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 semi-microburet. 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.

CAMBRIDGE, MASSACHUSETTS

(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]

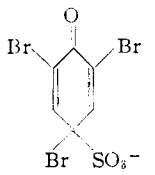
The Bromodesulfonation of Aromatic Sulfonate Salts. II. The Effect of Amino, Methoxy, Methyl and Nitro Substituents[1]

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_4^- 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

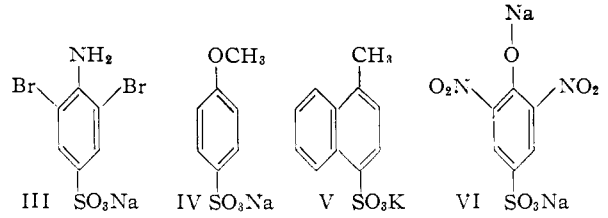
(1) This paper was presented in part at a symposium on aromatic substitution held by the Division of Organic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 20, 1956.

(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.

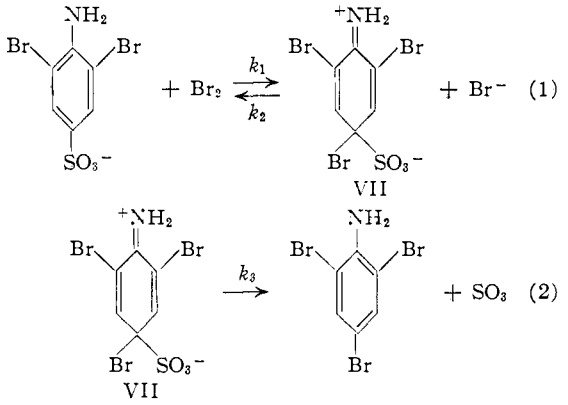
This paper reports the investigation of the kinetics and mechanism of the bromodesulfonation of the aromatic sulfonate salts



Previous investigators have shown that the products obtained in aqueous solution are, respectively: 2,4,6-tribromoaniline,[5,6] 4-bromoanisole,[7] 1-bromo-4-methylnaphthalene[8] and 4-bromo-2,6-dinitrophenol.[9-11]

A study of the rates of reaction as a function of (Br^-) shows that bromide ion retards the rate of product formation with III, IV and VI, but that the extent of this participation by bromide ion is dependent on the structure of the sulfonate salt. These results are explainable in terms of the usual mechanism for electrophilic substitution when there is a "steady state" concentration of an intermediate quinonoid, and they therefore constitute, together with the results of the previous paper,[3] strong experimental support for that theory. The mechanism presented here is similar to that proposed by Grovenstein and Henderson to account for the decrease in the rate of bromodecarboxylation of 3,5-dibromo-4-hydroxybenzoic and 3,5-dibromo-2-hydroxybenzoic acids with added sodium bromide.[12]

For the dibromo-*p*-aminobenzenesulfonate III the reaction scheme is



The SO_3 is hydrated to give sulfuric acid.

(5) J. J. Sudborough and J. V. Lakhumalani, *J. Chem. Soc.*, **111**, 41 (1917).

(6) O. Heinichen, *Ann.*, **253**, 268 (1889).

(7) A. N. Meldrum and M. S. Shah, *J. Chem. Soc.*, **123**, 1982 (1923); M. S. Shah, *et al.*, *J. Univ. Bombay*, **3**, 153 (1934). *C. A.*, **29**, 4747 (1935).

(8) L. F. Fieser and D. M. Bowen, THIS JOURNAL, **62**, 2103 (1940).

(9) E. Sakellarios, *Ber.*, **55**, 2846 (1922); *cf.* R. King, *J. Chem. Soc.*, **119**, 2105 (1921).

(10) M. M. Marqueyrol and P. Carré, *Bull. soc. chim. France*, [4] **27**, 127 (1920).

(11) Because 4-bromo-2,6-dinitrophenol reacts further with bromine under certain conditions, the products from this reaction are discussed separately in a later section.

(12) E. Grovenstein, Jr., and U. V. Henderson, Jr., THIS JOURNAL, **78**, 569 (1956); E. Grovenstein, Jr., and G. A. Ropp, *ibid.*, **78**, 2560 (1956).

Results

Reaction Kinetics.—The kinetics for the bromodesulfonation of III, IV, V and VI have been determined in water at $-0.10 \pm 0.02°$. The reaction rates were followed by removing aliquots, quenching with an iodide solution and titrating the liberated iodine with a known sodium thiosulfate solution. Starch was used as the indicator. Tables I and III summarize the findings.

The reactions were carried out essentially at a constant acidity and bromide concentration, in most cases, by having an initial concentration of sodium bromide and perchloric acid large enough that the amounts of acid and bromide produced in the reaction were small in comparison. The equilibrium constant for the formation of Br_3^- is 19.6 at 0.0° (equation 3)[13]; and, consequently, very little of the bromide produced during a reaction was converted to Br_3^-. For example, at 90% reaction in expt. 11 and 4 the ratios of Br_3^- to Br_2 are 0.01 and 0.005, respectively.

Second-order Kinetics.—By varying the initial ratio of the sulfonate salt to bromine by factors of 31, 13, 24 and 34 for III, IV, V and VI, respectively, the kinetics of these reactions were found to be second-order, that is, first order in each reactant.

Reactions with the anisole IV were homogeneous and followed the second-order equation to points beyond 93% completion when the anisole was in a fourfold excess but only to 60% completion when it was in a twofold excess. With the bromine in excess, the second-order expression was followed to only 35–40% completion. In all cases, the apparent rate constant for bromination increased with time, and, therefore, it appeared that *p*-bromoanisole, the reaction product, was undergoing further bromination. With V, 1-bromo-4-methylnaphthalene began to separate as an oil from the solution after about 25% reaction. The rate followed the second-order expression out to 40% reaction and then the rate constant drifted to a value 6 to 10% lower presumably because of bromine adsorbed on the product which thereby reduced the amount of bromine in solution. Reactions with the amine III gave a precipitation of 2,4,6-tribromoaniline after about 30% reaction, and the kinetics followed a second-order plot out to 60–70% reaction and then the rate decreased by about 10% apparently because of adsorption of bromine on the solid. Reactions with the dinitrophenol VI were homogeneous.

Bromide Dependence.—The kinetics of the reactions were studied as a function of bromide concentration over a change in $(Br^-)_0$ from zero to 0.15 *M*. The ionic strength was maintained constant by adjusting the amount of $(NaClO_4)_0$. Upon increasing $(Br^-)_0$ the rate constants decreased as shown in Tables I and III.

Ionic Strength.—Changes in the ionic strength had little effect on the rates.[14] For example, a change in ionic strength from 0.152 to 0.012 (expt. 6 and 10) changed the rate constant for the

(13) G. Jones and M. L. Hartmann, *Trans. Am. Electro. Soc.*, **30**, 295 (1916).

(14) The small salt effect is in line with the Brönsted equation which would predict no salt effect for the reaction of a neutral molecule, Br_2, with an ion.

bromodesulfonation of sodium dibromo-*p*-aminobenzenesulfonate from 6.02 to 5.91 liters/mole-sec. Similarly, only a small effect was noted with the *p*-methoxybenzenesulfonate IV (expt. 20 and 23). The essential point of interest is that small changes in media due to the substitution of one monovalent ion for another, at constant ionic strength, will not significantly alter the interpretation of the results which rely upon changes in rates by factors of 4 to over 1,000.

