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

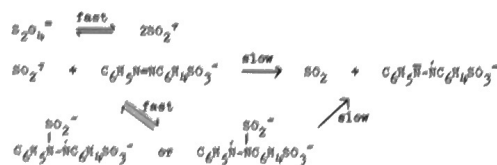C. R. WASMUTH, A. F. BRIDGES, K. W. CARR,
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ABSTRACT

For a series of 4-azobenzensulfonic acids, reduction by sodium dithionite in alkaline solution was found to be accelerated by electron-attracting substituents. A Hammett rho value of 2.8 was obtained for reduction at 25.0 C. in an aqueous solution 0.150 M in sodium hydroxide and 0.100 M in sodium sulfate.

INTRODUCTION

Sodium dithionite is a useful reagent for the reduction of aromatic azo compounds. The products are amines or hydrazo derivatives (Grandmougin 1906). The dithionite reduction of 4-azobenzenesulfonic acid has recently been found to be first order in 4-azobenzenesulfonate ion and one-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 p-nitrophenol (Wasmuth et al. 1964) and with oxygen (Rinker et al. 1960) in alkaline reaction media. Initial steps proposed for the dithionite reduction of 4-azobenzenesulfonic acid including the attack of the SO_2^- radical ion on the 4-azobenzensulfonate ion and the decomposition of an intermediate formed from these ions as possible rate-determining steps are

$$S_2O_4^= \underset{}{\overset{fast}{\rightleftharpoons}} 2SO_2^-$$

$$SO_2^- + C_6H_5N=NC_6H_4SO_3^= \overset{slow}{\longrightarrow} SO_2 + C_6H_5\dot{N}-NC_6H_4SO_3^=$$

In the present paper the relative rates of the reactions of some substituted 4-azobenzenesulfonic 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 erlenmeyer flask fitted with a two-hole stopper accommodating a nitrogen inlet tube extending to the bottom of the flask and a short outlet tube. A reaction was started by momentarily raising 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 mixture 0.150 M in sodium hydroxide, 0.100 M in sodium sulfate, and initially 0.0002-0.0006 M in

the azo compound. Temperature control was provided by a thermostated 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 pipet 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 Beer's law for each azo compound in the concentration range employed for the rate measurements.

The $Na_2S_2O_4$ content of the Fisher iron-free sodium dithionite used was found to be 79% by an iodometric method (Szekeres 1964). Eastman 6357 4-azobenzensulfonic acid was used without further purification. The sodium salts of 4'-bromo-4-azobenzenesulfonic acid, 4'-chloro-4-azobenzenesulfonic acid, 4'-methyl-4-azobenzenesulfonic acid, and 4'-methoxy-4-azobenzenesulfonic acid, were prepared by the methods of Janovsky (1887), Mentha and Heumann (1886), Mills (1895), and Inscoe et al. (1959), respectively. The 3'-chloro-4-azobenbenesulfonic 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, reprecipitated from aqueous solution by the addition of concentrated hydrochloric acid, recrystallized three times from benzene, and dried under vacuum at 56 C. The neutralization equivalent found for the sulfonic acid was 297.6 (calcd for $C_{12}H_9ClN_2O_5S$: 296.7). The melting point found was 109-110 C. Consistent with the structure indicated for the sulfonic acid were the isolation of m-chloroaniline as a product of the iron powder reduction of the acid in a dilute acetic acid solution and the isolation of 2-chlorobenzidine as a product of the reaction of stannous 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 Matheson, Coleman, and Bell m-chloroaniline and 2-chlorobenzidine prepared by treatment of 3-chloroazobenzene with stannous chloride in alcoholic hydrochloric acid solution (Burns et al. 1928). Loss of the sulfo group by displacement during the benzidine rearrangement of the intermediate hydrazo compound derived from 3'-chloro-4-azobenzenesulfonic acid would be likely in view of what is reported for the benzidine rearrangements of

