**SUBSTITUENT EFFECTS IN THE REDUCTION OF SOME 3'-OR 4'-SUBSTITUTED 4-AZOBENZENESULFONIC ACIDS BY SODIUM DITHIOHTE IN ALKALINE SOLUTION**


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**ABSTRACT**

For a series of 4-azobenzenesulfonic acids, reduction by sodium dithionite in alkaline solution was found to be accelerat ed by electron-attracting substituents. A Hammett's value of 5.8 was obtained for reactions at 25.0°C in an aqueous solution 0.15M in sodium hydroxide and 0.10M in sodium sulfate.

**INTRODUCTION**

Sodium dithionite is a useful reagent for the reduction of aromaticazo compounds. The products are amine derivatives of the azo compounds (Wasmuth, 1906). The dithionite reduction of 4-azobenzensulfonic acid has recently been found to be first order in 4-azobenzensulfonate ion and half-order in dithionite ion (Wasmuth et al., 1965). The same orders in dithionite ion and oxidant have been found for the reactions of sodium dithionite with para nitrophenol (Wasmuth et al., 1964) and with oxygen (Rinker, 1964) in alkaline reaction media. Initial steps proposed for the dithionite reduction of 4-azobenzensulfonic acid including the attack of the M° of the radical ion on the 4-azobenzensulfonate ion and the decomposition of an intermediate formed from these ions as possible rate-determining steps are:

\[ \text{M}^0 + \text{S}_2\text{O}_5^2- \rightarrow \text{M}^+ + \text{S}_2\text{O}_4^{2-} \]

\[ \text{M}^0 + \text{S}_2\text{O}_5^2- + \text{H}_2\text{O} \rightarrow \text{M}^+ + \text{S}_2\text{O}_4^{2-} + \text{OH}^- \]

In the present paper the relative rates of the reactions of some substituted 4-azobenzene sulfonic acids with sodium dithionite are reported.

**MATERIALS AND METHODS**

The reactions of sodium dithionite with the azo compounds were carried out in a 500 ml muffle furnace flask fitted with a two-hole stopper accommodating a sintered inlet tube extending to the bottom of the flask and a short outlet tube. A reaction was started by momentarily tapping the stopper and introducing a 380-2000 mg amount of sodium dithionite contained in a shallow polyethylene boat to a 300 ml volume of reaction mixtures 0.15M in sodium hydroxide, 0.10M in sodium sulfate, and initially 0.002-0.006 M in the azo compound. Temperature control was provided by a thermostatically controlled bath maintained at 25.0°C. The reactions were followed by absorbance measurements made at 430 millimicrons with a Beckman DU spectrophotometer on reaction mixture samples taken by syringe through the outlet tube during the first 500 seconds after mixing. Rate constants were calculated as previously described (Wasmuth et al., 1965). The variation of absorbance with concentration at 430 millimicrons was found to conform to the Beer-Lambert law for each azo compound in the concentration range employed for these measurements.

The Na2S2O5 content of the Fisher iron-free sodium dithionite used was found to be 79% by an iodometric method (Stockes, 1964). Eastman 6357 4-azobenzensulfonic acid was used without further purification. The sodium salts of 4'-bromo-4-azobenzensulfonic acid, 4'-chloro-4-azobenzensulfonic acid, 4'-methyl-4-azobenzensulfonic acid, and 4'-methoxy-4-azobenzensulfonic acid, were prepared by the methods of Janovsky (1987), Mentha and Heumus (1988), Mills (1985), and Inoue et al. (1959), respectively. The 3'-chloro-4-azobenzensulfonic acid used was prepared by allowing 3'-chloroazobenzene to react with 20% fuming sulfuric acid for one hour at 75°C. The product was separated by pouring the cooled reaction mixture into water, precipitated from aqueous solution by the addition of concentrated hydrochloric acid, recrystallized three times from benzene, and dried under vacuum at 55°C. The neutralization equivalent found for the sulfonic acid was 297.6 (calc'd for C12H10Cl3N2O5S, 297.7). The melting point found was 119-120°C. Compound with the structure indicated for the sulfonic acid was the isolation of m-chlorosalicylic acid as a product of the iron powder reduction of the acid in a dilute acetic acid solution and the isolation of 2-chlorobenzaldehyde as a product of the reaction of stannic chloride with the acid in concentrated hydrochloric acid solution. Identification of the products isolated was made by comparison of their IR spectra with the IR spectra of Manheim, C. R., B. G. Cleveland, and C. E. Harding, and G. E. Shackle, 1965. Kinetics of the Reduction of 4-Azobenzensulfonic Acid by Sodium Dithionite in Alkaline Solution. J. Soc. Dyers and Colorists, 81:433-436. Wasmuth, C. R., B. G. Cleveland, and C. E. Harding, 1966. Participation of the SO2 radical ion in the Reduction of Azo Compounds by Sodium Dithionite. J. Phys. Chem. 68: 423-425.

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![Graph](image-url)  
**Fig. 1. Variation of log k/k0 with Hammett sigma.**

**Table I**

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Rate Constant (k/k0)</th>
</tr>
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<tbody>
<tr>
<td>3'-Chloro</td>
<td>0.012</td>
</tr>
<tr>
<td>4'-Chloro</td>
<td>0.042</td>
</tr>
<tr>
<td>3'-Methyl</td>
<td>0.064</td>
</tr>
<tr>
<td>4'-Methyl</td>
<td>0.073</td>
</tr>
<tr>
<td>3'-Methoxy</td>
<td>0.086</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

The variation of the ratio of the three-substituted azo compounds constant, k/k0, to k, the three-substituted azo rate constant for the dithionite reduction of the parent 4-4-azobenzensulfonic ion, with the Hammett substituent constant sigma, is shown in Fig. 1 as a plot of log k/k0 against sigma for the series of substituted 4-azobenzensulfonates. The values of the rate constants are given in Table 1. The sigma values required were taken from the list compiled by McDaniel and Brown (1958). The variation in rate constant for the same, what limited series of compounds appears to follow the Hammett relationship

\[ \log \frac{k}{k_0} = \rho \sigma \]

The positive sign of the rho value obtained, 2.8, is indicative of development of negative charge at the reactive center of the reactant aromatic molecule in the transition state and thus does not appear to be inconsistent with the mechanisms proposed for the reaction with dithionite.

**LITERATURE CITED**