# The Alkaline Sulfide Reduction of Aromatic Nitro Compounds. XIII. The Processes in the Alkaline Sulfide Reduction of Aromatic Nitro Compounds*[1]

Shizunobu HASHIMOTO and Junzo SUNAMOTO*[2]

*Department of Applied Chemistry, Doshisha University, Karasuma-imadegawa, Kamikyo-ku, Kyoto*

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Goldschmidt and Larsen have presented evidence[1] that the reduction of sodium *m*-nitrobenzenesulfonate by an aqueous hydro sulfide saturated with hydrogen sulfide gives the corresponding nitroso, *N*-phenylhydroxylamino, and an anilino compound, but the anilino compound was not produced *via* the *N*-phenylhydroxylamino compound. Recently, Cope and Brown have suggested the formation of *N*-phenylhydroxylamine by gas chromatography in the reduction of nitrobenzene with an aqueous monosulfide containing ammonium chloride ($pH=10.5$).[2] On the other hand, in an earlier paper dealing with the kinetics of the aqueous monosulfide and with hydrosulfide reductions of sodium *m*-nitrobenzenesulfonate, we have suggested[3] that the monosulfide and hydrosulfide must be essentially identical in their reactions, a fact related to the hydrolytic equilibrium of the monosulfide.

The present investigation was undertaken to determine the alkaline sulfide reduction process of aromatic nitro compounds.

Table 1 shows the reduction products of nitro, nitroso, *N*-phenylhydroxylamino, azoxy, and azo compounds with the aqueous monosulfide or disulfide. The nitro compound gave only the corresponding amine, VI, with both sulfides. The nitroso compound gave VI together with VII, the product ratio of VI to VII being approximately unity in the monosulfide reduction. In the disulfide reduction, however, the yield of VII became much higher than that of VI. The monosulfide reduction of the *N*-phenylhydroxylamino compound was very slow under the conditions shown in Table 1; traces of VI and of VIII, the acidic rearrangement product of III, were detected on the paper chromatogram. On the other hand, in the disulfide reduction of III, the formation of VI and VII were observed, and the reduction rate of III became rather higher. Anlike the nitroso and *N*-phenylhydroxylamino compounds, the azoxy and azo compounds were reduced to give only the corresponding VII, derived from hydrazo compound. A small amount of VI given by the disproportionation of the hydrazo compound[4] was also detected.

The reduction of the nitro and nitroso compounds with the aqueous monosulfide and disulfide are shown in Fig. 1, while those of azoxy and azo compounds are shown in Fig. 2. The reduction rate of the nitro compound with an aqueous disulfide was very different from that with an aqueous

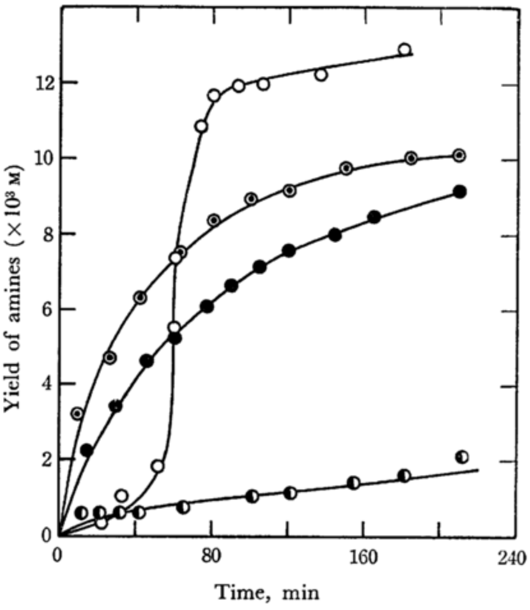

Fig. 1. Aqueous monosulfide and disulfide reduction of sodium *m*-nitro- and *m*-nitrosobenzene sulfonate at 35.0°C.

○: $(Ar\text{-}NO_2)=1.429\times10^{-2}$ M
$(Na_2S)=6.571\times10^{-2}$ M

●: $(Ar\text{-}NO_2)=1.563\times10^{-2}$ M
$(Na_2S_2)=1.926\times10^{-2}$ M

◐: $(Ar\text{-}NO)=1.430\times10^{-2}$ M
$(Na_2S)=13.14\times10^{-2}$ M

⊙: $(Ar\text{-}NO)=1.430\times10^{-2}$ M
$(Na_2S_2)=6.571\times10^{-2}$ M

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*[2] Present address: Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka.

