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The Alkaline Sulfide Reduction of Aromatic Nitro Compounds. XI. The Autocatalytic Reaction of the Monosulfide to the Disulfide in Aqueous Solution[*1]

Shizunobu HASHIMOTO, Junzo SUNAMOTO[*2] and Katsuhiko SATO

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

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The autocatalytic reactions of the aqueous monosulfide to the aqueous disulfide by an ultraviolet light, oxygen, and sodium *m*-nitrobenzene sulfonate have been investigated. The rate of the disulfide formation by the photo-oxidation of the aqueous monosulfide was given by the following equation: $d(S_2{}^{2-})/dt=k_0(S^{2-})^2/(S^{2-})_0{}^2$. Also in the reaction of aromatic nitro compound and aqueous monosulfide, the disulfide formation was observed prior to the amine formation. On the basis of the results obtained, the mechanisms of the alkaline sulfide reduction of aromatic nitro compounds have been discussed.

Sodium dithionite also is generally used as an usual reducing agent for the aromatic nitro compounds to the corresponding amines, as well as sodium sulfides. Recently, it has been presented that a radical reaction, which is dependent upon the homolytic fission of the weak S–S bond of dithionite, is involved in an alkaline dithionite reduction of aromatic nitro[1)] or azo compound.[2)] On the other hand, it has been also confirmed that sodium dithionite produces a thionite radical, $SO_2\cdot^-$, in a solid state[3)] or in an aqueous alkaline solution.[4)]

In an earlier paper dealing with the kinetics of the alkaline sulfide reduction of sodium *m*-nitrobenzene sulfonate,[5)] we have found that there is an induction period in the initial stage of this reaction and the radical autoxidation of the monosulfide to the disulfide is involved in this induction-period intervals. Furthermore, we have discussed about the correlation between the monosulfide and the disulfide reduction of aromatic nitro compounds and the pH dependence of the reactions.[6)]

In the present paper, we have investigated the autocatalytic reaction of the aqueous monosulfide solution with an ultraviolet light irradiation or other oxidizing agents on the view point of the reaction kinetics.

Experimental

Materials. All the reagents used in the present investigation were prepared and purified by the methods used in the preceding experiments.[5,6)]

Polarography. The polarographies of the alkaline sulfides were measured by the method in the previous report.[7)]

Spectrophotometry. A Shimadzu Bausch & Lomb Spectronic 20 or a Shimadzu Beckmann-type Model DU spectrophotometer was used for the measurements of the absorption spectra of the aqueous monosulfide and disulfide, and for those of the oxidation rates of the monosulfide to the disulfide.

Titration. The changes of the total sulfides and free alkali were followed as follows during the course of the reaction. A sample withdrawn from the reaction flask was placed in an Erlenmeyer flask with the excess of N/10 iodine and N/10 hydrochloric acid. After standing for about 30 min in the dark, it was backtitrated by N/10 sodium thiosulfate with starch, and thereafter it was further titrated by N/10 sodium hydroxide with methyl orange. The blanktest of course was undertaken for all the samples. Thereby, the total sulfides and the free alkali were calculated by Eqs. (1) and (2), respectively:

$$\text{The total sulfides}=\frac{1/2(a-b)}{c\times 10}\text{mol}/l \qquad (1)$$

where *a* is m*l* of the N/10 aqueous iodine solution added, *b* is m*l* of the titer of the N/10 aqueous sodium thiosulfate solution, and *c* is m*l* of the sample solution;

$$\text{The free alkali}=\frac{d-A}{10\times c}\text{mol}/l \qquad (2)$$

where *d* is m*l* of the titer of the N/10 aqueous sodium

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

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

2) C. R. Wasmuth, R. L. Donnel, C. E. Harding and G. E. Shankle, *J. Soc., Dyers & Colorists*, **81**, 404 (1965).

3) W. G. Hodgson, A. Neaves and C. A. Parker, *Nature*, **178**, 489 (1956).

4) B. Milicevic and G. Eigenmann, *Helv. Chim. Acta*, **46**, 192 (1963).

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

6) S. Hashimoto and J. Sunamoto, *ibid.*, **39**, 1207 (1966).

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

hydroxide solution and *A* is m*l* of the titer of *d* at the blanktest.

Reaction Procedures. A Taika Kagaku Photochemical Reaction Apparatus HLV-A was used for all the reactions. An appropriate amount of an aqueous sodium mono- or disulfide solution was placed in a reaction flask immersed in a thermostat regulated. It was deaerated and flushed by nitrogen at the given temperature and the reaction was commenced by the irradiation with an ultraviolet light. At appropriate time intervals aliquots were pressed out by nitrogen and subjected to analyses.

