a triethylamine or potassium acetate-dioxane solution were added. Before the yellow color had disappeared, the samples were measured at room temperature and −180°C (the *g*-factor was 2.05—1.95). As no electron spin resonance signals were detected, the radical concentration was presumed to be below 10^{-6} mol.

Summary

The formation of the "quinoid sulfene" intermediate, II, during the reaction between 3,5-dibromo-4-hydroxybenzenesulfonyl chloride and a weak base has been investigated by following the ultraviolet spectra of the reaction mixture. It has been suggested that the colorless precipitate formed as the final product of the reaction is an oligomer and has structure V.

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