Effect of Acidity.—Increasing the amount of $(HClO_4)_0$ at constant ionic strength showed that the rates of bromodesulfonation of III, IV and V are quite insensitive to acid. The amount of acid was increased by factors of 43 (expt. 2 and 7), 2 (expt. 11 and 19)[15] and 4 (expt. 29 and 33) with the sulfonate salts: III, IV and V, respectively. With the dinitro-*p*-phenolsulfonate VI, however, an increase in acid by a factor of 5 decreased the rate by a factor of 4.4 (expt. 39 and 44).

Bromination of *o*-Methoxybenzoic Acid.—The decrease in rate of bromination of *o*-methoxybenzoic acid accompanying a change in bromide concentration from 0.0025–0.15 *M* was found to be slightly greater than 4 (see Table II).

Calculation of Rate Constants.—The second-order rate constants, k_{obs}, were calculated by plotting log $(A_0 - B_0 + B)/B$ *vs.* time (see eq. 8), where A_0 is the initial concentration of the aromatic sulfonate salt and B is the apparent bromine concentration (equal to the titer of iodine in mole/l.) at a specified time. The graphical method was preferred to the direct calculation of k_{obs} for each point because it gives less weight to the value of B_0. The rate constants obtained by using experimental method 1, where checked, were reproducible to 1 to 3% of the average value. The wider variation occurred with those experiments which had shorter half-lives (*cf.* expt. 34 and 31 where the half-life was 80 sec.). The reproducibility of rate constants obtained with experimental method 2, where checked, was found to be *ca.* ±1.5% of an average value (*cf.* expt. 11 and 12). The accuracy of the data is also indicated by its fit to a second-order equation as the ratio of the initial concentration of reactants is varied and, in the case of III and IV, by the agreement with eq. 13 (see Fig. 1).

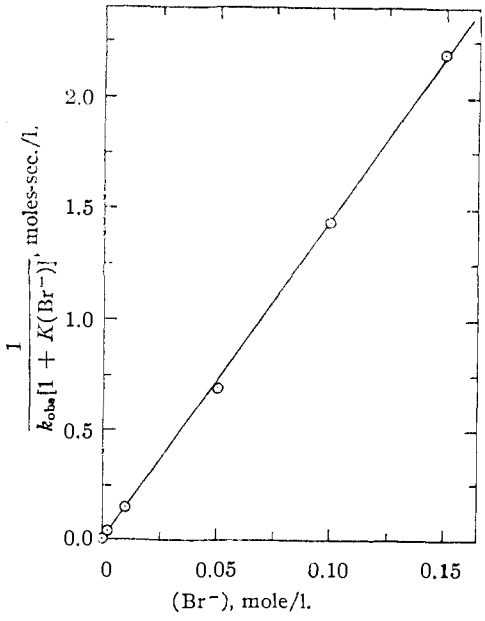


Fig. 1.—Plot of rate constants, corrected for Br_3^- effect, for the bromodesulfonation of sodium 3,5-dibromo-4-aminobenzenesulfonate *vs.* (Br^-).

(15) Also compare expt. 18 and 24 for an increase in acid by a factor of 5 but with a change of ionic strength.

Discussion

Kinetics of the Second-order Bromodesulfonation Reactions.—The second-order kinetics for the reaction of bromine with the dibromo-*p*-aminobenzenesulfonate (III), *p*-methoxybenzenesulfonate (IV) or 4-methylnaphthalenesulfonate (V), suggest a bimolecular mechanism between bromine and the aromatic sulfonate salt. Reactions with III, IV and V were insensitive to changes in acidity; this is in agreement with the expectations that the sulfonic acids would be completely ionized and that the anion would be the reactant. Further the observed independence of rate on acidity shows that neither HOBr nor H_2OBr^+ is the brominating agent.

A decrease in the rate of bromination as the bromide ion concentration is increased would be expected because of the decrease in bromine concentration due to tribromide ion formation

$$Br^- + Br_2 \rightleftharpoons Br_3^- \qquad (3)$$

for which the equilibrium constant is

$$K = \frac{(Br_3^-)}{(Br^-)(Br_2)} \qquad (4)$$

The second-order rate equation has the form

$$-\frac{dB}{dt} = -\frac{dA}{dt} = k(Br_2)(A) \qquad (5)$$

where k is the second-order rate constant, and A is the concentration of sulfonate salt, and B is the sum of bromine and tribromide ion (*i.e.*, the iodine titer of the solution). For a given experiment (Br^-) is essentially constant, and incorporating the bromine–tribromide ion equilibrium into the equation gives

$$-\frac{dB}{dt} = \frac{k}{1 + K(Br^-)}(B)[A_0 - (B_0 - B)] \qquad (6)$$

The equation shows that the reaction will follow a second-order rate law with an observed rate constant, k_{obs}, which obeys the relationship

$$k = k_{obs}[1 + K(Br^-)] \qquad (7)$$

Integration gives the rate equation used in finding k_{obs}

$$tk_{obs} = \frac{1}{A_0 - B_0} \ln\left[\frac{A_0 - B_0 + B}{B}\right]\left[\frac{B_0}{A_0}\right] \qquad (8)$$

The correction for reaction 3 has been applied to the data for the bromination of III, IV, V and *o*-methoxybenzoic acid and the corrected constants, $k_{obs}[1 + K(Br^-)]$, are given in Table I. It was found that $k_{obs}[1 + K(Br^-)]$ is nearly constant for the 4-methylnaphthalenesulfonate V and for *o*-methoxybenzoic acid. Table II summarizes the decrease in rate upon increasing $(Br^-)_0$ from 0.0025 to 0.15 *M*. With a value of $K = 19.6$,[13] eq. 7 pre-

