collected on a filter, washed with dilute sodium bicarbonate solution and recrystallized from 50 ml. of 95% ethanol with the addition of Darco. After washing with cold alcohol, the material was recrystallized again from alcohol to give 2.5 g. (38% yield) of pale-yellow product, m.p. 107–108°. Subsequent runs gave 17–22% yields of the anilide.

The other anilides in Table VI were prepared from the corresponding imines in the same manner.

Preparation of the Azomethine Dyes (III) (Tables I–IV). General Procedure.—Method A is carried out as follows: in a 1-l. beaker equipped with a stirrer was placed a solution of 0.01 mole of aroylacetanilide in 200 ml. of 95% ethanol. A solution of 5 g. of sodium carbonate in 50 ml. of water was added, followed by 0.011 mole (2.35 g.) of 4-amino-3-methyl-N,N-diethylaniline hydrochloride in 50 ml. of water. To the stirred mixture was added a solution of 0.04 mole of potassium ferricyanide in 100 ml. of water. Stirring continued for 15 min., and the dye was extracted with 250 ml. of ethyl acetate. The extract was washed several times with water and the solvent removed *in vacuo*. The residue was purified by chromatography over Doucil, with benzene or a mixture of ligroin (b.p. 60–90°) and acetone for development and elution; yield of dye 30–60%.

Method B, the use of silver chloride as the oxidant for preparation of the dyes, has been described previously.[5] The absorption spectra of the azomethine dye solutions, 8×10^{-5} molar concentration, for a 1-cm. thick sample against a water blank, were obtained with a General Electric recording spectrophotometer, using a constant spectral band width of 8 mμ.

Acknowledgment.—The authors thank Mr. E. E. Richardson, of these Laboratories, for the spectrophotometric curves.

ROCHESTER 4, N. Y.

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES OF HARVARD UNIVERSITY]

The Bromodesulfonation of Aromatic Sulfonate Salts. I. Sodium 3,5-Dibromo-4-hydroxybenzenesulfonate[1]

BY LAWRENCE G. CANNELL[2]

RECEIVED DECEMBER 20, 1956

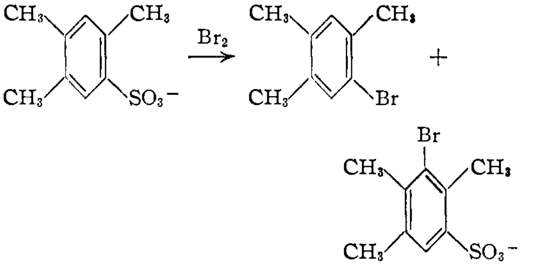
The reaction of bromine with sodium 3,5-dibromo-4-hydroxybenzenesulfonate (I) to give tribromophenol has been studied in aqueous solution at 25.0°. Ultraviolet and visible spectra show that the reactants combine immediately to give a reaction intermediate which has a 2,6-dibromo-2,5-cyclohexandien-1-one structure. Kinetics (measured iodometrically) give additional support to a mechanism (eqs. 4 and 5) comprised of the formation of the intermediate and Br^- in a fast reversible step which is followed by the first-order decomposition of the intermediate in a rate-determining step. Specifically, the kinetics are zero order in whichever reactant, bromine or I, is in excess and first order in the other. The equilibrium of the first step greatly favors the formation of the intermediate, but the reverse reaction can be demonstrated both kinetically and spectrophotometrically when sodium bromide is added. The significance of these results in regard to the mechanism of electrophilic aromatic substitution is discussed.

The bromodesulfonation reaction (eq. 1) has been investigated by measuring its reaction kinetics. Previous investigators have found that the reaction is greatly facilitated by amino, methoxy, hydroxy or alkyl substituents *ortho* or *para* to the sulfonic acid group, but that these substituents in the *m*-position do not promote bromodesulfonation.[3–7] The reaction, then, appears to be an example of electrophilic aromatic substitution.

$$Br_2 + ArSO_3^- + H_2O \rightarrow ArBr + HSO_4^- + HBr \quad (1)$$

Comparable reactions have been reported with chlorine as a desulfonating agent,[8] but molecular iodine does not give the reaction.[9]

That the bromodesulfonation reaction does not proceed by a free-radical mechanism is indicated from the reaction with alkylbenzenesulfonate salts. Here bromination occurs on the aromatic ring and not on the side chain where it would be expected if the reaction takes place by a free-radical mechanism.[12]



(2)

In certain special cases the replacement of a sulfonic acid group by *chlorine* appears to be a free-radical reaction,[13] but these exceptions are charac-

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[1] This paper was presented in part at a symposium on aromatic substitution held by the Division of Organic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 20, 1956.

[2] Shell Development Co., Emeryville, Calif. National Science Foundation post-doctoral fellow 1955–1956.

[3] R. L. Datta and J. C. Bhoumik, THIS JOURNAL, **43**, 303 (1921).

[4] J. J. Sudborough and J. V. Lakhumalani, *J. Chem. Soc.*, **111**, 41 (1917).