1) H. Goldschmidt and H. Larsen, *Z. physik. Chem.*, **71**, 437 (1910).

2) O. J. Cope and R. K. Brown, *Can. J. Chem.*, **40**, 2317 (1962).

3) S. Hashimoto and J. Sunamoto, This Bulletin, **39**, 1207 (1966).

4) S. Hashimoto and J. Sunamoto, *Yuki Gosei Kagaku Kyokaishi (J. Synth. Org. Chem. Japan)*, **24**, 1025 (1966).

TABLE 1. REDUCTION PRODUCTS IN AQUEOUS MONOSULFIDE OR DISULFIDE SOLUTION OF SODIUM *m*-NITROBENZENE SULFONATE AND ITS REDUCTION INTERMEDIATES

| Starting material and its concn. $\times 10^2$ M | Reducing agent and its concn. $\times 10^2$ M | Reduction condition °C | Reduction condition min | Reduction product* |
|---|---|---|---|---|
| I: 1.429 | M: 6.571 | 35 | 180 | VI |
| I: 1.563 | D: 1.926 | 35 | 250 | VI |
| II: 1.430 | M: 13.14 | 35 | 270 | VI and VII |
| II: 1.430 | D: 6.571 | 35 | 330 | VI $\gg$ VII |
| III: 1.514 | M: 7.669 | 35 | 300 | Almost unreacted, VI, (VIII) |
| III: 5.00 | D: 23.00 | 98 | 30 | VI $\gg$ VII |
| IV: 0.758 | M: 7.669 | 35 | 300 | VI (VII) |
| IV: 0.714 | D: 6.571 | 35 | 280 | VI (VII) |
| V: 0.740 | M: 13.14 | 35 | 350 | VI (VII) |
| V: 0.740 | D: 6.571 | 35 | 270 | VI (VII) |

* The products given by the other processes besides the reduction, as described in the text, are shown in parentheses.

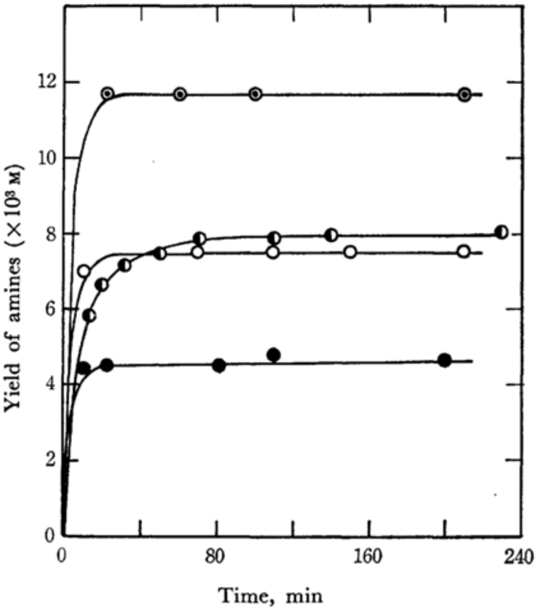


Fig. 2. Aqueous monosulfide and disulfide reduction of disodium *m*, *m'*-azoxy- and *m*, *m'*-azobenzene disulfonate at 35.0°C.

○: $(\text{Ar-N(O)=N-Ar}) = 0.758 \times 10^{-2}$ M $(\text{Na}_2\text{S}) = 7.669 \times 10^{-2}$ M

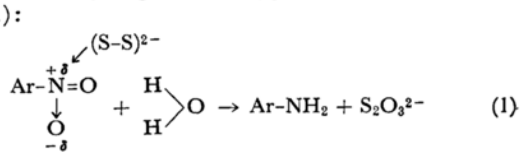
◐: $(\text{Ar-N(O)=N-Ar}) = 0.714 \times 10^{-2}$ M $(\text{Na}_2\text{S}_2) = 6.571 \times 10^{-2}$ M

●: $(\text{Ar-N=N-Ar}) = 0.740 \times 10^{-2}$ M $(\text{Na}_2\text{S}) = 13.14 \times 10^{-2}$ M