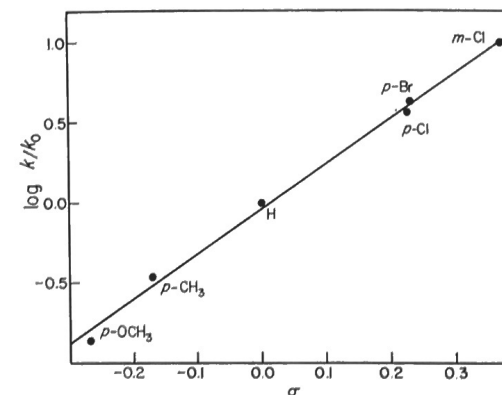sulfo-substituted aromatic hydrazo compounds (Ingold 1953).

Fig. 1. Variation of log k/k_0 with Hammett sigma.

TABLE I

RATE CONSTANTS FOR DITHIONITE REDUCTION

4-Azobenzenesulfonate ion	k, $l^{\frac{1}{2}}mole^{-\frac{1}{2}}sec^{-1}$
3'-Chloro	0.172
4'-Bromo	0.074
4'-Chloro	0.063
Unsubstituted	0.0172
4'-Methyl	0.0060
4'-Methoxy	0.0024

RESULTS AND DISCUSSION

The variation of the ratio of the three-halves order rate constant, k to k_0, the three-halves order rate constant for the dithionite reduction of the parent +4-azobenzenesulfonate ion, with the Hammett substituent constant sigma, is shown in Fig. 1 as a plot of log k/k_0 against sigma for the series of substituted 4-azobenzenesulfonates. The values of the rate constants

are given in Table I. The sigma values required were taken from the list compiled by McDaniel and Brown (1958). The variation in rate constant for the somewhat limited series of compounds appears to follow the Hammett relationship

$$\log \; k/k_0 \; = \; \rho\sigma$$

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

Burns, J. H., McCombie, and H. A. Scarborough. 1928. Some Substitution Products of Azobenzene. J. Chem. Soc. 2928-2936.

Grandmougin, E. 1906. Spaltung von Azofarbstoffen mit Natriumhydrosulfit. Ber. 39:2494-2497.

Ingold, C. K. 1953. Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca, New York, p. 633.

Inscoe, M. N., J. H. Gould, and W. R. Brode. 1959. The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. XXX. Photoisomerization of Azo Dyes in Aqueous Solution. J. Am. Chem. Soc. 81:5634-5637.

Janovsky, J. V. 1887. Beitraege zur Kenntniss der Azoverbindungen. Monatsh. Chem. 8:49-63.

McDaniel, D. H., and H. C. Brown. 1958. An Extended Table of Hammett Substituent Constants Based on the Ionization of Substituted Benzoic Acids. J. Org. Chem. 23:425.

Mentha, E., and K. Heumann. 1886. Ueber Derivate des Paramonochlorazobenzols. Ber. 19:2970-2974.

Mills, C. 1895. Some new Azo-compounds. J. Chem. Soc. 67: 925-933.

Rinker, R. G., T. P. Gordon, D. M. Mason, R. R. Sakaida, and W. H. Corcoran. 1960. Kinetics and Mechanism of the Air Oxidation of the Dithionite Ion ($S_2O_4^=$) in Aqueous Solution J. Phys. Chem. 64:573-581.

Szekeres, L. 1964. Zur Analyse der Dithionite. Z. Anal. Chem. 203:178-180.

Wasmuth, C. R., R. L. Donnell, C. E. Harding, and G. E. Shankle. 1965. Kinetics of the Reduction of p-Phenylazobenzenesulphonic Acid by Sodium Dithionite in Alkaline Solution. J. Soc. Dyers and Colourists. 81:403-405.

Wasmuth, C. R., C. Edwards, and R. Hutcherson. 1964. Participation of the SO_2^- Radical Ion in the Reduction of p-Nitrophenol by Sodium Dithionite. J. Phys. Chem. 68: 423-425.