[5] M. S. Van Dorssen, *Rec. trav. chim.*, **29**, 377 (1910); J. Obermiller, *Ber.*, **43**, 4361 (1909).

[6] A. N. Meldrum and M. S. Shah, *J. Chem. Soc.*, **123**, 1982 (1923).

[7] O. Heinichen, *Ann.*, **253**, 267 (1889).

[8] R. L. Datta and H. K. Mitter, THIS JOURNAL, **41**, 2028 (1919).

[9] Bromate,[2,8] iodate[2] or chlorate[2,8] salts in combination with the corresponding hydrohalic acid can also be employed as halogenodesulfonating agents.

[10] T. Callan and J. A. R. Henderson, *J. Soc. Chem. Ind.*, **41**, 161-T (1922).

[11] G. Heller, *Ber.*, **46**, 2703 (1913).

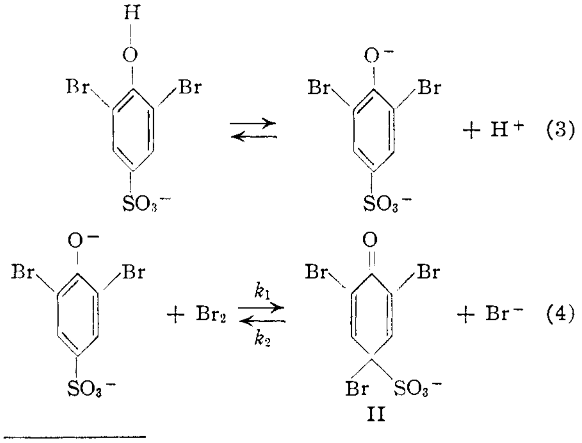
[12] W. Kelbe and K. Pathe, *ibid.*, **19**, 1546 (1886); W. Kelbe and H. Stein, *ibid.*, **19**, 2137 (1886).

[13] It was established by Kharasch and Eberly (1940) that, contrary to the claim of Eckert (*Ber.*, **58**, 313 (1925)), α- and β-anthraquinonesulfonic acids do not react with hydrochloric acid in the light to give the corresponding α- and β-chloroanthraquinones if oxygen is rigidly excluded from the system. However, if oxygen is present, the reaction studied by Eckert takes place readily. It was also established that, whereas water solutions of α- and β-anthraquinone sulfonic acids do not react with chlorine in the dark, a ready formation of the corresponding chloroanthraquinones takes place in the light. Results similar to the ones cited above have been obtained with anthraquinone-2,6-disulfonic acid. A free radical mechanism involving chlorine atoms has been postulated to explain these results. It was also established that bromine atoms do not replace sulfonic acid groups under the conditions cited above. A publication dealing with these findings will appear shortly (private communication from M. S. Kharasch).

terized by the presence of electron-withdrawing substituents and usually require much more vigorous conditions.[14]

Many investigators, studying aromatic substitution reactions wherein hydrogen is replaced, have interpreted their results in terms of quinonoid intermediates or transition states.[15] In particular, Melander cited such intermediates to account for the isotope effects in the nitration and sulfonation of benzene,[16] and Zollinger[17] has found evidence for their existence by studying the effect of base on diazonium coupling reactions.[17,18] Grovenstein and Henderson recently have reported, in a kinetic investigation of the bromodecarboxylation of dibromo-*o*- and -*p*-hydroxybenzoic acids to give 2,4,6-tribromophenol, that the rate dependence on (Br^-) strongly suggests that there is a quasi-stable quinonoid intermediate which can react with bromide ion to give starting materials.[19]

In the present work, the bromodesulfonation of sodium 3,5-dibromo-4-hydroxybenzenesulfonate (I) was investigated, and in a subsequent paper the bromodesulfonation of various other aromatic sulfonate salts will be discussed.[20] The findings presented in this paper show that I reacts with bromine according to the scheme[21,22]



(3)

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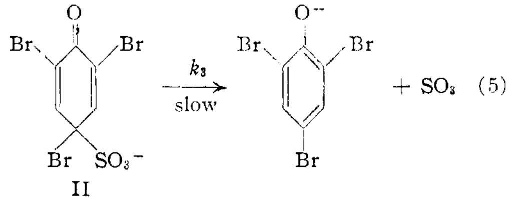

(5)

$$SO_3 + H_2O \longrightarrow H_2SO_4 \qquad (6)$$

The intermediate II is sufficiently stable that it can be detected spectroscopically. Kinetic and spectroscopic evidence confirm the presence of the equilibrium involving bromide ion which is shown in eq. 4, and the kinetic study indicates strongly that the rate-determining step is the unimolecular decomposition of the quinonoid, II.

