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The Alkaline Sulfide Reduction of Aromatic Nitro Compounds. VII. The Induction Period of the Sodium Monosulfide Reduction of Sodium *m*-Nitrobenzene Sulfonate*

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In the sodium monosulfide reduction of sodium *m*-nitrobenzene sulfonate, an induction period appears. The present investigation was undertaken in order to determine the causes of this induction period. The induction period is due not to the nitro compound, but to the reducing agent. The induction period is shortened by means of irradiation by ultraviolet light, the addition of potassium persulfate, ferric chloride, and α,α'-azobisisobutyronitrile, or under atmospheric conditions. On the other hand, the addition of phenol or alcohol lengthens the induction period. Further, on the basis of polarographic and spectroscopic studies of the induction period, it has been suggested that soduim disulfide is produced during this induction period. On the basis of these data, it seems reasonable to assume that, in the reduction of aromatic nitro compounds by sodium monosulfide, the reducing power of monosulfide is very small in itself, and that the nitro group is reduced by the disulfide produced by the radical oxidation of monosulfide. The formation of the sulfide ion radical and its dimerization appear to be responsible for the induction period of this reaction.

In an earlier presentation dealing with the kinetic studies of the alkaline sulfide reduction of sodium *m*-nitrobenzene sulfonate,(1) we reported that an induction period appeared in the sodium monosulfide reduction.

Although the alkaline sulfide reduction of aromatic nitro compounds is of much preparative significance, very little work has been carried out on it from the standpoint of reaction kinetics. One of the few available publications, with the exception of our own studies, is that of Goldschmidt and Larsen,(2) who measured the electric conductivity of the medium and followed the disappearance of sodium *m*-nitrobenzene sulfonate. However, they mistook the hydrosulfide for the monosulfide; when the aqueous monosulfide was prepared, gaseous hydrogen sulfide was introduced into the aqueous sodium hydroxide solution until the color of phenolphtalein disappeared. As sodium monosulfide undergoes hydrolysis, as is shown in Eq. 1, the sulfide which was prepared by Goldschmidt and Larsen is, then, hydrosulfide.

$$S^{2-} + H_2O \rightleftarrows SH^- + OH^- \qquad (1)$$

Another publication is that of Hojyo et al.,(3) who reported that the rate of the sodium monosulfide reduction of nitrobenzene in a 70 vol.% aqueous methanolic solution was too slow for the reaction to be followed kinetically. It may be supposed that they here observed the induction period which we later established.

The present investigation was undertaken in order to determine the causes of the appearance of the induction period in the sodium monosulfide reduction.

Experimental

Materials.—All the reactants and solvents were obtained commercially or by standard methods of preparation and were used after careful purification, either by distillation or by recrystallization. Sodium disulfide was freshly prepared by the method described in a previous paper.(4)

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* Presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

1) S. Hashimoto, J. Sunamoto and K. Oshima, presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo March, 1963.

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

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

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

Typical Procedure for Rate Measurements.—Appropriate amounts of a solvent, a nitro compound, and additives were placed in a 1000-ml. three-necked flask equipped with a reflux condenser, an outlet tube, and a nitrogen inlet tube with a trap containing the same solvent as the reaction flask. The flask was then immersed in a thermostat regulated and flushed by nitrogen at given temperatures for half an hour. The reaction was commenced by introducing a definite amount of an aqueous solution of sodium monosulfide which had previously been warmed to the reaction temperature. At appropriate time intervals aliquots (20 ml.) were withdrawn, poured into 20 ml. of a hydrochloric acid aqueous solution (1 : 2), and then warmed on a steam bath for half an hour.

Procedures for Irradiation.—In order to irradiate with ultraviolet light, a low-pressure mercury vapor lamp (2537 Å, 15 W.) was placed in the reaction flask; on the other hand, in order to irradiate with visible light, a National FCL-30D-SDL fluorescence lamp (4000—4500 Å, 20 W.) was set up at a distance of ca. 3 cm. from the reaction flask.

Analytical Procedures.—The above-mentioned acidic solutions were cooled below 10°C with ice, and the quantities of amine produced were determined by diazotizing titration according to the usual method.

Irradiation on an Aqueous Sodium Monosulfide Solution.—About 1000 ml. of a 1.33 mol./l. sodium monosulfide aqueous solution was placed in a flask equipped with a high-pressure mercury vapor lamp (3500—4000 Å, 100 W.), a reflux condenser, and an outlet tube. The flask was immersed in a thermostat regulated at 37—38°C, and then the internal atmosphere was substituted for nitrogen sufficiently. At appropriate time intervals samples were pressed out by nitrogen. The reaction was followed by the usual methods of acidimetry and iodometry and by polarography, as has previously been described.[4] The ultraviolet absorption spectra were run on a Shimadzu Beckmann-type Model-DU spectrophotometer, while the visible absorption spectra were run on a Shimadzu Bausch & Lomb Spectronic 20 photometer. Both absorption spectra were compared with that of an authentic solution of sodium disulfide. The coincidence was satisfactory.