TABLE I

SECOND-ORDER RATE CONSTANTS FOR BROMODESULFONATION REACTIONS AT $-0.10 \pm 0.02°$

Expt.	$(ArSO_3Na)_0 \times 10^4$	$(Br_2)_0 \times 10^4$	Concn. given in moles/liter $(HClO_4)_0$	$(NaBr)_0$	$(NaClO_4)_0$	Liters/mole-sec. k_{obs}	$k_{obs}[1 + K(Br^-)]$
			Sodium 3,5-dibromo-4-aminobenzenesulfonate				
1	25.0	1.92	0.100	0.0500	0	0.734	
2	5.00	3.00	.100	.0500	0	.744	
3	2.50	5.97	.100	.0500	0	.692	
4	5.00	2.74	.0023	0	0.1500	153	153
5	5.00	2.95	.0023	.0025	.1475	26.4	27.7
6	5.00	2.65	.0023	.0100	.1400	6.02	7.20
7	5.00	2.93	.0023	.0500	.1000	0.707	1.40
8	5.00	2.92	.0023	.1000	.0500	.236	0.699
9	5.00	2.99	.0023	.1500	0	.116	0.457
10	5.00	2.87	.0023	.0100	0	5.91	
			Sodium *p*-methoxybenzenesulfonate				
11	10.0	5.50	0.0100	0.0200	0.0300	0.184	
12	10.0	5.45	.0100	.0200	.0300	.189	0.264
13	15.0	5.58	.0100	.0200	.0300	.178	
14	20.1	5.53	.0100	.0200	.0300	.175	
15	2.51	5.13	.0100	.0200	.0300	.177	
16	2.20	7.93	.0100	.0200	.0300	.212	
17	10.0	5.08	.0100	.0050	.045	.322	.354
18	10.0	5.20	.0100	.0500	0	.0964	.191
19	10.0	4.72	.0200	.0200	.0200	.181	
20	5.00	2.83	.0015	.0100	0	.234	
21	5.00	2.62	.0023	0	.1500	.434	.434
22	5.00	2.94	.0023	.0025	.1475	.404	.424
23	5.00	2.95	.0023	.0100	.1400	.286	.342
24	5.00	2.84	.0023	.0500	.1000	.0986	.195
25	5.00	2.98	.0023	.1000	.0500	.0453	.134
26	5.00	3.08	.0023	.1500	0	.0254	.100
			Potassium 4-methylnaphthalenesulfonate				
27	5.00	2.80	0.0023	0.0025	0.1475	0.134	0.141
28	5.00	2.46	.0023	.0200	.1300	.0857	.120
29	10.0	2.11	.0023	.0200	.1300	.0985	.138
30	12.5	1.04	.0023	.0200	.1300	.0878	
31	2.50	5.08	.0023	.0200	.1300	.0992	
32	5.00	3.30	.0023	.1500	0	.0274	.108
33	10.0	2.31	.1023	.0200	.0300	.105	
			o-Methoxybenzoic acid				
34	5.00[a]	2.73	0.0103	0.0025	0.1475	19.1	20.0
35	5.00	2.50	.0103	.0025	.1475	18.0	18.9
36	5.00	2.95	.0103	.1500	0	3.70	14.6
37	5.00	2.82	.0103	.1500	0	3.90	15.4
38	5.00	2.55	.0206	.0025	.1475	13.0	

[a] $(CH_3OC_6H_4CO_2H)_0 \times 10^4$.

dicts a decrease by a factor of 3.76. For an increase from zero to 0.15 M $(Br^-)_0$ the factor is 3.94. The observed decrease of 4.5 and 4.8 for the 4-methylnaphthalenesulfonate V and *o*-methoxybenzoic acid, respectively, are in reasonable agreement with the calculated factor of 3.76.[16] However, for the *p*-methoxybenzenesulfonate IV and dibromo-*p*-aminobenzenesulfonate III the decrease in rate is too great to be accounted for by this correction for Br_3^- formation.

Therefore, the simple bimolecular mechanism scheme must be modified to account for this additional dependence on bromide ion. The proposed mechanism scheme is

$$ArSO_3^- + Br_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ar\begin{matrix}Br\\SO_3^-\end{matrix} + Br^- \qquad (9)$$

$$Ar\begin{matrix}Br\\SO_3^-\end{matrix} \xrightarrow{k_3} ArBr + SO_3 \qquad (10)$$

$Ar\begin{matrix}Br\\SO_3^-\end{matrix}$ is an intermediate having a quinonoid structure

(16) It appears that K would not be affected greatly by changes in ionic strength since this is the case in the closely analogous system for the formation of I_3^- from I_2 and I^-. For the latter system, the work of W. C. Bray and C. M. J. McKay (THIS JOURNAL, **32**, 914 (1910)) and L. I. Katzin and E. Gebert (*ibid.*, **77**, 5814 (1955)) indicates that the maximum variation in K for changes in the concentrations of KI, $NaClO_4$ and NaI under 0.15 M would be less than 12%. For a 12% increase in the value of K for the formation of Br_3^- from Br^- and Br_2, eq. 7 predicts a decrease of 4.2 in rate of bromodesulfonation. Experiments with *p*-methoxybenzenesulfonate III wherein (Br^-) was varied from 0.05 to 0.005 at $\mu = 0.06$ showed that the large deviations from eq. 7 were not due to a salt effect on K (see expt. 12, 17 and 18).

which is assumed to be in a "steady state" with respect to the reactants. This mechanism is basically the same as that proposed earlier for the bromodesulfonation of sodium 3,5-dibromo-4-hydroxybenzenesulfonate (I); however, the magnitude of the rate constants are such that in the absence of bromide ion the bromination step, eq. 9, is now rate-determining. If a "steady state" concentration is assumed for the quinonoid, Q, the reaction scheme given by eq. 9 and 10 predicts that

$$-\frac{dB}{dt} = k_3(Q) = \frac{k_3k_1(Br_2)(A)}{k_2(Br^-) + k_3} \qquad (11)$$

Equation 11 has then the same form as eq. 5, and by making a similar correction for the formation of Br_3^- (*cf.* eq. 6) the following expression is obtained

$$\frac{1}{k_{obs}[1 + K(Br^-)]} = \frac{1}{k_1}\left[\frac{k_2}{k_3}(Br^-) + 1\right] \qquad (12)$$

Equation 12 predicts that a plot of $(k_{obs}[1 + K(Br^-)])^{-1}$ against (Br^-) will give a straight line. When the experimental data for the bromination of the dibromo-*p*-aminobenzenesulfonate III and *p*-methoxybenesulfonate IV are plotted in this manner, straight line correlations are obtained (see Fig. 1). The agreement further verifies the correctness of the mechanism scheme given by eq. 9 and 10. The intercept at $(Br^-) = 0$ becomes equal to $1/k_1$; this value can also be determined directly. The slope is equal to k_2/k_1k_3, and it is therefore possible to determine k_2/k_3. For the anisole IV k_2/k_3 is equal to 22 l./mole, and for the amine II it is 2,200 l./mole. Since the (rate forward/rate reverse) $= k_2(Br^-)/k_3$, it follows that when $(Br^-)_0$ is 0.10 *M* the intermediate quinonoid VII, formed from the amine, returns to the initial reactants 220 times for every time it goes on to products.

When k_2/k_3 is small, eq. 12 reduces to eq. 7 (*i.e.*, the bromination step is rate-determining regardless of the bromide ion concentration).

Dibromo-*p*-aminobenzenesulfonate III. Effect of Acidity.—As noted above, the rate of bromodesulfonation of the amine III is unaffected by increasing $(HClO_4)_0$ from 0.0023 to 0.100 *M*. This indicates that the concentration of the compound undergoing bromination is not significantly changed over this range of acidity. Also, the ultraviolet spectrum of III, which has maxima at 298 and 253 mμ, does not change even though the composition of the solution is changed from 0.1 *M* $HClO_4$ to 0.1 *M* NaOH. Sodium *p*-aminobenzenesulfonate[17] undergoes a 19-fold decrease in absorption at λ_{max} 247 mμ in acid solution due to protonation of the amine group. Therefore, the data indicate that the amine III is so weak a base that it remains unprotonated even in 0.1 *M* $HClO_4$. This behavior is in line with the expected base strength of III. Gillois and Rumpf[18] have shown that the 2,6-dibromoanilinium ion has a pK_H of 0.35 at 25°; and since the pK_H for the N-protonated *p*-aminobenzenesulfonate ion is 1.35 log units less than that for the anilinium ion,[19] the expected pK_H for the N-protonated 3,5-dibromo-4-aminobenzenesulfonate ion is about −1.0. Therefore, in 0.1 *M* acid only about 1% of the amino groups would be protonated.