Results

When dilute aqueous solutions of the dibromo-*p*-phenolsulfonate I and bromine were mixed, the bromine color disappeared immediately even at 0°; however, the immediate addition of iodide gave an iodine titer equal to that of the bromine originally used. Also, when compound I was mixed with an equal molar amount of bromine, the spectrum of I disappeared and an absorption peak appeared at 280 mμ (see Fig. 1). The peak height decreased slowly over a period of several hours, and the final spectrum closely resembled that of 2,4,6-tribromophenol. The iodine titer of the solution decreased with time. The kinetics were found to be first-order in bromine and zero-order in the dibromo-*p*-phenolsulfonate when the latter was in excess (see Table I). In a 0.15 *M* sodium bromide solution, the color of the tribromide ion appeared, and the rate of reaction was decreased by a factor of 1.6. When the dibromo-*p*-phenolsulfonate was in excess, the first-order rate constant, k_3, was equal to the slope of the line obtained by plotting ln (B) *vs.* t (where B is the iodine titer of the solution in moles/l. at time, t). The reproducibility of the rate constants were within 3%. The experiments were carried out at a constant ionic strength in order to avoid any interfering salt effect. The effect of ionic strength was not studied except to note that changes in the region 0.6 to 0.16 μ had little effect on the rate (see experiment 5).

With bromine in excess, the kinetics were found to follow the rate equation where A_0 is the initial

$$(B_0 - B)/t = k'(A_0) \qquad (7)$$

concn. of I (see Table II). The data show the reaction to be zero order in bromine and first order in the dibromo-*p*-phenolsulfonate. Further work, which is discussed later in this paper, was undertaken in order to relate k_3 to k'.

Discussion

Spectral Measurements.—Spectral measurements provide not only evidence for a reaction intermediate but make it possible to assign the intermediate a 2,5-cyclohexadienone structure. Mixing an aqueous solution of sodium 3,5-dibromo-4-hydroxybenzenesulfonate (I) with an equal molar amount of bromine in water brought about the immediate disappearance of the bromine color. Also, the spectrum of I, which has only a

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[14] These reactions are carried out at 90–250° with chlorine or a chlorate salt and hydrochloric acid; see K. Lauer, *J. prakt. Chem.*, **135**, 182 (1932); H. Schilling, *Ber.*, **46**, 1066 (1913); P. Friedländer, S. Karamessinis and O. Schenk, *ibid.*, **45**, 55 (1922); V. V. Koslov, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 289 (1947); *C. A.*, **42**, 550 (1948).

[15] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 330–363; W. A. Waters, *J. Chem. Soc.*, 727 (1948).

[16] L. Melander, *Arkiv Kemi*, **2**, 211 (1951); U. Berglund-Larsson and L. Melander, *ibid.*, **6**, 219 (1953).

[17] Hch. Zollinger, *Helv. Chim. Acta*, **38**, 1597 (1955).

[18] See also W. M. Shubert and P. C. Myhre, Abs. of Am. Chem. Soc. Meeting, Atlantic City, N. J., September 16–21, 1956, p. 58-O.

[19] E. Grovenstein, Jr., and U. V. Henderson, Jr., THIS JOURNAL, **78**, 569 (1956). Their argument has been further strengthened by isotopic fractionation work; see E. Grovenstein, Jr., and G. A. Ropp, *ibid.*, **78**, 2560 (1956).

[20] L. G. Cannell, THIS JOURNAL, **79**, 2932 (1957).

[21] Datta and Bhoumik (ref. 3) have reported that I and an equal molar amount of bromine give a quantitative yield of 2,4,6-tribromophenol.

[22] The scheme shows bromination taking place with the phenoxide anion rather than with the phenol, although experiments have not yet shown this directly. Evidence has been found[20] that ionization of the phenol precedes the bromodesulfonation of sodium 4-hydroxy-3,5-dinitrobenzenesulfonate. Also, Grovenstein and Henderson[19] found that the rate of bromodecarboxylation of 3,5-dibromo-4-hydroxybenzoic acid is inversely proportional to $(H^+)^2$ and concluded that bromination occurs after the loss of two protons.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE BROMODESULFONATION OF SODIUM 3,5-DIBROMO-4-HYDROXYBENZENESULFONATE

		Concn. given in moles/liter					
Expt.	Temp., °C.	$(\mathrm{ArSO_3Na})_0 \times 10^4$	$(\mathrm{Br_2})_0 \times 10^4$	$(\mathrm{HClO_4})_0$	$(\mathrm{NaBr})_0$	$(\mathrm{NaClO_4})_0$	10^3k_3, min.$^{-1}$
1	24.93	10.00	5.04	0.0100	0	0.1500	5.49
2	24.93	30.00	4.58	.0100	0	.1500	5.35
3	24.93	50.0	3.25	.0100	0	.1500	5.67
4	24.93	10.0	5.48	.0300	0	.1300	5.69
5	24.93	20.0	5.20	.0100	0.0200	.0300	5.34
6	24.93	10.0	5.41	.0100	.1500	0	3.32[a]
7	24.93	10.0	5.34	0	0	.1600	7.38
8	−0.10	5.12	2.61	.0023	.0025	.1475	0.197
9	−0.10	5.12	2.97	.0023	.1500	0	0.127[a]

[a] See footnote 28.

