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The Alkaline Sulfide Reduction of Aromatic Nitro Compounds. XII. ESR Studies of the Alkaline Sulfide Reduction of the Aromatic Nitro Compound*[1]

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The ESR techniques were used in order to examine the presence of the radical species in the alkaline sulfide reduction of aromatic nitro compounds and in the photooxidation of an aqueous monosulfide solution. The ESR spectra were clear when observed by ultraviolet-light irradiation on an aqueous monosulfide solution: they were the signals of a singlet, with a *g*-value of 2.002 ± 0.001 and a maximum slope width of 3.1 gauss, and a doublet, with a *g*-value of 2.00 ± 0.001 and a coupling constant of 114 gauss. The singlet was identified as the signal of the sulfide ion radical, $S\cdot^-$, while it was most reasonable to assume the doublet to be signals due to the interaction of the sulfide ion radical with the hydrosulfide or the hydroxide in the solution. On the other hand, ESR spectra were also observed in the reaction of sodium *m*-nitrobenzene sulfonate with an aqueous monosulfide solution; these spectra were identical with the sulfide ion radical and the radical-anion of the nitro compound. On the basis of the results obtained, we have discussed the mechanisms of the alkaline sulfide reduction of aromatic nitro compounds and these reduction intermediates.

In previous investigations dealing with the kinetics of the aqueous monosulfide reduction of sodium *m*-nitrobenzene sulfonate,¹⁾ the photochemical oxidation of an aqueous monosulfide solution,²⁾ and the aqueous hydrosulfide reduction of azoxybenzene,³⁾ we have proposed that the autoxidation of monosulfide to disulfide may always occur and that this autoxidation may proceed via the formation of a sulfide ion radical, $S\cdot^-$.

In the present investigation, the ESR techniques were used in order to confirm practically the assumptions hitherto presented by us.¹⁻³⁾ From the results obtained, we have discussed the reaction mechanisms of the alkaline sulfide reduction of aromatic nitro compounds and these reduction intermediates.

Experimental

Materials. Analytical grade crystal sodium monosulfide and ammonium sulfide, and crystal potassium monosulfide commercially obtained were used an aqueous solution without further purification. Sodium polysulfides were prepared from sodium monosulfide, and elemental sulfur, by the method used in a previous paper.⁴⁾ The aqueous alkaline sulfide solutions prepared were analyzed exactly before use by the usual iodometry.

Sodium *m*-nitrobenzene sulfonate and its reduction intermediates, such as the corresponding nitroso, azoxy, and azo compounds, were obtained by the standard methods of preparation and were used after careful purification until no impurities were detected in them on their paper chromatograms. They were also exactly analyzed before use by the usual diazometry.

ESR Measurements. The paramagnetic resonance spectra were observed using a JES-3BX, X-band spectromater with a field modulation of 100 kc/sec, and a TE_{102} mode cavity with a flattened quartz cell (thickness, 1 mm; width, 8 mm; length, 50 mm). As the standard of the *g*-value and the hyperfine splitting of the radicals, DPPH (α, α'-diphenyl-β-picrylhydrazyl) was applied to the cavity. The UV irradiation (2537 Å, 15W) was undertaken at a distance of 0.5—1 cm from the absorption cell, wherein a sample solution was placed for an appropriate duration; thereafter the absorption cell was immediately applied to the cavity.

The electron beam was irradiated from a Van de Graaff accelarator on a common glass beaker, wherein the sample had been placed. The irradiation dose was 2×10^7 rad.

The reaction of the alkaline sulfide solution with the nitro compound or its reduction intermediates was

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[1] *1 Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

1) S. Hashimoto and J. Sunamoto, This Bulletin, **39**, 100 (1966).

2) Part XI: S. Hashimoto and J. Sunamoto and K. Sato, *ibid.*, **40**, 2860 (1967).

3) S. Hashimoto and J. Sunamoto, *Yuki Gosei Kagaku Kyokaishi (J. Synth. Org. Chem. Japan)*, **24**, 1225 (1966).

4) S. Hashimoto and J. Sunamoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 669 (1965).

undertaken under proper conditions in a flask different from the absorption cell; thereafter the reaction mixtures were again placed in the absorption cell prior to the ESR measurements.

Results and Discussion

ESR Spectra of Irradiated Aqueous Monosulfide. Because we had first supposed that the radical produced from aqueous monosulfide would be very unstable if it did exist, the ESR spectra were measured with a frozen sample using liquid nitrogen or under an outside irradiation on the sample placed in the cavity. However, no ESR spectra at all were observed by these method, nor did any changes in the aqueous monosulfide appear. Therefore, the sample placed in the absorption cell was next irradiated prior to the ESR measurements. The sample, which had been colorless before irradiation, gradually turned yellow upon irradiation, and clearly the disulfide formation was observed. The resulting solution was immediately measured; thereby very clear ESR spectra could be observed.