TABLE II

DECREASE IN RATE OF BROMODESULFONATION ON INCREASING $(Br^-)_0$ FROM 0.0025 TO 0.1500 *M* AT 0.0°

Sodium 3,5-dibromo-4-aminobenzenesulfonate	230 (1300)[a]
Disodium salt of 3,5-dinitro-4-hydroxybenzenesulfonic acid	246
Sodium 4-methoxybenzenesulfonate	16
Potassium 4-methylnapthalenesulfonate	4.5
o-Methoxybenzoic acid	4.8
Predicted decrease due to Br_3^- effect only	3.76

[a] Experimentally determined for a change from $(Br^-)_0 = 0$ to $(Br^-)_0 = 0.15$ *M*. This value should be compared to a predicted decrease for the effect of Br_3^- formation of 3.94.

Destabilization of the Quinonoid State in Phenols by *o*-Nitro Groups.—The disodium salt of 4-hydroxy-3,5-dinitrobenzenesulfonic acid (VI), in contrast to the salt of dibromo-*p*-phenolsulfonic acid I, gave a very rapid reaction with bromine even at 0°, and the kinetics showed that the decomposition of the quinonoid intermediate was not rate-determining at low bromide concentrations.

The data (see Table III) can be summarized as follows: (1) the kinetics were second order. (2) An increase in (Br^-) from 0.0025 to 0.1500 *M* decreased the reaction rate by a factor of 246; the rate constant is still decreased by bromide by a factor of 65 after taking into account the Br_3^- effect (*cf.* Table II). The dependence of the rate on bromide ion was thus very similar to that found for the dibromo-*p*-aminobenzenesulfonate (III); the bromination step is rate-determining at low $(Br^-)_0$, but as $(Br^-)_0$ is increased, the desulfonation reaction begins to become rate-determining. (3) The rate was inversely dependent on acid (an increase in acid by a factor of 5 resulted in a 4.4-fold decrease in rate), and this stands as evidence that it is the phenoxide anion which undergoes bromination. The mechanism is comparable to that given in eq. 1 and 2.

The proposed explanation is given in the form of a potential energy curve, Fig. 2, which compares the bromodesulfonation of I and VI. It is well known that the introduction of a nitro group *ortho* to an OH group greatly increases the acidity of the phenol. This is attributed largely to the resonance stabilization of the anion.[20] A similar interaction would be expected in the ground state of the doubly charged anion of VI and, therefore, Fig. 2 shows a lower energy for the ground state of VI than for I. However, in the transition state, for the bromination step this interaction is partly lost because the phenoxide anion is being converted to a carbonyl group, and the C–C double bonds are becoming localized in positions unfavorable to resonance between the phenol oxygen and the nitro groups. Therefore, in the transition state, the energy difference between I and VI is considerably reduced.

It has been shown that quinones become better

(17) For previous work, see, for example, H. Böhme and J. Wagner, *Arch. Pharm.*, **280**, 255 (1942); *C. A.*, **37**, 2517 (1943).

(18) M. Gillois and P. Rumpf, *Bull. soc. chim. France*, **21**, 112 (1954).

(19) R. O. MacLaren and D. F. Swinehart, THIS JOURNAL, **73**, 1822 (1951).

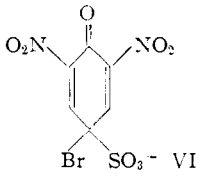
(20) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 346.

TABLE III

KINETIC DATA FOR THE BROMODESULFONATION OF DISODIUM SALT OF 3,5-DINITRO-4-HYDROXYBENZENESULFONIC ACID AT $-0.10 \pm 0.02°$

Expt.	Concn. given in moles/liter $(NaOArSO_3Na)_0 \times 10^4$	$(Br_2)_0 \times 10^4$	$(HClO_4)_0$	$(NaBr)_0$	$(NaClO_4)_0$	Liters/mole sec. k_{obs}	$k_{obs}[1 + K(Br^-)]$
39	5.00	2.69	0.0200	0.0025	0.1475	13.1	13.7
40	5.00	2.56	.0200	.0100	.1400	2.26	2.70
41	1.60	5.56	.0200	.0100	.1400	2.40	
42	20.00	1.67	.0200	.0100	.1400	2.37	
43	5.00	2.67	.0200	.0100	.1500	0.0532	0.210
44	5.00	2.70	.100	.0025	.0675	3.00	

oxidizing agents when substituted with electronegative groups and that the nitro group is particularly effective in this regard.[21] Therefore, the potential energy of the tribromoquinonoid intermediate is represented in Fig. 2 as being less than that for the bromodinitroquinonoid intermediate VIII.



VIII

Finally, in the desulfonation step, as the C–S bond is broken the C–C double bonds again become delocalized and the resonance energy between the phenoxide anion and the nitro groups can again be important. Consequently, the activation energy for the desulfonation step for VI is much less than that for I. The over-all result is that in the absence of bromide ion the rate of desulfonation is increased to such a great extent that it is now no longer rate controlling. But the quinonoid has sufficient stability that with bromide ion the reverse reaction to give starting materials can take place and the desulfonation step then becomes important as the rate-determining step.

It should be noted that this change is brought about not by replacing one activating group by another but by modifying it through *ortho* substituents. The activation is clearly due to a combination of the phenoxide anion and the nitro groups and can be described as a resonance interaction. This is shown by the observation that potassium 4-methoxy-3-nitrobenzenesulfonate gives a much slower reaction with bromine than does sodium 4-methoxybenzenesulfonate (IV). The deactivating effect that introducing a nitro group has on the rate of bromination of sodium *p*-methoxybenzenesulfonate IV thus illustrates the effect which is usually observed: the nitro group retards electrophilic aromatic substitution by an inductive effect. In the bromination of the dinitrophenol VI the nitro groups must also deactivate the ring by an inductive effect, but this is completely hidden by the resonance interaction. The difference in the kinetics of bromination of the dibromophenol I and the dinitrophenol VI demonstrates that the rate-determining step in aromatic electrophilic substitution can be changed by the modification of substituents.

Dinitro-*p*-phenolsulfonate VI. Products.—

(21) L. F. Fieser, THIS JOURNAL, **52**, 5204 (1930); **51**, 3101 (1929).