TABLE II

KINETIC DATA FOR THE REACTION OF SODIUM 3,5-DIBROMO-4-HYDROXYBENZENESULFONATE WITH EXCESS BROMINE AT 24.93 ± 0.02°

	Concn. given in moles/liter					
Expt.	$(\mathrm{ArSO_3Na})_0 \times 10^4$	$(\mathrm{Br_2})_0 \times 10^4$	$(\mathrm{HClO_4})_0$	$(\mathrm{NaBr})_0$	$(\mathrm{NaClO_4})_0$	$10^3k'$, min.$^{-1}$
10	2.40	5.03	0.0100	0	0.1500	8.37
11	2.40	10.1	.0100	0	.1500	8.46
12	2.40	4.92	.0100	0	.1500	6.76
13	1.20	5.23	.0100	0	.1500	8.62

k' is defined by equation 7.

small amount of absorption at longer wave lengths than 230 mμ, is replaced by a spectrum having one large peak with a λ_{max} at 278–279 mμ (see Fig. 1). On the basis that all of the dibromo-*p*-phenolsulfonate has been brominated, the new compound has an ϵ of 11,400. That the compound actually is an intermediate was shown by the observation that the absorption at 279 mμ decreased over a period of several hours and finally the spectrum closely resembled that of 2,4,6-tribromophenol, the reaction product under these conditions.

The identity of the intermediate as the 2,5-cyclohexadien-1-one (II), with the chief absorption being due to a conjugated carbonyl group, was indicated strongly by comparison with spectra previously reported by other investigators. Price has shown that 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one (III) has a λ_{max} at 280 mμ with an ϵ of 9,700 in chloroform.[23] Elston, Peters and Rowe[24] reported that 2,4,6-tribromo-4-chloro-2,5-cyclohexadien-1-one has a λ_{max} at 275–280 mμ with an ϵ of 10,000, and Denivelle and Fort have made similar observations with other structurally similar compounds.[25] The spectral evidence then shows that the formation of the 2,5-cyclohexadienone (eq. 4) is fast and indicates that the desulfonation step is rate-determining.

Kinetic Measurements with Bromine and Excess Sodium Dibromo-*p*-phenolsulfonate.—Kinetic measurements both confirm the presence of a reaction intermediate and show that the rate-determining step is its decomposition. The addition of aqueous potassium iodide to a solution of the intermediate II, immediately after its preparation, liberated iodine quantitatively equal to the amount of bromine used. The amount of iodine liberated from aliquots of the reaction mixture decreased with time and so constitutes additional proof that there is a reaction intermediate. Thus it appears that iodide completely reverses eq. 4 to give iodine and I, and such an explanation is in accord with the accompanying change in the ultraviolet spectrum.[26]

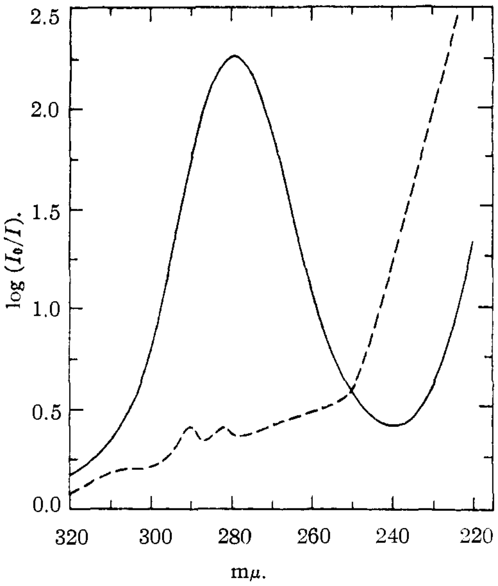

Fig. 1.—Ultraviolet spectra of quinonoid intermediate: ------, sodium 3,5-dibromo-4-hydroxybenzenesulfonate; ——, after mixing the sulfonate salt with an equal molar amount of Br_2 (taken in water at 25°).

The mechanism shown in eq. 4 and 5 predicts the following regarding the reaction kinetics: (a) when the initial amount of the dibromo-*p*-phenolsulfonate salt is in excess, the reaction will be zero order in I and first-order in bromine with the rate constant being k_3; and (b) when bromine is in excess, the reaction will be first order in the dibromo-*p*-phenolsulfonate salt and zero order in bromine with the rate constant being again k_3 since in both cases the rate-determining step would be the unimolecular decomposition of the intermediate quinonoid. The rates were followed iodometrically at 24.93 ± 0.02° Result (a) was kinetically verified; the initial ratio of the dibromo-*p*-phenolsulfonate salt I to bromine was varied from 2 to 15 and the first-order rate constant remained essentially constant as Table I shows. The value of k_3 is 5.51×10^{-3} min.$^{-1}$ and the intermediate has a half-life of 126 min. When the initial ratio of I to bromine was 15, the data followed a first-order rate law to 90% completion, but when it was 2 the first-order equation was followed only to 56% completion. This indicated that bromine was reacting further with the reaction product and subsequent

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(23) J. A. Price, THIS JOURNAL, **77**, 5436 (1955).

(24) C. H. R. Elston, A. T. Peters and F. M. Rowe, *J. Chem. Soc.*, 367 (1948).