Results and Discussion

The first investigation was undertaken in order to examine which species, the nitro compound or the reducing agent, exhibits an induction period in the reduction with sodium monosulfide. The results when the initial concentrations of the nitro compound and sodium monosulfide were changed with a varying molar ratio of the two reactants are shown in Figs. 1 and 2. The initial concentration of the reducing agent had an effect on both terms, the induction-period intervals and the rate of the main reaction. However, the initial concentration of the nitro compound had an effect only on the main reaction. It may, therefore, be concluded that the induction period is due not to the nitro compound, but to the reducing agent. Further, when nitrobenzene was used instead of sodium *m*-nitrobenzene sulfonate in the sodium monosulfide reduction, though the rate of the main reaction became slower, the induction period was certainly observed.

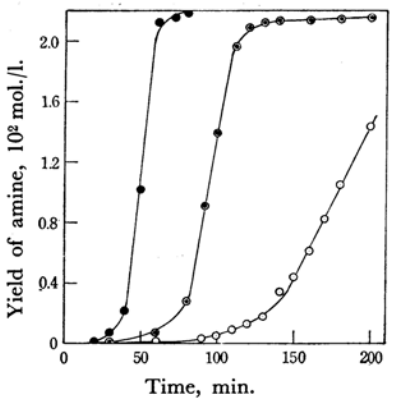

Fig. 1. Effect of initial concentration of reducing agent.

○ : Exp. No. 12 in Table I
⊙ : Exp. No. 17
● : Exp. No. 20

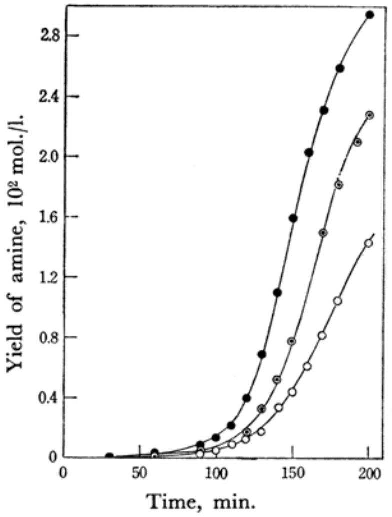

Fig. 2. Effect of initial concentration of nitro compound.

○ : Exp. No. 12 in Table I
⊙ : Exp. No. 25
● : Exp. No. 26

The rate of the main reaction is given by runs in which the initial concentrations of the nitro compound and sodium monosulfide were interchanged; it is certain that the rates can be expressed by Eq. 2:

$$d(\mathrm{Ar{-}NH_2})/dt = k_3(\mathrm{Ar{-}NO_2})(\mathrm{Na_2S})^2 \qquad (2)$$

This equation is the same as that given for the sodium hydrosulfide reduction in a previous presentation.[1]

Some complementary data on the induction-period intervals and the calculated apparent

TABLE I. THIRD-ORDER RATE CONSTANTS FOR REDUCTION OF SODIUM *m*-NITROBENZENE SULFONATE BY SODIUM MONOSULFIDE AQUEOUS SOLUTION

Exp. No.	(Ar–NO$_2$) 10^2 mol./l.	(Na$_2$S) 10^2 mol./l.	Additives 10^2 mol./l.	Temp. °C	Induction period min.	Rate constant k_3, min^{-1} mol^{-2} l^{-2}
1	1.563	5.625	None	35	121	2.790
2	1.563	5.625	None	35	42	3.416[a]
3	1.563	5.625	(FeCl$_3$)=0.031	35	78	2.710
4	1.563	5.625	(FeCl$_3$)=0.031 (K$_2$S$_2$O$_8$)=0.032	35	45	2.770
5	1.563	5.625	(NaHCO$_3$)=5.625	35	126	2.123
6	1.563	5.625[b]	None	35	0	—
7	1.563	5.625[b]	(FeCl$_3$)=0.031	35	0	—
8	1.563	9.631	None	35	45	2.331
9	1.563	9.631	None	35	120	0.844[c]
10	1.563	9.631	None	35	118	1.010[d]
11	1.563	9.631	None	35	118	0.067[e]
12	2.178	6.507	None	30	128	2.109
13	2.178	6.507	(K$_2$S$_2$O$_8$)=0.533	30	20	3.741
14	2.178	6.507	(NaOH)=5.926	30	123	2.537
15	2.178	6.507	(ABIN)=0.136	30	116	2.066
16	2.178	6.507	(Phenol)=0.856	30	Very slow	Very small
17	2.178	11.73	None	30	74	1.725
18	2.178	11.73	None	30	60	1.715[f]
19	2.178	11.73	None	30	64	1.435[g]
20	2.178	19.49	None	30	40	1.281
21	2.682	5.126	None	30	138	0.917
22	2.682	5.126	None	30	138	5.676[h]
23	2.682	5.126	(Na$_2$S$_2$O$_3$)=1.499	30	138	0.761
24	2.682	5.126	(Na$_2$S$_2$)=0.769	30	0	7.975
25	4.347	6.507	None	30	125	1.763
26	6.533	6.507	None	30	113	1.562