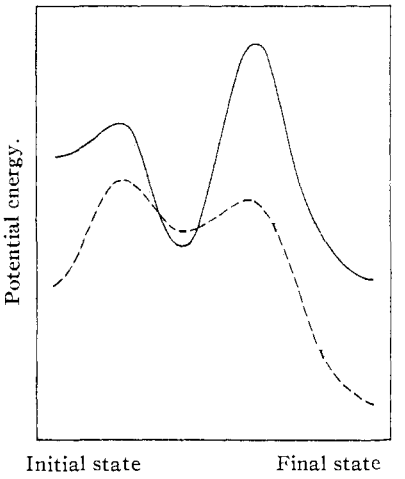
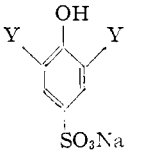


Fig. 2.—Bromodesulfonation of
—— Y is Br, (I)
------ Y is NO_2, (VI)



Sakellarios reports that the reaction of VI with an equal molar amount of bromine water at 24–30° gives a 93% yield of 4-bromo-2,6-dinitrophenol before recrystallization.[9] Marqueyrol and Carré report that VI with an equal molar amount of bromine in water gives a crude product which contains 31.7% bromine (a bromodinitrophenol has 30.4%) wherein the main product is 4-bromo-2,6-dinitrophenol.[10] With excess bromine at room temperature they reported that the crude product contained 45% bromine (54% required for a dibromonitrophenol) from which the chief product isolated was 2-bromo-4,6-dinitrophenol[22] and a smaller amount of 2,4-dibromo-6-nitrophenol. They further showed by titration data that VI reacted with more than a molar amount of bromine. The replacement of a nitro group on 4-bromo-2,6-dinitrophenol by bromine is not surprising in view of other work which shows that picric acid will brominate in aqueous solution at room temperature to give 2-bromo-4,6-dinitrophenol.[23]

Dinitro-*p*-phenolsulfonate VI. Side Reactions.—The reaction rate measurements, reported in this

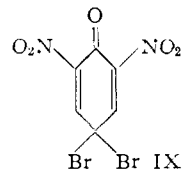
(22) Marqueyrol and Carré suggest that 4-bromo-2,6-dinitrophenol, the initial reaction product, isomerizes in the presence of excess bromine into 2-bromo-4,6-dinitrophenol (*cf.*, H. E. Armstrong, *J. Chem. Soc.*, **13**, 520 (1875); H. Gordon, *Chem. News*, **63**, 221 (1891)).

(23) J. Castets, *J. pharm. chim.*, **13**, 46 (1916); *C. A.*, **10**, 1486 (1916); *cf.* H. E. Armstrong, *Ber.*, **6**, 649 (1873).

paper, also show that the dinitrophenolsulfonate VI will react with more than one mole of bromine. The reaction of VI with excess bromine followed a second-order rate law (having the same value of k as that obtained when bromine was not in excess, see Table III) until 0.5 mole of bromine had been taken up for each mole of VI initially present. The apparent rate constant then began to increase and bromination continued at a rapid rate until *ca.* 1.5 moles of bromine had disappeared and the reaction finally approached the stoichiometry of two moles of bromine consumed per mole of VI. These data suggest that, as reported by Marqueyrol and Carré, 2,4-dibromo-6-nitrophenol was a reaction product.

When the dinitrophenolsulfonate VI was in excess, the reaction followed a second-order rate to 70–75% completion after which the rate began to slow down with a very pronounced decrease occurring after 85% completion. Even though the initial ratio of VI to bromine was changed from 2 to 12, the decrease in the rate constant occurred at closely the same point in the reaction. This indicated that the reaction responsible for the decrease in rate did not involve VI but was evidently between bromine and the reaction product, 4-bromo-2,6-dinitrophenol.

In summary, it may be said that the initial reaction product is 4-bromo-2-6-dinitrophenol but that secondary bromination reactions become kinetically important after 50 to 75% reaction. It appears that 4-bromo-2,6-dinitrophenol brominates to give a reaction product, or intermediate, which slows down the rate of disappearance of bromine by tying up some of the bromine in a way such that it is less effective as a brominating agent but will, in the analytical method, still react with iodide to give iodine. With excess bromine, however, bromination occurs to give 2,4-dibromo-6-nitrophenol. In considering possible secondary bromination products it is interesting to note that 4-bromo-2,6-dinitrophenol might be expected to give the cyclohexadienone (IX) just as tribromophenol gives 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one.[24] However,



IX

apparently phenols containing a nitro group *ortho* or *para* to the OH group have not given isolable cyclohexadienones. This is not surprising since, as noted above, hydroquinones which are substituted with nitro groups become more difficult to oxidize to the corresponding quinones.

Comparison of the Bromodesulfonation Reactions.—The kinetics of the bromodesulfonation of I, III, IV and V, together with the spectral data, can be used to divide these compounds according to the stability of the intermediate quinonoid: (1) Bromination of sodium 3,5-dibromo-4-hydroxybenzenesulfonate (I) gives zero-order kinetics for the reactant (bromine or I) present in excess, and first-order kinetics for the other. The most evident explanation of the kinetics requires that the phenolsulfonic acid upon mixing with bromine is immediately transformed into a quinonoid intermediate II and demands that the *intermediate be present in large concentration.* This was verified by ultraviolet absorption spectra of the aqueous solution in this case. The rate-determining step is then the decomposition of the intermediate. Other phenols of closely similar structure would be expected to behave analogously.[25]

(2) By contrast, the kinetics for the bromination of potassium 4-methylnaphthalene-1-sulfonate (V) indicate a bimolecular mechanism between the sulfonate anion and Br_2; the reaction follows second-order kinetics which are first-order with respect to each reactant. The kinetics require *only a transition state,* and it is not necessary to propose that there is a reaction intermediate. The decrease in rate of bromodesulfonation as bromide ion concentration is increased can be satisfactorily accounted for by assuming that the equilibrium for the formation of Br_3^- from bromine is independent of the bromodesulfonation reaction and that Br_3^- is inert as a brominating agent.

These kinetics are not distinguishable from the usual bromodeprotonation reactions as is illustrated in the present work by the bromination of *o*-methoxybenzoic acid. Other workers have found similar results with bromodeprotonation reactions. Wilson and Soper[26] reported similar kinetics for the bromination of *o*-nitroanisole in water and so have Grovenstein and Henderson[12] for the bromination of 2,6-dibromophenol.

(3) The bromination of sodium *p*-methoxybenzenesulfonate (IV) and sodium 3,5-dibromo-4-aminobenzenesulfonate (III) also follows second-order kinetics, but here it was found necessary to postulate a *steady state concentration* of a reaction intermediate in order to account for the dependence of rate on (Br^-). When the observed rate constant was corrected for Br_3^- formation, the decrease in rate is only partly accounted for (see Table II). The magnitude of this additional decrease depends on the structure of the compound; the factor is 4 for sodium *p*-methoxybenzenesulfonate and 57 for sodium 3,5-dibromo-4-aminobenzenesulfonate upon changing the $(Br^-)_0$ from 0.0025 to 0.1500 *M*. This additional decrease in rate can be accounted for by a mechanism (eq. 9 and 10) which includes the reaction of bromide ion with a quinonoid intermediate to regenerate the starting sulfonate anion and Br_2. The rate-determining step is the attack of bromine on the sulfonate anion at low bromide concentrations but, as the concentration of bromide is increased, the step involving the elimination of SO_3 becomes rate-determining.

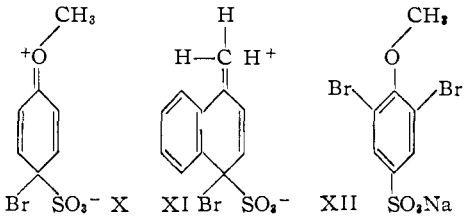
The substituent stabilizes the quinonoid structure by double bond formation with the benzene ring. The dibromo-*p*-phenolsulfonate I eliminates

(24) See ref. 3 for discussion and also refs. 22–26 of that paper.

(25) Sodium 3,5-dichloro-4-hydroxybenzenesulfonate in aqueous solution upon mixing with an equal molar amount of bromine water was found to give an immediate disappearance of the bromine color and a new absorption peak at 271–272 mμ of ϵ = 12,400. This behavior is closely similar to that for the dibromophenolsulfonate I and indicates that bromodesulfonation is by an identical mechanism.