(25) L. Denivelle and R. Fort, *Compt. rend.*, **238**, 1132 (1954); L. Denivelle, R. Fort and J. Favre, *ibid.*, **237**, 340 (1953).

(26) That the quinonoid intermediate II should oxidize iodide ion to iodine is in accord with its proposed structure. Structurally similar compounds, such as III, give the characteristic reactions of hypohalites. III with aqueous KI gives iodine and tribromophenol; J. H. Kastle and A. S. Loevenhart, *Am. Chem. J.*, **27**, 32 (1902); J. H. Kastle and J. W. Gilbert, *ibid.*, **27**, 43 (1902).

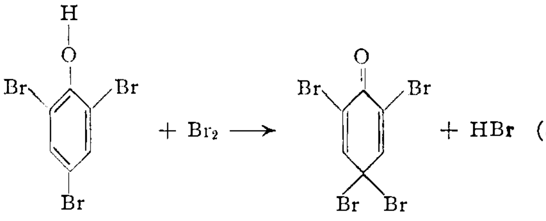
experiments, discussed below, confirmed this conclusion.

The reversibility of reaction 4 with Br^- was demonstrated by changing the initial concentration of bromide ion from zero to 0.15 M at constant ionic strength. At the higher bromide ion contration, the reaction mixture was yellow-orange rather than colorless; this is explainable on the basis that Br^- reverses reaction 4 to give the dibromo-*p*-phenolsulfonate anion and Br_2, which is then converted into Br_3^-. The latter has a characteristic yellow-orange color.[27] In line with this explanation, it was found that the over-all reaction rate was decreased by a factor of 1.6.[28]

An approximate value of the activation energy for the desulfonation step can be calculated by using experiments at 25 and 0°. These give a value of $\Delta H^{\ddagger} = 22.6$ kcal./mole.

Dependence of Rate on Acidity.—The desulfonation reaction (eq. 5) could be written alternatively as a two-step reaction: first protonation of the carbonyl oxygen and second elimination of SO_3 to give the phenol rather than the phenoxide ion. This mechanism is ruled out, however, by the observation that a threefold increase in the initial concn. of acid, at constant ionic strength, gives very little change in rate (note expt. 4 in Table I). Also, the disappearance of bromine color was still immediate upon mixing the reactants. It was noted further that a change of $(HClO_4)_0$ from 0.01 M to zero (expt. 7) increased the rate only by 34%.

Reaction of Bromine with Tribromophenol.—Halogeno-2,5-cyclohexadien-1-ones, such as III, are prepared by the reaction of 2,4,6-trihalogenophenols with bromine.[23-26] It was found that the mixing of aqueous solutions of 2,4,6-tribromophenol and bromine at 25° gave an immediate disappearance of bromine color, appearance of a faint yellow color which could be attributed to III and appearance of an absorption max. at 279 mμ of $\epsilon = 8600$ (calculated by assuming complete reaction). The peak at 279 mμ, as discussed above, is due to the presence of the conjugated carbonyl of III. Therefore, reactions 4 and 8 are analogous in that both occur very rapidly at 25° and give a 2,5-cyclohexadien-1-one.



(8)

III

Kinetic Measurements with Excess Bromine and Sodium Dibromo-*p*-phenolsulfonate.—With bromine in excess the reaction kinetics are more complicated but give further support for the mechanism shown in eq. 4 and 5. All of the tribromophenol produced in reaction 5 would be converted into the tetrabromo-2,5-cyclohexadienone III in accord with equation 8. This alone, however, would not decrease the titer of the solution; nor would it decrease the concentration of the intermediate II; consequently, the rate of decomposition of the intermediate as determined by titration would be unchanged. Experimentally, however, it was found that more than twice the molar amount of bromine was consumed (per mole of the dibromo-*p*-phenolsulfonate salt initially present) and that the rate was much faster than that given by a first- or second-order expression. The data fit the empirical relationship given in eq. 7 and follow this straight line relationship beyond the point necessary for the consumption of two moles of bromine for one mole of dibromo-*p*-phenolsulfonate initially present (see Fig. 2). The data, given in Table II, show that doubling the concentration of I doubles the value of $(B_0 - B)/t$ but that doubling the amount of bromine has no effect on the rate.

The kinetics show that more reactions are occurring than those given in eq. 5 and 6, but as predicted by this reaction scheme, the rate is *zero order in bromine*. The initial rate of reaction follows eq. 7 wherein the concentration of I appears to the first power, and, therefore, the data support the further prediction of the mechanism scheme (eq. 5 and 6) that the rate should be first-order in sodium dibromo-*p*-phenolsulfonate. The one further prediction of the mechanism scheme is that k_3 will be the same whether I or bromine is in excess. In order to verify or disprove the latter, it was necessary to investigate the nature of the side reactions which become important when bromine is in excess and to find a way of comparing k' and k_3.