Results and Discussion

Absorption Spectra of Aqueous Monosulfide and Disulfide Solutions. Table 1 shows the absorption bands of the aqueous sodium monosulfide and disulfide solution. The both sulfides have strong absorption at 230 mμ, and only the aqueous disulfide has, in addition, an absorption at 360 mμ. Evidently the yellow of the aqueous disulfide is due to the absorption in a visible region. In either cases, the relation between the absorption intensities and the concentrations was good accordance with the Lambert-Beer's law in rather wide range of the concentrations ($\sim 6\times 10^{-3}$ M). The measurements of the reaction rates were, therefore, followed the changes of these absorption intensities by photometry.

TABLE 1. ABSORPTION BANDS OF AQUEOUS MONOSULFIDE AND DISULFIDE

Sulfide	λ_1(mμ), ε_1	λ_2(mμ), ε_2
Aqueous monosulfide	230 (4000)	—
Aqueous disulfide	230 (5600)	360 (223)

Conversion of Aqueous Monosulfide with L-V Lamp[*3] Irradiation. As is shown in Fig. 1, the aqueous monosulfide solution, which was first colorless, gradually turned yellow upon the irradiation with the L-V lamp under nitrogen atmosphere. The absorption, thereby, appeared at 360 mμ and it increased in the intensity with proceeding of the reaction. It shows evidently the formation of disulfide during the course of the reaction. As previously assumed,[5] the radical oxidation of the monosulfide to the disulfide may occur as follows:

$$(S^{2-}\cdot H_2O) \xrightarrow{h\nu} (S^{2-}\cdot H_2O)^* \longrightarrow S\cdot^- + H\cdot + OH^- \quad (3)$$

At this time, the generation of hydrogen gas was of course observed. No changes of the aqueous monosulfide solution occurred at all in the dark. When the initial concentration of the aqueous monosulfide was rather lower, the disulfide once produced apparently decreased.

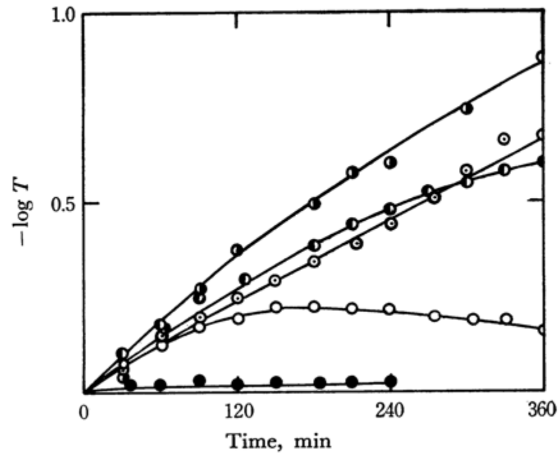

Fig. 1. L-V lamp irradiation on aqueous monosulfide solution at 35.0°C under nitrogen atmosphere.
Initial concn. of aqueous monosulfide;
○: 1.53×10^{-3} M, ◐: 3.93×10^{-3} M
◑: 7.35×10^{-3} M, ⊙: 16.3×10^{-3} M
●: 16.3×10^{-3} M, irradiated with the H-V lamp

When compared with under the same condition, the oxidation of the monosulfide to the disulfide with the H-V lamp[*4] irradiation was much slower than that with the L-V lamp irradiation (Fig. 1, curves No. 4 and 5). Seemingly the differences by the light source may be due to the absorption wavelength of the aqueous monosulfide.

On the other hand, the results followed the changes of the total sulfides and the free alkali are listed in Table 2. The total sulfides obviously decreased, though the decrease was less than that expected the monosulfide completely to change into the disulfide, while no comparable changes of the free alkali were observed.

Conversion of Aqueous Monosulfide or Disulfide Solution with H-V Lamp Irradiation. In order to examine the further photodecomposition of the disulfide produced from the monosulfide, the H-V lamp was irradiated on an aqueous disulfide solution. Clearly from Fig. 2, the absorption of the disulfide at 360 mμ rapidly decreased in its intensity. Under the condition as is shown in Fig. 2, the aqueous monosulfide solution irradiated also showed the absorption at 360 mμ and it gradually increased in the intensity. The absorptions of the aqueous monosulfide and disulfide at 230 mμ decreased together upon irradiation.