(26) W. J. Wilson and F. G. Soper, *J. Chem. Soc.*, 3376 (1949), see also D. H. Derbyshire and W. A. Waters, *ibid.*, 564 (1950).

a proton from the OH group to give an intermediate quinonoid with a carbonyl group (II); the experiments show that this structural change (of those considered in this paper) is the most effective way of stabilizing a quinonoid.[27] With the dibromo-*p*-aminobenzenesulfonate III and the *p*-methoxybenzenesulfonate IV, double bond formation in the quinonoid can be brought about by forming an imine salt VII and oxonium cation X, respectively. For the methylnaphthalenesulfonate V a double bonded structure cannot be drawn but rather the transition state can be written as a resonance hybrid of various structures, one of which is the hyperconjugation structure XI.



Br SO_3^- X XI Br SO_3^- XII SO_3Na

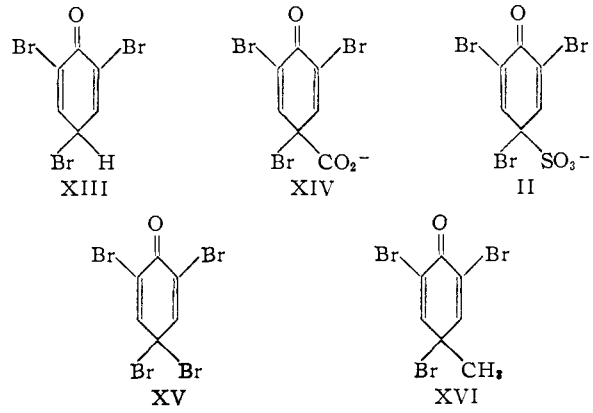
Sodium 3,5-dibromo-4-methoxybenzenesulfonate (XII), in contrast to IV, was found to undergo no appreciable reaction with bromine at 25°, and even at 98° the reaction was slow. This fact can be explained by noting that, because of steric repulsion, the bromine atoms keep the methyl group from being planar with the ring, and therefore, the oxygen can form only a partial double bond with the ring. Much of the activating effect of the oxygen is then lost and XII is relatively unreactive.[28]

Structural Features which Favor the Formation of Stable Quinonoid Intermediates.—The decomposition of a quinonoid intermediate may be written as

$$Ar\begin{matrix}X\\Y\end{matrix} \longrightarrow ArY + X \qquad (13)$$

where X is the group being replaced, Y is the group which became bonded to Ar in the initial step of the substitution reaction, and $Ar\begin{matrix}X\\Y\end{matrix}$ is the reaction intermediate with a quinonoid structure. It is apparent that an additional means of increasing the stability of a quinonoid is to increase the activation energy for the decomposition step (*i.e.*, choose X such that the energy of activation for breaking the C–X bond is raised). The experimental work discussed above showed that, for bromodesulfonation at least, the OH group is more effective in stabilizing a quinonoid structure than any of a variety of other substituents. Therefore, for comparison purposes a series of phenols will be chosen wherein X is varied. Ar is chosen to be the 3,5-dibromo-4-hydroxyphenyl group; X is $-CO_2^-$, $-SO_3^-$, Br (or Cl) or $-CH_3$; and Y is Br (*i.e.*, the intermediates were derived by bromination of ArX). The various intermediates or stable compounds are XIV, II, XV and XVI, respectively, for the above-named substituents.

The relative stabilities of these quinonoids will now be compared. The work reported in this paper shows that in aqueous solution at 0° the



XIII XIV II XV XVI

bromodecarboxylation of 3,5-dibromo-4-hydroxybenzoic acid was so rapid that the reaction was practically finished after 7 sec.[29] The intermediate II at 25° has a half-life of 126 min. Bromination of tribromophenol with aqueous bromine leads to the formation of the isolable 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one (XV).[24] Bromination of 2,6-dibromo-4-methylphenol leads to the cyclohexadien-1-one XVI which Fries and Oehmke have isolated and characterized.[30,31]

The increase of the stability of the intermediates where X is Br or CH_3 over those where X is $-CO_2^-$ or $-SO_3^-$ can be attributed to the higher energy of activation necessary for the breaking of the C–Br or C–CH_3 bond in the cyclohexadienones, XV and XVI, respectively, as indicated in reaction 13. The greater stability of the intermediate II where X is $-SO_3^-$ over that where X is $-CO_2^-$ can be explained in a similar manner. The case where X is hydrogen was studied by Grovenstein and Henderson[12] who found that the rate of bromination was *ca.* 200 times faster than that for X = $-CO_2^-$, and since in the latter case they demonstrated that the bromination reaction is reversible with bromide ion, whereas the former reaction showed little or no tendency for reversal, it would appear that the rupture of the C–CO_2^- bond of the intermediate XIV requires a higher activation energy than does the

(27) When the solvent is such that the phenol does not ionize appreciably, the stabilizing effect is not forthcoming. This is illustrated by the work of A. A. Yasnikov and E. A. Shilov (*Doklady Akad. Nauk S.S.S.R.*, **78**, 925 (1951); *C. A.*, **46**, 5009 (1952)) who report that 2,4,6-tribromophenol in anhydrous acetic acid will not brominate to give XV but that a small amount of water is necessary as a proton acceptor to bring about the reaction.

(28) *Cf.* ref. 20, pp. 157–160 and 238–243.

(29) XIV can be referred to here as a reaction intermediate because Grovenstein and Henderson have shown, as previously cited, that in 80% acetic acid–water 20% the kinetics of this bromodecarboxylation reaction require a "steady state" intermediate.[12]

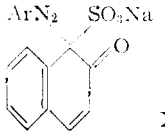
(30) K. Fries and G. Oehmke, *Ann.*, **462**, 6 and 16 (1928); Fries and co-workers assigned this and many other closely related compounds a cyclohexadienone structure on the basis of chemical evidence (see K. Fries and E. Brandes, *Ann.*, **542**, 48 (1939); K. Fries and H. Engel, *ibid.*, **439**, 232 (1924)). In support of this view, G. M. Coppinger and T. W. Campbell (THIS JOURNAL, **75**, 734 (1953)) have assigned a compound formed by the bromination of 2,6-di-*t*-butyl-4-methylphenol as 4-bromo-2,6-di-*t*-butyl-4-methyl-2,5-cyclohexadien-1-one by means of its infrared spectrum.

(31) For examples showing the use of substituting agents other than bromine see: M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, **19**, 978 (1954); L. E. Forman and W. C. Sears, THIS JOURNAL, **76**, 4977 (1954); H. E. Albert and W. C. Sears, *ibid.*, **76**, 4979 (1954).

rupture of the C–H bond in XIII to give tribromophenol.

The unique feature of the intermediate II is that it is stable enough to be formed in large concentrations yet unstable enough that it will decompose at a conveniently measurable rate in a manner typical of substitution reactions (eq. 13). Thus, it is an ideal case for kinetic investigation.