a) Inside irradiation of ultraviolet light, 2537 Å, 15 W.
b) Sodium disulfide
c) In 33.1 vol.% aqueous methanolic solution
d) In 33.1 vol.% aqueous isoproply alcohol solution
e) Nitrobenzene in 33.1 vol.% aqueous methanolic solution
f) Outside irradiation of visible light, 4000—4500 Å, 30 W.
g) Outside irradiation of visible light under atmospheric condition
h) Under atmospheric condition

third-order rate constants are shown in Table I.

The Effect of Light.—The effect of light on the induction period was also investigated. As is shown in Fig. 3, the induction periods were shortened by means of the inside irradiation of ultraviolet light and the outside irradiation of visible light, compared with the dark reaction. Of course, the effect was far better in the former, In neither case, however, was any effect on the main reaction observed.

On the basis of these data, it is reasonable to assume that the induction period contains a radical reaction, but the main reaction perhaps contains an ionic reaction.

Barret and his co-workers presented evidence that the sulfate ion radical was formed by the irradiation by ultraviolet light of an aqueous or methanolic sulfate solution.[5] It may be similarly

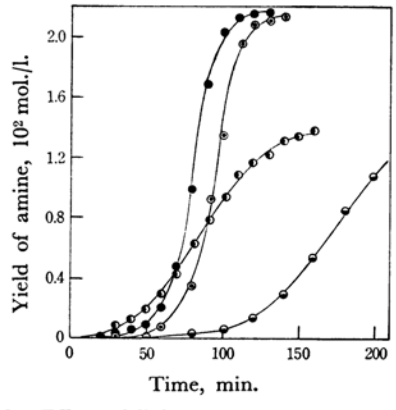

Fig. 3. Effect of light.
◒ : Exp. No. 1 in Table I
◐ : Exp. No. 2
⊙ : Exp. No. 17
● : Exp. No. 18

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[5] J. Barret, M. F. Fox and A. L. Mansell, *Nature*, **200**, 257 (1963).

reasonable to assume the following processes for the formation of the sulfide ion radical:

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

The disulfide ion is immediately produced by the coupling of two sulfide ion radicals:

$$2S\cdot^{-} \rightarrow (S\text{-}S)^{2-} \quad (4)$$

Therefore, it was supposed that the reduction of the nitro group was proceeded by that of the disulfide ion produced.

The Effect of the Solvent.—Figure 4 shows that the induction-period intervals are longer in an aqueous alcoholic solution than in an aqueous solution. It can be considered that the sulfide ion radical was deactivated by the solvent.

$$S\cdot^{-} + \text{Solvent} \rightarrow \text{Deactivated species} \quad (5)$$

It is well known that the α-hydrogen of alcohol is more easily abstracted by the radical than is the hydrogen of water.⁶⁾ Also, the rate of the main reaction became a little solwer in an aqueous alcoholic solution than in an aqueous solution. This observation may be reasonable since the solubility of sodium *m*-nitrobenzene sulfonate is decreased, and the diminished solvent polarity may also be responsible.

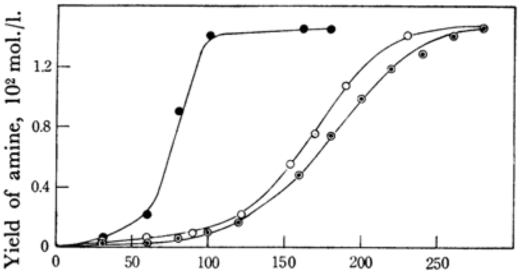

Fig. 4. Effect of solvent.
● : Exp. No. 8 in Table I
⊙ : Exp. No. 9
○ : Exp. No. 10