On the other hand, also from the changes of the total sulfides and the free alkali shown in Table

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[*3] L-V lamp stands for the low-pressure mercury vapor lamp (2537 Å, 15 W).

[*4] H-V lamp stands for the high-pressure mercury vapor lamp (3500—4000 Å, 100W).

TABLE 2. CHANGES OF TOTAL SULFIDES AND FREE ALKALI
Irrad.: 2537 Å, 15 W, in N_2, at 35.0°C

	$(S^{2-})_0=1.53\times10^{-3}$ M			$(S^{2-})_0=3.93\times10^{-3}$ M	
t min	Total sulfides 10^3 M	Free alkali 10^2 M	t min	Total sulfides 10^3 M	Free alkali 10^2 M
0	1.53	1.40	0	3.93	1.24
120	1.18	1.35	125	3.18	1.15
240	1.05	1.36	300	2.55	1.03
360	1.03	1.40			

	$(S^{2-})_0=7.35\times10^{-3}$ M			$(S^{2-})_0=16.3\times10^{-2}$ M	
t min	Total sulfides 10^3 M	Free alkali 10^2 M	t min	Total sulfides 10^3 M	Free alkali 10^2 M
0	7.35	2.72	0	16.3	3.23
180	7.25	2.70	120	15.4	3.58
360	6.16	2.59	240	14.8	3.58
			360	14.3	3.20

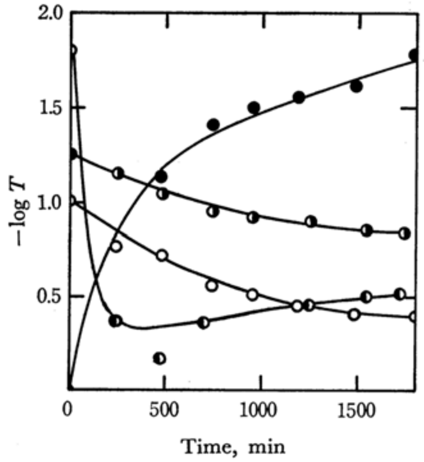

Fig. 2. H-V lamp irradiation on aqueous monosulfide and disulfide solution at 37.5°C, under nitrogen atmosphere.
$(S^{2-})_0=1.33\times10^{-2}$ M, $(S_2{}^{2-})_0=1.13\times10^{-2}$ M
○: absorption intensity at 230 mμ of aqueous monosulfide
◑: absorption intensity at 230 mμ of aqueous disulfide
●: absorption intensity at 360 mμ of aqueous monosulfide
◐: absorption intensity at 360 mμ of aqueous disulfide

3, it is clear that the disulfide itself is further photochemically reacts. Though the reason is still not clear, at the same time, about ten per cent of the free alkali decreased in the amounts during the course of the oxidation of the monosulfide with the H-V lamp irradiation. Furthermore, the following of the reaction by polarography confirmed the formation of the disulfide in the monosulfide reaction, as well as the decrease of that in the disulfide reaction itself.

We have previously found[5] that the addition of a trace of the disulfide makes the induction period disappear in the aqueous monosulfide reduction of sodium *m*-nitrobenzene sulfonate, and assumed that it may be dependent upon the chain reaction with the sulfide ion radical produced by the homolytic fission of the disulfide as follows:

$$(S\text{–}S)^{2-} \underset{k}{\overset{k'}{\rightleftarrows}} S^{-}\cdot + S^{-}\cdot \tag{4}$$

Therefore, the reaction of Eq. (4) may be a little reversible, though k is of course much larger than k'. Further studies are in progress on this point by the ESR spectroscopy of an aqueous disulfide solution and will be reported on the following paper.

Seemingly the almost of disulfide will react with water to give an oxide of sulfide. When the H-V lamp was used to the aqueous disulfide solution, in fact, the anodic mercury oxidation wave of the polarography owing to the formation of the thiosulfate, which was not observed before irradiation, was observed on a polarogram and gradually increased in the wave-height with the proceeding of the reaction.