Figure 1 shows typical ESR spectra of aqueous monosulfide irradiated with ultraviolet light. Surprisingly, the radical species obtained has a very long lifetime, and the absorption intensities hardly decayed at all for a long time. Table 1 shows the relationship between the absorption intensities and the time used in carrying out the measurements.

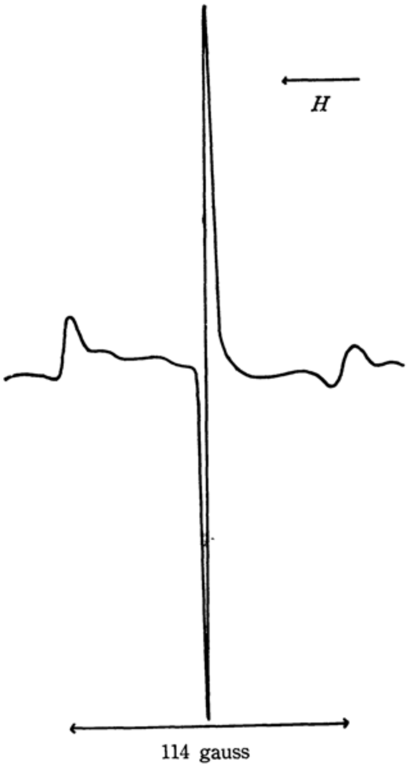

Fig. 1. ESR spectrum of aqueous monosulfide solution UV irradiated.
$(Na_2S)=0.75\times10^{-2}$ M
Irrad.: for 1/2 hr
Measurement: 15 min after

Table 1. Decay of ESR absorption intensities of aqueous monosulfide solution irradiated

$(S^{2-})_0=1.5\times10^{-2}$ M t sec	 Intensity (arbit. unit)	$(S^{2-})_0=7.5\times10^{-2}$ M t sec	 Intensity (arbit. unit)
360	195	1440	133
660	193	2340	128
1080	186		

As Fig. 1 shows, a very strong and narrow singlet, with a maximum slope width of 3.1 gauss, and a weak and marble doublet, with a coupling constant of 114 gauss, were observed. The g-value of the central narrow absorption was 2.002±0.001, while that of the doublet was 2.001±0.001. Because of the composition of the sample solution, these spectra must be dependent upon the sulfide. Furthermore, from the g-value and so forth, the central singlet is certainly the sulfide ion radical, $S\cdot^-$.

Gardner and Fraenkel have presented a one-line ESR spectrum of molten sulfur, the g-value whereof is 2.024.[5] Similarly, sulfur dissolved in oleum also gives a one-line ESR spectrum,[6] the g-value of which is 2.026±0.03; the maximum slope width of the singlet is 4 gauss. In both cases, the singlets observed have been assigned to the sulfur-free radical. Clearly the singlet observed in our experiments can be separated from the spectra of the free radicals of sulfur or polysulfur.

Recently, Milićević and Eigenmann have reported evidence[7] for the thionite radical, $SO_2\cdot^-$, obtained by means of the ESR technique. The ESR spectrum observed by them was also a narrow singlet, with a g-value of 2.0054±0.0004, in an aqueous alkaline solution of sodium dithionite. Their results approach ours for the irradiated aqueous monosulfide solution.

On the other hand, it has been found that the species which gives the doublet is different from that which gives the central singlet. When the micro power from klystron is made larger, though the central singlet was easily saturated, the doublet lines were saturated only with difficulty. Furthermore, when the lines were irradiated with an electron beam instead of an ultraviolet light, considerable changes occurred in the amplitude of the singlet line relative to the doublet lines, as is shown

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5) D. M. Gardner and G. K. Fraenkel, *J. Am. Chem. Soc.*, **78**, 3279 (1956).

6) D. M. Gardner and G. K. Fraenkel, *ibid.*, **78**, 6411 (1956).

7) B. Milićević and G. Eigenmann, *Helv. Chim. Acta*, **46**, 192 (1963).