Decomposition of 2,4,4,6-Tetrabromo-2,5-cyclohexadienone (III) in Dilute Aqueous Solution.—Separate experiments showed that III decomposes in dilute aqueous solution to give at least two products.[29] The disappearance of III with time was followed by the decrease of iodine titer of the solution. For these experiments III was produced in aqueous solution by mixing aqueous solutions of bromine and tribromophenol at concentrations of 2×10^{-4} M or less. The ratio of the initial concentration of tribromophenol to bromine was varied from 4 to 0.5 (see Table III), and the initial concentration of III was varied by a factor of about 3.6. The reaction can be described approximately as being zero order with respect to whichever reactant (bromine or tribromophenol) is in excess and first-order with respect to the other reactant. Thus, over the range of concentrations studied, the reaction appeared to be first-order

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[27] In the ultraviolet region, Br_3^- has a large absorption peak at 267 mμ with an appreciable absorption at 279 mμ. When the reaction mixture was 0.15 M in NaBr, the spectrum showed a shift of the max. at 279 mμ to 276–278 mμ with an increase in absorption at 267 mμ. These observations are also in agreement with the above explanation.

[28] Since the analytical method gives the rate of the over-all reaction and the conversion of bromine to the intermediate 2,5-cyclohexadienone (II) was not complete at the outset of the reaction in 0.15 M NaBr, the smaller value of the rate constant serves only to show that the over-all reaction is slowed down and does not indicate a change in the value of k_3.

[29] Grovenstein and Henderson[19] report that in a study of the bromodecarboxylation of 3,5-dibromo-4-hydroxybenzoic acid to give tribromophenol, the bromine consumption (as determined by the liberation of iodine with KI) after 256 hr. is just that calculated for the reaction of one mole of bromine. Therefore, under these conditions (in 80% acetic acid and 0.1 M HBr) there is no subsequent decrease in the iodine titer.

with respect to III. The kinetic relationship was followed to 60–70% reaction after which the rate increased. The rate constant for the decomposition of III was found to be 2.24×10^{-2} min.$^{-1}$ which is four times as great as that for the decomposition of quinonoid intermediate II. The identity of the products of the decomposition was not established; however, the end-point of the iodine titration indicated that at least two products were being formed. One product gave no reaction with iodide whereas the other product (pink in color) gave a slow reaction with iodide to give iodine. Thus, the immediate titration of a sample, after mixing with potassium iodide solution, required about one-third less sodium thiosulfate than that required if the solution were allowed to stand for 45 min. before titration; but further standing produced no additional increase in titer. The same instability of the end-point from titration was observed with the reaction of sodium dibromo-*p*-phenolsulfonate (I) with excess bromine. Here, for example, aliquots of the pink reaction solution, after standing alone for 15 hr., gave no immediate production of iodine; however, after 45 minutes, with iodide solution, the molar amount of iodine was equal to about one-third that of the initial amount of I. The first iodometric end-point was used to calculate the rate constants in Table III and to give the data in Table II which fit eq. 7.

Kinetic Analysis of the Complex System.—The following method was devised in order to obtain a method of comparing k' and k_3. The entire reaction scheme can be summarized as a four-step reaction series: reaction 4 followed by reactions 5 and 8 with the fourth step being the decomposition of the tetrabromocyclohexadienone III to give products, designated only as P_2, which do not give an immediate reaction with aqueous potassium iodide. With P_1 to represent tribromophenol, the scheme is

$$\begin{gathered} \mathrm{I} + \mathrm{Br_2} \xrightarrow{\text{fast}} \mathrm{II} + \mathrm{Br^-} \\ \mathrm{II} \xrightarrow[k_3]{\text{slow}} \mathrm{P_1} \\ \mathrm{P_1} + \mathrm{Br_2} \xrightarrow{\text{fast}} \mathrm{III} \\ \mathrm{III} \xrightarrow[k_4]{\text{slow}} \mathrm{P_2} \end{gathered} \qquad (9)$$

The sequence can be treated kinetically as a two-step first-order series reaction

$$\mathrm{I} \xrightarrow{k_3} \mathrm{P_1} \xrightarrow{k_4} \mathrm{P_2} \qquad (10)$$

The decrease in the iodine titer with time $(B_0 - B)$, is equal to $(P_1 + 2P_2)$. Equations[30] giving the values of P_1/A_0 and P_2/A_0 as a function of time were used to calculate values of $(P_1 + 2P_2)/A_0$ by taking the values of k_3 and k_4 to be 5.51×10^{-3} min.$^{-1}$ and 2.24×10^{-2} min.$^{-1}$ (see Table III), respectively. A plot of $(P_1 + 2P_2)/A_0$ against time shows that this function gives an almost straight line having a slope of 7.0×10^{-3} min.$^{-1}$ between $(P_1 + 2P_2)/A_0$ equals zero to 0.88.[31]