Rate of Photo-oxidation of Monosulfide to Disulfide. Assuming that the formation of the sulfide ion radical by Eq. (3) is much rapid and that the other deactivations besides the dimerization of the sulfide ion radicals could be neglected, the formation rate of the disulfide can be given most simply by Eq. (5):

$$\frac{d(S_2{}^{2-})}{dt} = k(S\cdot^{-})^2 \risingdotseq k(S^{2-})^2 \tag{5}$$

Because, if the reaction of Eq. (3) is very much fast, (S^{2-}) will be almost equal to the concentration of the sulfide ion radical, $(S\cdot^{-})$, represented by Eq. (6):

TABLE 3. CHANGES OF TOTAL SULFIDES AND FREE ALKALI
Irrad.: 3500—4000 Å, 100W, in N_2, at 37.5°C

	$(S^{2-})_0=1.33\times10^{-2}$ M			$(S^{2-})_0=1.13\times10^{-2}$ M	
t min	Total sulfides 10^2 M	Free alkali 10 M	t min	Total sulfides 10^2 M	Free alkali 10 M
0	1.33	2.29	0	1.13	2.38
480	1.08	2.14	480	0.96	2.35
960	0.96	2.11	960	0.86	2.35
1200	0.95	2.09	1260	0.84	2.35
1800	0.84	2.06	1740	0.79	2.32

$$(S\cdot^-) = (S^{2-})_0 - 2(S_2{}^{2-}) \tag{6}$$

where $(S^{2-})_0$ is the initial concentration of the aqueous monosulfide. Upon integration of Eq. (5) substituted by Eq. (6), the result is

$$kt = \frac{(S_2{}^{2-})}{(S^{2-})_0\{(S^{2-})_0 - 2(S_2{}^{2-})\}} \tag{7}$$

Rearrangement of Eq. (7) yields Eq. (8):

$$-\frac{1}{\log T} = \frac{1}{k\cdot\varepsilon_{360}\cdot d\cdot(S^{2-})_0{}^2}\cdot\frac{1}{t} + \frac{2}{\varepsilon_{360}\cdot d\cdot(S^{2-})_0{}^2} \tag{8}$$

where ε_{360} is the absorption coefficient of the aqueous disulfide solution at 360 m, ($\varepsilon_{360}=223$), d is the cell length ($d=1$ cm), and T is the transmittance at 360 mμ, respectively. Upon plotting $-1/\log T$ against $1/t$ on the basis of the experimental results obtained, a good linear relationships were obtained as are shown in Fig. 3. Clearly from Fig. 3, in addition, the tangents of the straight lines obtained, α, were almost constant independent upon the initial concentration of the aqueous monosulfide:

$$\alpha = \frac{1}{k\cdot\varepsilon_{360}\cdot d\cdot(S^{2-})_0{}^2} = \text{const.} \tag{9}$$

Thus Eq. (10) can be given:

$$\frac{d(S_2{}^{2-})}{dt} = k_0\frac{(S^{2-})^2}{(S^{2-})_0{}^2} \tag{10}$$

where

$$k_0 = \frac{1}{\alpha\cdot\varepsilon_{360}\cdot d} \tag{11}$$

In the photo-oxidation of the monosulfide with the UV irradiation, thus, the initial formation rate of the disulfide can be given by the zeroth-order equation with respect to the concentration of the aqueous monosulfide and it is in proportion to only the light absorbed. The zeroth-order rate constants estimated graphically and the initial concentrations of the aqueous monosulfide are shown in Table 4.

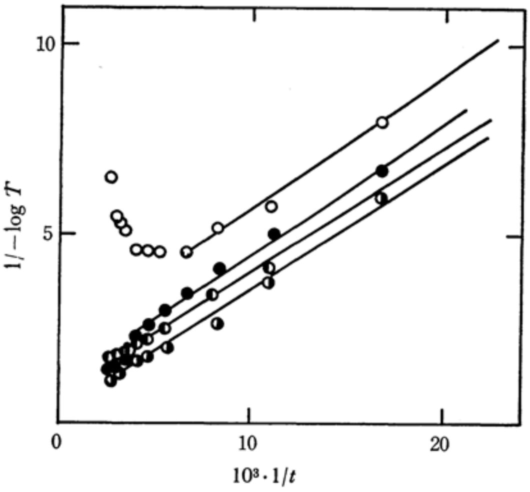

Fig. 3. $1/t$ *vs.* $1/-\log T$.
Irrad.: 2537Å, 15W, at 35.0°C, under nitrogen atmosphere
Initial concn. of aqueous monosulfide;
○: 1.53×10^{-3} M, ◐: 3.93×10^{-3} M
◑; 7.35×10^{-3} M, ●: 16.30×10^{-3} M

TABLE 4. ZEROTH-ORDER RATE CONSTANTS OF PHOTOOXIDATION OF AQUEOUS MONOSULFIDE SOLUTION AT 35.0°C

Initial concn. of aq. monosulfide soln., 10^3 M	Additives M	k_0 10^5 mol l^{-1} min^{-1}
1.46	None	1.16
3.67	None	1.21
7.33	None	1.11
14.66	None	1.13
7.33	(NaOH)$=1.04\times10^{-1}$	0.85
7.33	(NaOH)$=2.60\times10^{-1}$	0.75
14.66[a]	None	very small

a) A sample irradiated with the H-V lamp; others were irradiated with the L-V lamp.