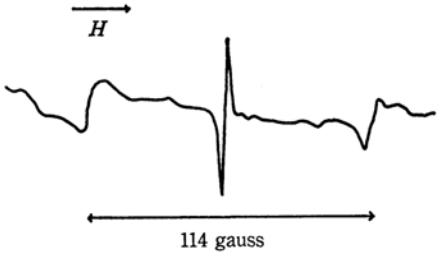

Fig. 2. ESR spectrum of aqueous monosulfide solution electron irradiated.
$(Na_2S)=0.725$ M
Dose: 2×10^7 rad

in Fig. 2. At this time a remarkable anisotropy was also observed on the doublet lines. It may be reasonable to consider that the radical produced was adsorbed on the surface of the quartz cell. However, both the signals, the singlet and doublet, were always observed together under the different conditions, and no changes in the width, the coupling constant, or the *g*-values occurred.

Semenov has presented evidence[8] that crystal hydrogen sulfide gives ESR spectra consisting of a singlet due to the sulfur-free radical and a doublet due to the hydrosulfide free radical, upon radiation-irradiation, and that the *g*-value and the coupling constant of the doublet are 2.00 and 28 gauss respectively. In our experiments, the sulfide ion radical may be produced as the following processes have previously suggested[1,2]:

$$(S^{2-}H_2O) \xrightarrow{h\nu} S\cdot^- + H\cdot + OH^- \qquad (1)$$

$$H\cdot + H\cdot \rightarrow H_2 \qquad (2)$$

$$S\cdot^- + S\cdot^- \rightarrow (S\text{-}S)^{2-} \qquad (3)$$

$$S^{2-} + H_2O \rightleftharpoons SH^- + OH^- \qquad (4)$$

$$H\cdot + SH^- \rightarrow S\cdot^- + H_2,\ \mathit{etc.} \qquad (5)$$

The qualitative generation of hydrogen gas was observed in practice, but the hydrogen atom was not observed by the ESR technique. No other radical, such as the hydroxyl radical, was observed in the present experiment. Therefore, assuming that the doublet may be dependent upon the interaction of the sulfide ion radical with the counter ion, the ESR spectra of the aqueous potassium sulfide and the aqueous ammonium sulfide solutions were determined by the same method used for the aqueous sodium monosulfide. However, no changes at all in the ESR spectra with the counter ion occurred in this experiment either. From these results, it may be reasonable to assume in our experiments that the doublet lines appear as a result of a certain split of the sulfide ion radical as a result of interaction with the hydrosulfide or the hydroxide in the aqueous solution:

$$S\cdot^- \cdots\cdots OH^- \quad \text{or} \quad S\cdot^- \cdots\cdots SH^-$$

Correlation between the Radical Concentration and the Initial Concentration of Aqueous Monosulfide. In order to examine the correlation between the absorption intensities of the singlet and the initial concentration of the aqueous monosulfide, aqueous monosulfide solutions of different concentrations, within 1.5×10^{-4} M and 0.75 M, were irradiated with ultraviolet light for 30 min; the ESR measurements were then immediately carried out. However, no comparable changes with the initial concentration of the aqueous monosulfide solutions occurred, within the range of experimental error, in the relative intensity of the singlet.

ESR Spectra of Aqueous Polysulfide Solutions. In earlier papers we have found that an aqueous solution of disulfide fades even in the dark, as well as in the absence of any other oxidizing agents, and have assumed that a slight homolytic fission of disulfide may occur in an aqueous solution.[1,2] In the present paper, the aqueous disulfide not irradiated was examine by ESR spectroscopy. Surprisingly, the aqueous disulfide itself, which had been allowed to stand in the dark under a nitrogen atmosphere for a month after having been prepared, give ESR spectra which were identical with that of the aqueous monosulfide irradiated. Upon irradiation with an UV light on the aqueous disulfide solution, of course, the absorption intensities of the signals increased. From these results, it seems most reasonable to conclude that the sulfide ion radical apparently exists in the aqueous disulfide solution not irradiated also and that there exists a small but obvious reversibility between the disulfide and the sulfide ion radical upon the homolytic fission of the S–S bond:

$$(S\text{-}S)^{2-} \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} S\cdot^- + S\cdot^- \qquad (6)$$

Moreover, we have found that the aqueous trisulfide and tetrasulfide solution not irradiated give ESR spectra. These spectra were also identical with that of the aqueous monosulfide irradiated. Interestingly, the absorption intensity of the singlet observed in the trisulfide was approximately equal to that to the tetrasulfide; moreover, the intensities also approached that observed in the irradiated monosulfide, which was expected to be in a stationary state, as Table 2 shows.