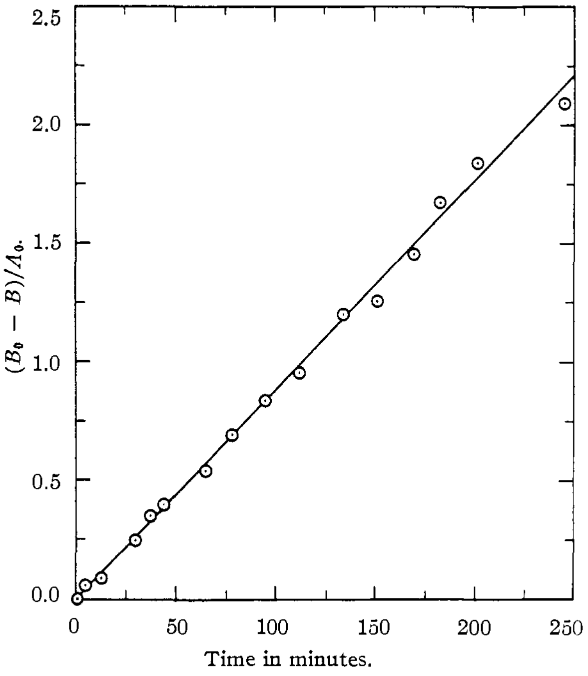

Fig. 2.—Reaction of sodium 3,5-dibromo-4-hydroxybenzenesulfonate with excess bromine; $A_0 = 1.20 \times 10^{-4}$ mole/l., $(\mathrm{Br_2})_0 = 5.23 \times 10^{-4}$ mole/l.

This calculated value is 16% lower than the experimental value for k' of 8.1×10^{-3} min.$^{-1}$ (the average of Table II). Because the experiments also show that there is an additional uptake of bromine which is not considered in eq. 9, the agreement is considered close enough to give support to the scheme shown in eq. 9. Therefore, the kinetics as a whole indicate that the mechanism of the bromodesulfonation of sodium 3,5-dibromo-4-hydroxybenzenesulfonate (I) is the same when bromine is in excess as it is with I in excess. The mechanism for the latter case has been shown above to be that given in eq. 4 and 5.

TABLE III

REACTION OF 2,4,6-TRIBROMOPHENOL WITH BROMINE, DECOMPOSITION OF 2,4,4,6-TETRABROMO-3,5-CYCLOHEXADIENONE IN WATER 24.93 ± 0.02°

	Concn. given in moles/liter					
Expt.	$(\mathrm{Br_3C_6H_2OH})_0 \times 10^4$	$(\mathrm{Br_2})_0 \times 10^4$	$(\mathrm{HClO_4})_0$	$(\mathrm{NaBr})_0$	$(\mathrm{NaClO_4})_0$	10^2k, min.$^{-1}$
14	1.95	0.487	0.0100	0	0.1500	2.55
15	1.95	0.765	.0100	0	.1500	2.24
16	1.93	1.01	.0100	0	.1500	2.24
17	1.89	1.52	.0100	0	.1500	2.12
18	1.79	4.43	.0100	0	.1500	1.86

Experimental

Sodium 3,5-Dibromo-4-hydroxybenzenesulfonate (I).—Sodium *p*-phenolsulfonate (one mole, Eastman White Label), sodium bromide (3.5 moles) and hydrochloric acid (4.3 moles) were dissolved in one l. of hot water. An aqueous solution of sodium bromate (0.7 mole) was added dropwise to the hot reaction mixture while it was stirred vigorously with a mechanical stirrer. The mixture was cooled and most of the excess acid was neutralized with aqueous sodium hydroxide. After standing, the mixture was filtered and, following treatment with Norite, the filtrate was reduced in volume. Compound I separated upon cooling and was recrystallized from water three times and once from 90%

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[30] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 153.

[31] Differentiation of the equations shows that the function goes through a maximum at $(P_1 - 2P_2)/A_0$ equal to 0.34 with a value of 7.3×10^{-3} min.$^{-1}$ but that in the region zero to 0.88 the average slope is about 7.0×10^{-3} min.$^{-1}$.

ethanol by cooling to −15°. When dried to constant weight at 100° the crystals pulverized.[32]

Anal. Calcd. for $C_6H_3Br_2O_4SNa$: C, 20.36; H, 0.85; Br, 45.16. Found: C, 20.17; H, 0.87; Br, 45.05.

2,4,6-Tribromophenol (Eastman Practical Grade) was recrystallized four times from ethanol, m.p. 94-95°, lit. m.p. 94°.[33]

Kinetic Measurements of the Bromodesulfonation Reaction of I.—Measurements were carried out in distilled water at 24.93 ± 0.02°. The concentrations of the reactants and rate constants are given in Tables I and II. The following reagents were used: sodium perchlorate, Fisher Purified Grade recrystallized from water; sodium bromide, Mallinckrodt Reagent Grade; perchloric acid, C.P. Grade; and the bromine was a center fraction, b.p. 58°, of refractionated Merck Reagent Grade. Stock solutions of I (0.0200 *M*), standardized perchloric acid and bromine water (*ca.* 5 × 10^{-3}) were used in preparing the reaction mixtures. Sodium perchlorate and sodium bromide were weighed out separately for each experiment. The reaction mixture was prepared, at the reaction temperature, by mixing a solution (a) containing sodium perchlorate and I with an equal volume (250 or 500 ml.) of a solution (b) containing bromine, perchloric acid and sodium bromide. The rate was followed by withdrawing aliquots (26.59 ml.), pipetting each aliquot into 10 ml. of 0.8% aqueous potassium iodide, and titrating the liberated iodine immediately with a standardized sodium thiosulfate (*ca.* 0.0027 *N*) solution measured from a semimicroburet. Starch was used as the indicator. The normality of the sodium thiosulfate solution was determined periodically by titrating against a standard potassium iodate solution. Sixteen to twenty points were taken in each experiment. When I was in excess, there was no problem with bromine volatility. However, when bromine was in excess, the loss of bromine became important (as determined by blank determinations) after one-third to one-half of the solution had been removed. Therefore, the volume of the solutions (a) and (b) was increased to 500 ml. and less than one-half of the mixture was used.