Naphthols would be expected to give more stable quinonoids than phenols. An example pertinent to this paper, because it could be considered as a desulfonation reaction occurring in two steps, is given in the work of Rowe and co-workers. They showed that the reaction of aryldiazonium salts in aqueous solution with 2-hydroxynaphthalenesulfonic acid leads to compounds having the quinonoid structure XVII.[32] The salts of these compounds have been isolated and are referred to as "stabilized diazonium salts" since with strong mineral acid they decompose to give the same compound as that obtained from β-naphthol and the aryldiazonium salt.



XVII

Experimental

Sodium 3,5-Dibromo-4-aminobenzenesulfonate (III).—An aqueous solution of the salt was prepared by treating an aqueous solution of sulfanilic acid (Mallinckrodt Analytical Reagent) with sodium bromate and hydrobromic acid according to the directions of Heinichen.[6] The sodium salt was isolated by evaporation of the solution after neutralizing with sodium hydroxide and recrystallized twice from water and twice from 90% ethanol to give fine needles. The salt was dried at 200°.[33]

Anal. Calcd. for $C_6H_4Br_2NO_3SNa$: C, 20.42; H, 1.14; Br, 45.28. Found: C, 20.69; H, 1.28; Br, 45.21.

Sodium *p*-methoxybenzenesulfonate (IV) was prepared by the method of Moody[34] by sulfonating anisole (Eastman White Label). The salt was recrystallized twice from water, twice from 90% ethanol and dried at 100°.

Anal. Calcd. for $C_7H_7SO_4$: C, 40.00; H, 3.36; S, 15.25. Found: C, 40.23; H, 3.32; S, 15.01.

Potassium 4-methylnaphthalene-1-sulfonate (V) was prepared by the method of Fieser and Bowen.[8] The salt was recrystallized three times from water and twice from ethanol-water and dried at 100°, m.p. of *p*-toluidine salt 227–229° (lit.[8] m.p. 228–230°).

Sodium 3,5-dibromo-4-methoxybenzenesulfonate (XII) was prepared by treating I with a twofold excess of dimethyl sulfate in aqueous sodium hydroxide. Upon reducing the volume of the solution, XII separated out and was recrystallized twice from aqueous sodium hydroxide and once from water and dried at 200°. The product showed no violet coloration upon treating with aqueous ferric chloride.

Anal. Calcd. for $C_7H_5Br_2O_4SNa$: C, 22.84; H, 1.37; Br, 43.43. Found: C, 23.00, 23.13; H, 1.24, 1.47; Br, 43.31.

Disodium Salt of 3,5-Dinitro-4-hydroxybenzenesulfonate (VI).—By the substitution of sodium for potassium salts, the monosodium salt of the dinitrophenolsulfonic acid was prepared by the method given by Friedlaender.[35] The monosodium salt was recrystallized from water and converted into the disodium salt by the addition of sodium carbonate. No more carbonate was added than that required to neutralize the acid as was indicated by the effervescence of carbon dioxide. The disodium salt was recrystallized three times from water and dried to constant weight at 120°.[36]

Anal. Calcd. for $C_6H_2N_2O_8SNa_2$: C, 23.38; H, 0.65; N, 9.09. Found: C, 23.30; H, 0.68; N, 9.04.

Potassium 4-Methoxy-3-nitrobenzenesulfonate.—*o*-Nitroanisole (Matheson-Coleman and Bell) was sulfonated with chlorosulfonic acid by the method of Gnehm and Knecht.[37] The potassium salt was prepared from the acid and purified by recrystallization from water, m.p. of the sulfonyl chloride derivative 65.5–66.5° (lit.[37] m.p. 66°).

***o*-Methoxybenzoic acid** was prepared by treating sodium salicylate with dimethyl sulfate in aqueous base. The product was recrystallized several times from ethanol, m.p. 101–101.5° (lit.[38] m.p. 100–101°).

Sodium 3,5-dichloro-4-hydroxybenzenesulfonate was prepared from sodium *p*-phenolsulfonate (Eastman White Label) by chlorination with $NaClO_3$/HCl in a procedure similar to that used for the preparation of sodium dibromo-*p*-phenol sulfonate by bromination.[3]

3,5-Dibromo-4-hydroxybenzoic acid was prepared by the bromination of *p*-hydroxybenzoic acid (Eastman White Label) in aqueous solution by a hydrobromic acid–sodium bromate mixture. The acid was recrystallized three times from chloroform, m.p. 271.5–272.5° (cor.), lit.[39] m.p. 267–268°.

Measurement of the Bromodesulfonation Reaction.—The kinetics of the bromodesulfonation of the amine II, anisole III, methylnaphthalene IV and dinitrophenol VI were measured at −0.10 ± 0.02°. The data are summarized in Tables I and III. Distilled water was used as the solvent. The reagents were the same as previously described.[3] Solutions of the reactants were prepared by mixing at the reaction temperature equal volumes of solution (a) which contained the aromatic sulfonate salt and sodium perchlorate with solution (b) which contained bromine, sodium bromide and perchloric acid. In the case of VI, the perchloric acid was equally divided between (a) and (b). The acid was added to prevent hydrolysis of the bromine and also to determine the effect of acidity on rates. Solutions of the sulfonate salts (0.0200 *M*), standardized perchloric acid and bromine water (*ca.* 5×10^{-3} *M*) were used in preparing the reaction mixtures. Sodium perchlorate and sodium bromide were weighed out separately for each experiment.

Two methods of mixing the reactants were employed. Method 1 consisted of mixing separate 25.0-ml. portions of solutions (a) and (b) for each point taken. Method 1 was used for the faster reactions and for those in which the reaction product began to separate from solution before reaction was complete. The $(Br_2)_0$ was determined by using samples of solution (b) as blanks both at the time the experiment was started and also toward the conclusion of the experiment. It was thus shown that the loss of bromine by the volatilization was small over the time interval necessary to conduct an experiment. All reactions were carried out in glass stoppered flasks.

Method 2, which was used for the slower completely homogeneous reactions, consisted of mixing equal volumes of solutions (a) and (b), usually 250 ml. each, and then following the reaction by withdrawing a sample (26.59 ml.) by pipet. Between operations, the pipet was cooled at the bath temperature. The reaction time was taken as that from the mixing of the solutions until one-half of the pipet was emptied. The initial bromine concentration was determined by removing an aliquot immediately after mixing or by removing an aliquot from solution (b) in which case a compensating volume was taken from (a) also and discarded. Method 2 was used in expt. 11 to 29 inclusive; all other experiments in Tables I and III followed the procedure of method 1.

About 16 points were taken in each experiment. With a fast reaction, the first point was taken after 4 sec. The reaction was stopped by mixing each sample with 10 ml. of 0.8% aqueous potassium iodide in method 1 or by pipetting

(32) F. M. Rowe, E. Levin, A. C. Burns, J. S. H. Davis and W. Tepper, *J. Chem. Soc.*, 690 (1926); F. M. Rowe, E. Levin and A. T. Peters, *ibid.*, 1065 (1931).

(33) Analyses were performed by Schwarzkopf Microanalytical Lab., Woodside 77, N. Y., unless otherwise noted.

(34) G. T. Moody, *Chem. News*, **66**, 247 (1892).

(35) P. Friedlaender, "Fortschritte der Teerfarben Fabrikation," Vol. I, Julius Springer, Berlin, 1888, p. 324.

(36) Analysis was by Elek Micro Analytical Lab., Los Angeles 16, Calif.