Effect of Hydroxide Ion Concentration. The monosulfide is almost completely hydrolyzed into the hydrosulfide and the hydroxide in an aqueous solution:

$$S^{2-} + H_2O \rightleftharpoons SH^- + OH^- \tag{12}$$

Therefore, the hydroxide concentration in the

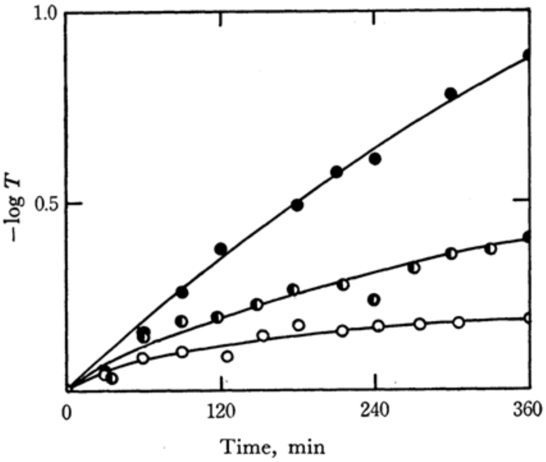

Fig. 4. Effect of sodium hydroxide at 35.0°C, upon irradiation, under nitrogen atmosphere.
●: $(\mathrm{S^{2-}})_0=7.33\times10^{-3}$ M
◐: ●+$(\mathrm{NaOH})=1.04\times10^{-1}$ M
○: ●+$(\mathrm{NaOH})=2.60\times10^{-1}$ M

medium have large effects on the autoxidation rates of the aqueous monosulfide upon irradiation. As are shown in Fig. 4 and Table 4, in fact, the autoxidation rates of the aqueous monosulfide became lower with increasing of the hydroxide concentrations.

The species to give the sulfide ion radical should be expected to either a certain complex between the monosulfide and water or a hydrosulfide itself produced by the hydrolysis of the monosulfide as Eq. (12). But, from the view point of the pH dependence of the reaction rates, the sulfide ion radical may be rather expected to be formed from the hydrosulfide than from the complexes.

$$\begin{array}{l}
[(\mathrm{S}\cdot^{-}\mathrm{H_2O^{-}}) \rightleftharpoons (\mathrm{S^{2-}}\cdot\mathrm{H_2O})] \xrightarrow{h\nu} \\
\qquad\qquad\qquad\qquad \upharpoonleft\!\downharpoonright \\
\qquad\qquad\qquad\qquad \mathrm{SH^{-}} + \mathrm{OH^{-}} \\
\rightarrow [(\mathrm{S^{2-}}\cdot\mathrm{H_2O}) \rightleftharpoons (\mathrm{S}\cdot^{-}\mathrm{H_2O^{-}})]^{*} \qquad\qquad (13) \\
\qquad \upharpoonleft\!\downharpoonright \qquad\qquad\qquad\quad \downarrow \\
\quad (\mathrm{SH^{-}} + \mathrm{OH^{-}})^{*} \rightarrow \mathrm{S}\cdot^{-} + \mathrm{H}\cdot + \mathrm{OH^{-}}
\end{array}$$

If so, the correlation between the monosulfide and the hydrosulfide in the alkaline sulfide reductions of aromatic nitro compounds⁶⁾ can be smoothly explained.

Oxidation with Potassium Persulfate. In the aqueous monosulfide reduction of sodium *m*-nitrobenzene sulfonate, the addition of potassium persulfate made the induction-period intervals shorter,⁵⁾ and it has been assumed that the formation of the sulfide ion radical from the monosulfide was induced by the persulfate. In this paper, we have examined whether the oxidation of the monosulfide to the disulfide occurs by the addition of the persulfate into the aqueous monosulfide solution not containing aromatic nitro compound, even in the dark. Figure 5 shows that the oxidation of the monosulfide can proceed, even in the dark, with the addition of the persulfate and that the reaction rate increases with the increment of the additive. Also, after a reaction of a long duration, the disulfide produced faded and its fading rate were almost constant independent upon the initial concentration of the persulfate added. The disulfide produced might further react to give an oxide of sulfide as in the previous cases above mentioned, in which the H-V lamp was irradiated on the aqueous disulfide solution. Seemingly the persulfate added will oxidize the monosulfide as in Eqs. (14) and (15):⁵⁾