Reaction of 2,4,5-Tribromophenol with Bromine.—Solutions of 2.00 × 10^{-4} *M* tribromophenol were prepared by dissolving 0.0662 g. of the phenol in hot distilled water and then diluting to one l. upon cooling. The desired amounts of sodium perchlorate and sodium bromide were dissolved in a measured amount of tribromophenol solution. Standardized perchloric acid was added and, after bringing to 24.93 ± 0.02°, the solution was then mixed with bromine water such that the total volume was one liter. The initial concentration of tribromophenol was calculated from the volume of 2.00 × 10^{-4} *M* solution used to prepare the reaction mixture. The disappearance of bromine together with tetrabromocyclohexadienone III and other compounds which with iodide liberate iodine was followed. Aliquots (50 or 26.59 ml.) were withdrawn, added to 10 ml. of 0.8% potassium iodide solution, and the liberated iodine was titrated with standardized sodium thiosulfate solution. The reaction was homogeneous throughout the course of the reaction. The data are given in Table III. When tribromophenol was in excess, the values of the first-order rate constant, k_1, were taken as being equal to the slope of a plot of ln (B) *vs.* time, where B is the iodine titer in moles/l. With bromine in excess, k_4 was taken as being equal to the slope of a plot of ln $(A_0 - B_0 + B)$ *vs.* time.

Ultraviolet spectra were taken in distilled water on a Cary recording spectrophotometer, model 11.

Acknowledgment.—The author wishes to express his gratitude to Dr. F. H. Westheimer for his encouragement and helpful discussions throughout the course of this work. The author is also indebted to the National Science Foundation for financial support.

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[32] Analysis was performed by Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y.

[33] I. Heilbron, *et al.*, "Dictionary of Organic Compounds," Vol. IV, Eyre and Spottiswoode Ltd., London, 1953, p. 551.

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES OF HARVARD UNIVERSITY]

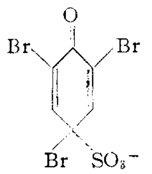
The Bromodesulfonation of Aromatic Sulfonate Salts. II. The Effect of Amino, Methoxy, Methyl and Nitro Substituents[1]

BY LAWRENCE G. CANNELL[2]

RECEIVED DECEMBER 20, 1956

The kinetics of the bromodesulfonation of a series of *p*-substituted aromatic sulfonate salts have been studied in aqueous solution at 0°. The results give additional experimental support to the theory that electrophilic aromatic substitution reactions proceed by way of quinonoid intermediates. The following *p*-substituents were studied: amino (III), methoxy (IV), methyl (V), and hydroxyl, with *m*-nitro groups (VI). All four compounds gave second-order kinetics, but they varied in regard to their dependence of rate on (Br^-). The kinetics for V showed little or no additional dependence on Br^- aside from that required by Br_3^- formation. However, with III, IV and VI it was found that decreases in rate occurred which cannot be accounted for by the Br_3^- effect alone (*cf.* Table II). The kinetics can be accounted for by a mechanism wherein bromine and the sulfonate anion undergo a *reversible* reaction to give Br^- and a "steady state" concentration of a quinonoid intermediate. To complete the reaction, the quinonoid intermediate decomposes in a unimolecular step (*cf.* eq. 1 and 2). Structural features affecting the stability of quinonoid reaction intermediates are discussed.

In a previous paper the bromodesulfonation of sodium 3,5-dibromo-4-hydroxy benzenesulfonate (I) was reported.[3] Spectral and kinetic data showed that the formation of a 3,5-cyclohexadien-1-one (II) as a reaction intermediate took place immediately upon mixing the reactants, and that the rate-determining step was the first-order decomposition of the quinonoid II to give tribromophenol.[4] Since the bromodesulfonation reaction is an example of electrophilic aromatic substitution,[3] this work constitutes a clear example of electrophilic aromatic substitution proceeding by way of a quinonoid intermediate.



II

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[1] This paper was presented in part at a symposium on aromatic substitution held by the Division of Organic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 20, 1956.

[2] Shell Development Co., Emeryville, Calif. National Science Foundation post-doctoral fellow, 1955–1956.

[3] L. G. Cannell, THIS JOURNAL, **79**, 2972 (1957).

[4] In aqueous solution at 25° the half-life of the intermediate was found to be 126 min.