(37) R. Gnehm and O. Knecht, *J. prakt. Chem.*, **74**, 92 (1906).

(38) I. Heilbron, *et al.*, "Dictionary of Organic Compounds," Vol. III, Eyre and Spottiswoode Ltd., London, 1953, p. 281.

(39) Reference 38, Vol. II, p. 91.

an aliquot into aqueous potassium iodide in method 2. The sample was then analyzed immediately for the amount of iodine liberated by titrating against a standardized sodium thiosulfate solution measured from a semimicroburet. Starch was used as an indicator.

A reaction mixture which was 6.7×10^{-3} *M* in potassium 4-methoxy-3-nitrobenzenesulfonate and 4.3×10^{-3} *M* in bromine was kept at 50°; it was found that slightly less than half of the bromine disappeared after 17 hr. Sodium 3,5-dibromo-4-methoxybenzenesulfonate (XII) with bromine gave no appreciable reaction at 25°; but when a reaction mixture containing 6.7×10^{-3} *M* XII and 4.6×10^{-3} *M* bromine was heated in a sealed tube at 98°, the amount of bromine decreased to 2.4×10^{-3} *M* after 1.5 hr.

Bromodecarboxylation of 3,5-Dibromo-4-hydroxybenzoic Acid.—The procedure was similar to method 1 discussed above for the bromodesulfonation experiments. Solution (a) was prepared by dissolving 1.00×10^{-3} mole of the dibromohydroxybenzoic acid with 1.65×10^{-3} mole of NaOH in one l. of water. Solution (b) contained 4.84×10^{-4} mole/l. of Br_2; 25 ml. of each solution were mixed at 0°. The reaction was so rapid that with a time of 7 sec. it was over 90% complete.

Ultraviolet spectra were taken in aqueous solution on a Cary spectrophotometer, model 11.

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[CONTRIBUTION FROM JOHN HARRISON LABORATORY, UNIVERSITY OF PENNSYLVANIA, AND BROOKHAVEN NATIONAL LABORATORY]

The Free Radical Phenylation of 2,4-Dinitrotritiobenzene[1]

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The conversion of 2,4-dinitrotritiobenzene to 2,4-dinitrobiphenyl by treatment with benzoyl peroxide proceeds with the displacement of just one-half of the tritium. This proves that the product-determining step does not involve breaking the tritium- (or hydrogen-) carbon bond.

Two mechanisms have been advanced for free radical substitution in the benzene ring. One[2] involves initial hydrogen abstraction followed by coupling of two radicals.

$$C_6H_5\cdot + ArH \longrightarrow C_6H_5H + Ar\cdot \xrightarrow{C_6H_5\cdot} ArC_6H_5 \quad (1)$$

The other involves initial addition to the aromatic nucleus, followed by hydrogen abstraction.[2a,3]

$$C_6H_5\cdot + ArH \longrightarrow \left[\begin{array}{c} C_6H_5 \\ Ar \\ H \end{array}\right] \xrightarrow{R\cdot} RH + ArC_6H_5 \quad (2)$$

In order to obtain more unequivocal evidence, we have studied the phenylation of 2,4-dinitrotritiobenzene, since mechanism 1 should show a substantial isotope effect while mechanism 2 would have little or none.

Experimental

2,4-Dinitrotritiobenzene was prepared by dissolving 2,4-dinitrobenzoic acid (5 g.) in 5 ml. of tritiated water (20 mc./10 ml.) heated at 125°, followed by decarboxylation of 5 g. of the tritiated acid by heating to 240° in 25 ml. of quinoline with 0.02 g. of copper chromite catalyst. After thorough washing of an ether solution, evaporation and recrystallization from 95% ethanol, 1.5 g. (38%) of tritiated *m*-dinitrobenzene, m.p. 108–108.8°, was obtained. This sample was mixed with 40 g. of unlabeled material and recrystallized once more from ethanol. One sample prepared in this way assayed[4] for 51.7 ± 1.6 mμc./mg. of hydrogen, a second for 22.8 ± 0.7 mμc./mg. of hydrogen.

2,4-Dinitrobiphenyl.—A mixture of 4.3 g. of benzoyl peroxide (0.02 mole) and 29.6 g. of tritiated *m*-dinitrobenzene (0.2 mole) was heated, gradually increasing the temperature from 75 to 100° over a period of 5 hr. After dissolving in 400 ml. of ether, the product was washed with five 50-ml. portions of 10% sodium bicarbonate, with three 50-ml. portions of 15% hydrochloric acid and three 50-ml. portions of water. Drying and evaporation left a solid residue which was distilled at 0.4 mm. to remove most of the excess *m*-dinitrobenzene (b.p. 98° (0.4 mm.)). The still residue was extracted with 150 ml. of boiling methanol. After cooling to room temperature and evaporation to 10 ml., the precipitate was collected and recrystallized four times from methanol to yield 0.7 g. (16%) of 2,4-dinitrobiphenyl. Before assay, 0.1 g. of this material in 5 ml. of benzene was put through a column of magnesium oxide.[5] After development with additional benzene, elution of the purple band with benzene, followed by evaporation of the benzene and recrystallization from methanol gave material melting at 109.3–110°. The results of tritium assay are summarized in Table I.

TABLE I

TRITIUM CONTENT OF *m*-DINITROBENZENE AND 2,4-DINITROBIPHENYL (MμC./MG. OF HYDROGEN)

Sample	$C_6H_4(NO_2)_2$ (exptl.)	$C_6H_5C_6H_3(NO_2)_2$ (exptl.)	$C_6H_5C_6H_3(NO_2)_2$ (calcd.)[a]
1	51.7 ± 1.6	13.2 ± 0.4	12.9 ± 0.4
2	22.8 ± 0.7	5.54 ± 0.17	5.7 ± 0.2

[a] Calculated assuming starting material is exclusively 2,4-isomer and that replacement of hydrogen and tritium occur at identical rates.

An authentic sample of 2,4-dinitrobiphenyl was prepared by mixed Ullmann coupling of 2,4-dinitrochlorobenzene and iodobenzene in 3.5% yield,[6] m.p. 109.3–110°.[7] This showed no depression of melting point when admixed with the preceding sample.

Anal. Calcd. for $C_{12}H_8N_2O_4$: C, 59.01; H, 3.26; N, 11.47. Found: C, 58.96; H, 3.25; N, 11.39.

Discussion

The agreement of the tritium content of the

(1) Research carried out in part under the auspices of the U. S. Atomic Energy Commission.

(2) (a) W. A. Waters, *J. Chem. Soc.*, 727 (1948); (b) H. Lobel, G. Stein and J. Weiss, *ibid.*, 2704 (1950).

(3) C. C. Price, "Reactions at the Carbon–Carbon Double Bond," Interscience Publishers, Inc., New York, N. Y., 1946; D. H. Hey, A. Nechvatal and T. S. Robinson, *J. Chem. Soc.*, 2892 (1951).

(4) Tritium assay was performed at Brookhaven by Dr. D. R. Christman.

(5) K. Cruse and R. Mittag, *Z. anal. Chem.*, **131**, 273 (1950).

(6) By the procedure of N. Kornblum and D. L. Kendall, THIS JOURNAL, **74**, 5182 (1952).

(7) H. C. Gull and E. E. Turner, *J. Chem. Soc.*, 496 (1929).