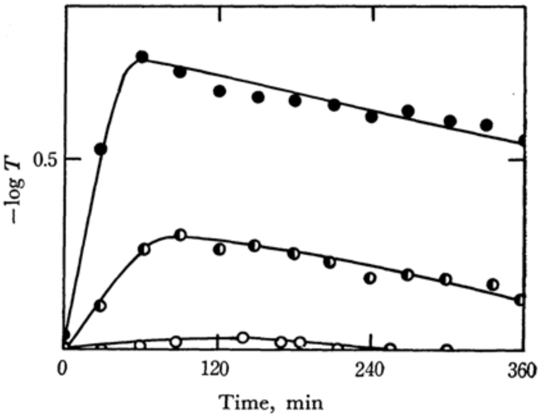

Fig. 5. Effect of potassium persulfate at 35.0°C, in the dark, under nitrogen atmosphere.
$(\mathrm{S^{2-}})_0=7.33\times10^{-3}$ M
○: $(\mathrm{K_2S_2O_8})=2.36\times10^{-4}$ M
◐: $(\mathrm{K_2S_2O_8})=1.18\times10^{-3}$ M
●: $(\mathrm{K_2S_2O_8})=2.36\times10^{-3}$ M

$$\mathrm{S^{2-}} + \mathrm{S_2O_8{}^{2-}} \rightarrow \mathrm{SO_4{}^{2-}} + \mathrm{SO_4}\cdot^{-} + \mathrm{S}\cdot^{-} \qquad (14)$$

$$\mathrm{SO_4}\cdot^{-} + \mathrm{S^{2-}} \rightarrow \mathrm{SO_4{}^{2-}} + \mathrm{S}\cdot^{-} \qquad (15)$$

Oxidation with Air. In the comparison between the air oxidation and the photo-oxidation of the aqueous monosulfide under the same condition, the apparent oxidation rate of the photo-oxidation was faster than that of the air oxidation and the disulfide formation was hardly observed through the reaction. However, the rate of the decrease of the total sulfides in the air oxidation was slightly higher than that in the other. It may be reasonable to assume that the disulfide might be oxidized to give an oxide of sulfide as soon as produced and no disulfide formation might be apparently observed. In fact, as are shown in Table 5, when the aqueous disulfide was air-oxidized, the fading of the disulfide and the decrease of the polarographic oxidation-wave owing to the disulfide in the wave-height, together with the shift of its peak potential to anode side, were obviously observed. After the reaction, in addition, a new anodic oxidation wave due to the thiosulfate appeared at −0.17 V *vs.* SCE. On the

TABLE 5. AIR OXIDATION OF AQUEOUS DISULFIDE SOLUTION
$(S_2^{2-})_0 = 1.5$ M, Flow speed of air: 60 m*l*/min, at bp, for 20 hr
Condition of ac polarography: $(S_2^{2-}) = 1.5 \times 10^{-3}$ M, at 28.0°C, V *vs.* SCE

Sample	E_1 V	h_1 $\mu\mho$	E_2 V	h_2 $\mu\mho$	E_3 V	h_3 $\mu\mho$	E_4 V	h_4 μ—
Before oxidation	—	—	—	—	−0.65,	95	−0.91,	662
After oxidation	−0.17,	450	−0.44,	45	−0.69,	95	−0.86,	380

TABLE 6. AIR OXIDATION OF AQUEOUS MONOSULFIDE SOLUTION
$(S^{2-})_0 = 5.0$ M, Flow speed of air: 80 m*l*/min, at bp, for 15 hr
Condition of ac polarography: $(S^{2-})_0 = 5.0 \times 10^{-3}$ M, at 28.0°C, V *vs.* SCE

Sample	E_1 V	h_1 $\mu\mho$	E_2 V	h_2 $\mu\mho$	E_3 V	h_3 $\mu\mho$	E_4 V	h_4 $\mu\mho$
Before oxidation	—	—	—	—	−0.65,	110	−0.84,	605
After oxidation	—	—	—	—	−0.65,	120	−0.84,	645
*	−0.14,	430	−0.44,	—	−0.70,	100	−0.83,	240

* A sample which was allowed to stand for 5 days in the laboratory after the primary determination of ac polarography.

other hand, in the air oxidation of the aqueous monosulfide, the reaction solution which was colorless before oxidation gradually turned yellow and as is shown in Table 6 the increase of the wave-heights of the third and the fourth wave confirmed the formation of the polysulfide.[7] Also, when a dilute aqueous monosulfide solution was allowed to stand for a long time under atmospheric condition, the appearance of an anodic oxidation wave owing to the thiosulfate and the decrease of the third and the fourth wave in their heights were observed.