We have previously reported evidence[4] that the polarographic oxidation potentials of the aqueous sulfides shift to the cathod side with an increase in the sulfur contents in sodium sulfides, $x=$ 1—4 in Na_2S_x, and that interdependently their absorption waves also increase in wave hight. Considering these previous facts, coupled with the present results of the ESR spectroscopy, one may

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[8] N. N. Semenov, "XVIIIth International Congress of Pure and Applied Chemistry, Special Lectures," Butterworths, London (1962), p. 353.

TABLE 2. ESR SPECTRA OF AQUEOUS POLYSULFIDE SOLUTIONS

Sulfide	Concn. M	Absorption intensity (Arbitrary unit)
S_3^{2-}	0.831	126[a]
S_4^{2-}	0.831	130[a]
S^{2-}	0.750	126[b]

a) A sample allowed to stand for 45 days after preparing.

b) A sample allowed to stand for 60 min after irradiation.

assume that the polysulfides are reversibly disproportionate in their aqueous solutions, as in Eq. (7):

$$2S_x^{2-} \rightleftharpoons S_2^{2-} + S_{x-2}^{2-} \qquad (7)$$

In polarography, of course, the anodic oxidation potentials would be observed as the average of Eq. (7).[4] On the other hand, as is clear from the correlation between Eqs. (6) and (7), the ESR signal would be observed as the sulfide ion radical even in an aqueous polysulfide solution. However, it would be very difficult to clarify the behavior of the polysulfides in aqueous solutions on the basis of our present results only.

ESR Spectra of Reaction Products of Sodium *m*-Nitrobenzene Sulfonate with Aqueous Monosulfide. Kolker and Waters have shown, by ESR spectroscopy,[9] that a radical-anion of nitrobenzene and a thionite radical can be easily formed in the aqueous alkaline dithionite reduction of nitrobenzene. We have also previously reported evidence that disulfide formation occurs prior to the amine formation in the aqueous monosulfide reduction of sodium *m*-nitrobenzene sulfonate, and have assumed that radical reaction is involved in this reaction.[1,2] The ESR technique was also used in order to confirm this previously-proposed problem.

When the initial concentration of the nitro compound was rather low in this reaction, the singlet of the above-mentioned sulfide ion radical was clearly observed and the presence of the radical species was confirmed (Fig. 3-a). Furthermore, when the initial concentration of the nitro compound was increased, the radical-anion of the nitro compound was evidently detected in the sample allowed to stand for 3·½ hours after the reaction had begun (Fig. 3-b). This radical-anion observed was also very stable, much like the sulfide ion radical previously described. As is shown in Fig. 3-b, the ESR spectra of this radical-anion of *m*-nitrobenzene sulfonate comprise a widely-separated nitrogen triplet, which is further split into a quartet and a doublet by ring protons.

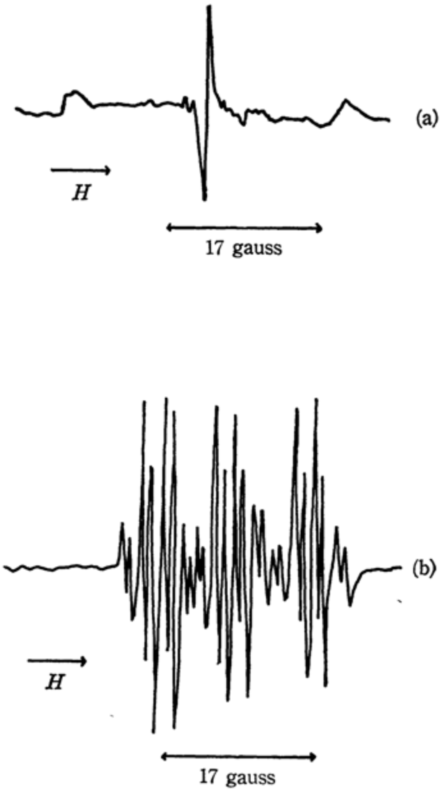

Fig. 3. ESR spectra of reaction products of sodium *m*-nitrobenzene sulfonate with aqueous monosulfide solution.

(a) $(Ar\text{-}NO_2)=0.91\times10^{-3}$ M $(Na_2S)=0.66\times10^{-1}$ M)
A sample allowed to stand for 1·⅔ hr after beginning the reaction.

(b) $(Ar\text{-}NO_2)=0.46\times10^{-1}$ M $(Na_2S)=0.66\times10^{-1}$ M
A sample allowed to stand for 3·½ hr after beginning the reaction.

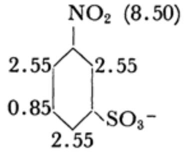

Fig. 4. Coupling constants of ring protons, in our experiments.