⊙: $(\text{Ar-N=N-Ar}) = 0.740 \times 10^{-2}$ M $(\text{Na}_2\text{S}_2) = 6.571 \times 10^{-2}$ M

monosulfide.[3,5] Anlike the monosulfide reduction of the nitro compound, that of the nitroso compound had no induction period and its reduction rate was much slower throughout the reaction. On the other hand, the disulfide reduction of the nitroso compound proceeded at approximately the same rate as that of the nitro compound. The monosulfide reduction rate of the *N*-phenylhydroxylamino compound was much lower than that of the nitroso compound, but the disulfide reduction rate was the same as those of the nitro and nitroso compounds. Our findings concerning the reduction rates listed above are consistent with the results obtained by Cope and Brown,[2] although our point of view was somewhat different from theirs. In the reduction of the azoxy and azo compounds, no comparable differences in the reduction rates were observed between the monosulfide and the disulfide reduction. In these cases, the initial reduction rates were rather high, and the reactions reached an apparent equilibrium rather early.

On the basis of the data thus obtained, it seems most reasonable to conclude that, in the alkaline sulfide reductions of sodium *m*-nitrobenzenesulfonate, but not the hydrogen sulfide reduction, methanilic acid will be directly produced from the nitro compound upon the attack of the disulfide on the positively-charged nitrogen of the nitro group[6] and upon the subsequent rapid interchange between hydrogen and oxygen, as is shown in Eq. (1):



$$\text{Ar-}\overset{+\delta}{\text{N}}\text{=O} \ (\swarrow (\text{S-S})^{2-}),\ \text{N} \rightarrow \underset{-\delta}{\text{O}} + \text{H}_2\text{O} \rightarrow \text{Ar-NH}_2 + \text{S}_2\text{O}_3^{2-} \qquad (1)$$

No nitroso, *N*-phenylhydroxylamino, azoxy, or azo compounds is intermediately produced during the course of the reduction of the nitro compound. In the monosulfide or the hydrosulfide reduction, the disulfide is produced by the radical oxidation

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[5] S. Hashimoto and J. Sunamoto, This Bulletin, **39**, 100 (1966).

[6] M. Hojyo, Y. Takagi and Y. Ogata, *J. Am. Chem. Soc.*, **82**, 2459 (1960).

of the monosulfide or the hydrosulfide with light, oxygen, and so forth.[5,7,8]

### Experimental

**Materials.** The sodium monosulfide (M) and disulfide (D), sodium *m*-nitrobenzenesulfonate (I), sodium *m*-nitrosobenzenesulfonate (II), disodium *m*,*m*'-azoxybenzenedisulfonate (IV), and disodium *m*,*m*'-azobenzenedisulfonate (V) were the same as those used in previous papers.[3,8] The sodium *m*-(*N*-phenylhydroxylamino)benzenesulfonate (III) was prepared by the zinc reduction of the corresponding nitro compound, I; the sulfonate thus obtained, when recrystallized from aqueous methanol, was found to be chromatographically pure. Their purities were exactly determined before use by the usual reduction-diazometry.

**Rate Measurement.** The procedure for the rate measurements and analyses were the same as in the method described earlier.[3,5]

When a nitroso, azoxy, or azo compound was reduced by aqueous alkaline sulfide, the corresponding hydrazo compound was obtained. After the benzidine rearrangement of the hydrazo compound with hydrochloric acid, the amine produced was determined by diazometry. When *m*-(*N*-phenylhydroxylamino)benzenesulfonate was reduced by aqueous monosulfide under the same conditions as those used in the reduction of the nitro or nitroso compound, the reduction rate of the former was much slower and most of the reactant was recovered.

The reaction was also followed by paper chromatography. The chromatograms were developed with *n*-butanol containing concentrated hydrochloric acid (4 : 1 by vol.). The $R_f$ values and the detections were as follows: *m*-aminobenzenesulfonate (VI), $R_f=0.30$, reddish orange upon diazotization and coupling with $\alpha$-naphthol-4-sulfonate (method A) or orange, with *p*-dimethylaminobenzaldehyde (method B); *m*, *m*'-benzidinedisulfonate (VII), $R_f=0.05$, red, with A or orange, with B; III, $R_f=0.22$, yellow, with B; and 2-hydroxy-5-aminobenzenesulfonate (VIII), $R_f=0.13$, dull red, with A or yellow, with B. No other materials were observed.

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7) Part XI: S. Hashimoto, J. Sunamoto and K. Sato, This Bulletin, **40**, 2860 (1967).

8) Part XII: S. Hashimoto, J. Sunamoto and A. Aoki, *ibid.*, **40**, 2867 (1967).