On the basis of these results obtained, it may be reasonable to assume that, when the aqueous monosulfide solution was air-oxidized, the disulfide produced was immediately further oxidized to give an oxide, such as the thiosulfate, as follows:[5]

$$2S^{2-} + 3O \rightarrow SO_3\cdot^- + S\cdot^- \tag{16}$$

$$SO_3\cdot^- + 2S^{2-} \rightarrow S_2O_3^{2-} + S\cdot^- \tag{17}$$

$$2S\cdot^- \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} (S\text{-}S)^{2-} \tag{18}$$

$$(S\text{-}S)^{2-} + 3O \xrightarrow[\text{very fast}]{} S_2O_3^{2-} \tag{19}$$

Conversion of Aqueous Disulfide Solution in the Dark. In order to examine the behavior of the disulfide itself, when being absent from light, oxygen, or any other oxidizing agents, the aqueous disulfide solution was allowed to stand in the dark. Figure 6 shows that the disulfide apparently fades in the dark, even in the absence of any oxidizing agents, and that the fading rate approaches to those of the disulfide produced in the persulfate-oxidation or the air oxidation: the rates were approximately given by the zeroth-order reaction.

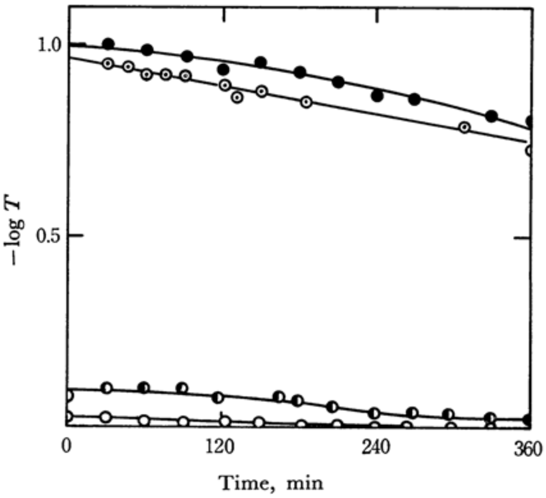

Fig. 6. Conversion of aqueous disulfide at 35.0°C, in the dark under nitrogen atmosphere.
○: $(S^{2-})_0 = 7.33 \times 10^{-5}$ M + $(S_2^{2-})_0 = 3.67 \times 10^{-5}$ M
◐: $(S^{2-})_0 = 7.33 \times 10^{-5}$ M + $(S_2^{2-})_0 = 3.67 \times 10^{-4}$ M
●: $(S^{2-})_0 = 7.33 \times 10^{-5}$ M + $(S_2^{2-})_0 = 3.67 \times 10^{-3}$ M
⊙: $(S_2^{2-})_0 = 3.53 \times 10^{-3}$ M

Effect of Aromatic Nitro Compound. In the previous experiment two of the authors (S. H. and J. S.) have found[8] that, in the aqueous monosulfide reduction of sodium *m*-nitrobenzene sulfonate, the disulfide formation occurs prior to the amine formation in the absence of light and any other oxidizing agents besides the nitro compound, and that there are induction period in the amine formation and the disappearance of the nitro

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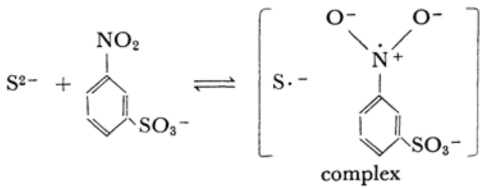
[8] S. Hashimoto and J. Sunamoto, Presented at the 17th Annual Symposium of the Organic Reaction Mechanisms, Tokyo, November, 1966.