The coupling constants observed are given in Fig. 4. Although the ESR spectra of the radical-anion of *m*-nitrobenzene sulfonate itself have never yet been presented by any other investigators, those of analogous compounds, such as *m*-dinitrobenzene, have been observed by alkali-metal reduction[10] or by polarographic reduction.[11] These

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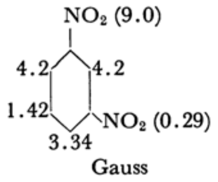
9) P. L. Kolker and W. A. Waters, *Proc. Chem. Soc.*, **1963**, 55.

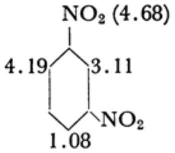
10) R. L. Ward, *J. Am. Chem. Soc.*, **83**, 1296 (1963).

11) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).



(a)

By alkali-metal reduction[10]

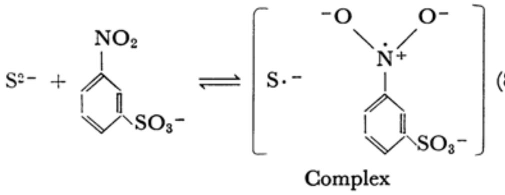


(b)

By polarographic reduction[11]

Fig. 5. Coupling constants of ring protons, in the literature.

results are given in Fig. 5. As is clear from Fig. 5, the coupling constants of the ortho- and the para-positions to the nitro group were different from each other. In our results, however, the ortho- and para-ring proton coupling constants were equivalent, unlike those expected from the electronic characters of the nitro and the sulfonate groups. In our earlier investigation dealing with the kinetics of the disulfide formation in the above reaction,[2] we have suggested that there exists the following equilibrium:



(8)

$$\text{Complex} \rightleftharpoons \text{S}\cdot^- + (\text{Ar-}\dot{\text{N}}\text{O}_2)^- \qquad (9)$$

If the ESR spectrum of the radical-anion of *m*-nitrobenzene sulfonate is due to the 1-electron reduction complex, as in Eq. (8), the coupling constants of the ortho- and para-ring proton may be affected by some interaction of the sulfide ion radical with the nitro compound, and, of course, this radical species may have a long lifetime, similar to the sulfide ion radical.

Furthermore, when *m*-nitrobenzene sulfonate (0.46×10^{-1} M) was reduced by an aqueous monosulfide solution (0.68×10^{-1} M), the ESR signal corresponding to the radical anion of the nitroso compound has also been observed, as is shown in Fig. 6. In this case, the center of the spectrum has superimposed on it a single line, which we have described as due to the sulfide ion radical derived from the monosulfide. When *m*-*m*'-azoxy- or *m*-*m*'-azobenzene disulfonate was reduced by the method used for the corresponding nitro or nitroso compound, however, only the signal of the sulfide ion radical was observed; none of the other signals to be expected from the azoxy or azo compound were observed at all. From these results, it is clear in any case that the radical reactions are involved in the alkaline sulfide reduction of aromatic nitro compounds or their reduction intermediates.

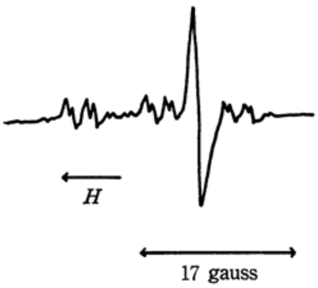


Fig. 6. ESR spectrum of reaction product of sodium *m*-nitrosobenzene sulfonate with aqueous monosulfide solution.
$(\text{Ar–NO})=0.46\times10^{-1}$ M; $(\text{Na}_2\text{S})=0.68\times10^{-1}$ M
A sample allowed to stand for 6·½ hr after mixing of reactants.

Conclusion

In order to confirm our previous assumption that the radical reaction may be involved in the alkaline sulfide reduction of aromatic nitro compounds or their reduction intermediates, we used ESR techniques. In both solutions, an irradiated aqueous monosulfide solution and an aqueous polysulfide solution not irradiated, the ESR spectra were obviously observed. The radicals detected, one of which was identical with the sulfide ion radical derived from the monosulfide, had very long lifetimes. On the other hand, also in the aqueous monosulfide reduction of sodium *m*-nitrobenzene sulfonate or its reduction intermediates, such as the corresponding nitroso, azoxy, or azo compound, the ESR signal of the sulfide ion radical was always observed. From the results obtained in the present investigation, the presence of radical reactions in the alkaline sulfide reduction of aromatic nitro compounds or their reduction intermediates, which was hitherto only assumed, has been practically confirmed.

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