compound. In the present experiment, the disulfide formation was determined in the aqueous monosulfide reduction of sodium *m*-nitrobenzene sulfonate in the dark under nitrogen atmosphere. Since sodium *m*-nitrobenzene sulfonate also have an absorption at 360 mμ ($\varepsilon_{360}=46.8$), which is the characteristic absorption band of the aqueous disulfide, the absorbances of the reaction mixtures at zero hour were proportional to the initial concentration of the nitro compound. However, when the concentration of the nitro compound was corrected, all of the absorbances returned to origin. The corrected concentrations or absorbances of the disulfide were not measured in this experiments, because only relative concentrations were necessary to the later discussion. As are shown in Fig. 7, though the disulfide formation hardly occurred when the very small amount of the nitro compound ($10^{-3}-10^{-4}$ M) were added, the disulfide formations were, however, evidently observed when the amount of the nitro compound added became larger (10^{-2} M∼). In addition, the induction-period intervals appeared also in the disulfide formation itself. With the increase of the initial concentration of the aqueous monosulfide, the induction-period intervals shortened and the rate of the disulfide formation became lower. These phenomena, the dependence of the induction-period intervals in the disulfide formation on the initial concentrations of the reactants, were analogous to those in the amine formation. From these results, it is clear that the nitro compound itself may induce the generation of the sulfide ion radical and the subsequent disulfide formation. Therefore, the following reactions *via* a certain complex, such as 1-electron reduction complex, may be probable for the formation of the sulfide ion radical:



(20)

$$\text{complex} \rightleftharpoons \text{S}\cdot^{-} + (\text{Ar-}\dot{\text{N}}\text{O}_2)^{-} \qquad (21)$$

Assuming these processes, the induction-period intervals of the disulfide formation and the subsequent amine formation in the aqueous monosulfide reduction of aromatic nitro compound can be smoothly explained. In this case, the rate determining step of the sulfide-ion-radical formation perhaps may be the stage of Eq. (21) on the basis of the correlations between the rate of the amine formation and that of the disulfide formation and between the initial concentrations of reactants and the both reaction rates.

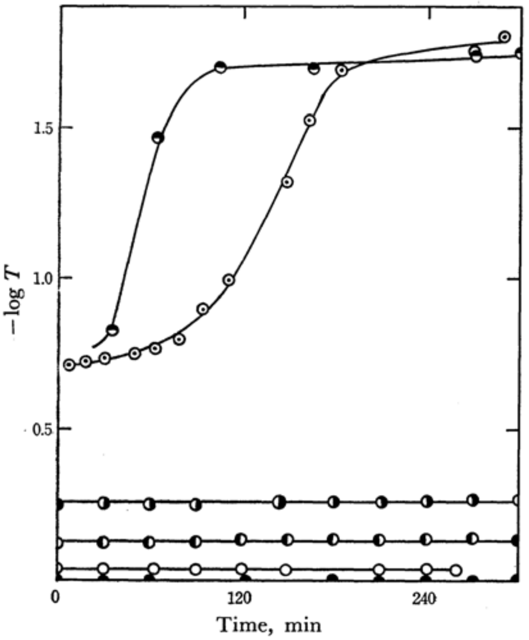


Fig. 7. Disulfide formation in reaction of nitro compound and aqueous monosulfide solution, in the dark under nitrogen atmosphere at 35.0°C.

●: $(\text{S}^{2-})_0=6.65\times10^{-3}$ M
○: ●+(Ar-NO_2)$=5.0\times10^{-4}$ M
◐: ●+(Ar-NO_2)$=2.50\times10^{-3}$ M
◑: ●+(Ar-NO_2)$=5.0\times10^{-3}$ M
◓: $(\text{S}^{2-})_0=9.83\times10^{-2}$ M
 +(Ar-NO_2)$=1.39\times10^{-2}$ M
⊙: $(\text{S}^{2-})_0=5.29\times10^{-2}$ M
 +(Ar-NO_2)$=1.51\times10^{-2}$ M

Cope and Brown also have stated the evidence[9] in parallel with our investigations that the induction period in the disappearance of nitrobenzene and the disulfide formation are observed during the course of the ethanolic monosulfide reduction of nitrobenzene. Although their findings are consistent with our results, their point of view is somewhat different from ours. From the present investigation, clearly their assumption for the disulfide formation is mistaken.

On the other hand, Kolker and Waters presented the evidence by ESR spectroscopy[1] that the radical-anion of nitro compound and the thionite radical can be easily formed in an aqueous sodium dithionite reductions of aromatic nitro compounds. If the processes assumed above as Eqs. (20) and (21) are correct, an anion radical of the nitro compound may certainly exist together with the sulfide ion radical also in our experiments. Further investigation is in progress on this point by ESR spectroscopy and will be reported on a following paper.

Thanks are due to Mr. Kenji Izumoto for his assistance in some of the experimental work.

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[9] O. J. Cope and R. K. Brown, *Can. J. Chem.*, **39**, 1695 (1961).