The Effect of Air.—Figure 5 shows that the induction period was only a little, though obvioulsy, shortened under the atmospheric conditions than a nitrogen atmosphere. It was earlier known that the oxidation of aqueous sodium sulfite is an auto-oxidation,⁷⁾ and that it is very sensitive to light and air in a chain oxidation process.⁸⁾ It may be reasonable to assume that the effect of air on the auto-oxidation of a sodium monosulfide solution is the same as on the auto-oxidation of a sodium

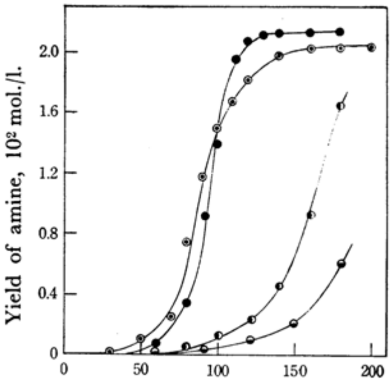

Fig. 5. Effect of air.
⊙ : Exp. No. 17 in Table I
● : Exp. No. 19
◒ : Exp. No. 21
◐ : Exp. No. 22

sulfite solution; it may also be reasonable to suggest that the processes is as follows, for example:

$$S\cdot^{-} + 3O \rightarrow SO_3\cdot^{-} \quad (6)$$

$$SO_3\cdot^{-} + S^{2-} \rightarrow SO_4^{2-} + S\cdot^{-} \quad (7)$$

In this case, however, it is necessary to reduce the rate of the main reaction with the air oxidation of the sodium disulfide produced.

The Effect of Sodium Disulfide and Sodium Thiosulfate.—The effects of the oxidation products of sodium monosulfide were also investigated. The addition of a catalytical amount of sodium disulfide made the induction period disappear. It may be reasonable to assume that the disulfide ion will make up for the sulfide ion radical, as in Eq. 8, and may be useful as an initiator:

$$(S\text{-}S)^{2-} \rightarrow S\cdot^{-} + S\cdot^{-} \quad (8)$$

However, the addition of sodium thiosulfate had scarcely any effect on the induction period or on the main reaction.

The Effect of ABIN and Phenol.—The addition of ABIN (α,α'-azobisisobutyronitrile) shortened the induction period, but it had scarcely any effect on the rate of the main reaction. On the other hand, the addition of phenol, which is often used as an inhibitor or a retarder for a radical reaction,⁹⁾ made the rate of the over-all reaction much slower.

The Effect of Potassium Persulfate and Ferric Chloride.—The salt of some metals of a variable valency is used as a radical source for a polymerization in an aqueous solution, such as a redox polymerization or an emulsion polymerization. If the induction period is due to the radical oxidation of sodium monosulfide to sodium disulfide,

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6) C. F. Wells, *Trans. Faraday Soc.*, **57**, 1703 (1961).

7) N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," translated by J. E. S. Bradley, Vol. I, Pergamon Press, New York (1958), p. 178.

8) H. L. J. Bäckström., *Z. physik. Chem.*, **B25**, 122 (1934).

9) P. G. Ashmore, "Catalysts and Inhibition of Chemical Reactions," Butterworth, London (1963), p. 266.

as was previously assumed, it may naturally be supposed that these salts have an effect on the induction period. In fact, the addition of a catalytical amount of potassium persulfate or ferric chloride shortened the induction period, as is shown in Fig. 6. When both salts were used together, it shortened it greatly.

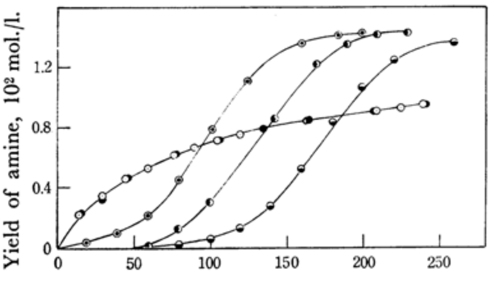

Fig. 6. Effect of ferric chloride.
◒ : Exp. No. 1 in Table I
◐ : Exp. No. 3
⊙ : Exp. No. 4
○ : Exp. No. 6
● : Exp. No. 7

At the present time, the sulfide ion radical is believed to be formed as follows:

$$Fe^{3+} + 2S^{2-} \rightarrow Fe^{2+} + 2S\cdot^{-} \qquad (9)$$

$$S_2O_8{}^{2-} + S^{2-} \rightarrow SO_4{}^{2-} + SO_4\cdot^{-} + S\cdot^{-} \qquad (10)$$

$$SO_4\cdot^{-} + S^{2-} \rightarrow SO_4{}^{2-} + S\cdot^{-} \qquad (11)$$

In a system containing potassium persulfate and ferrous chloride, the formation of the ion radical is believed to start as follows¹⁰⁾:

$$Fe^{2+} + S_2O_8{}^{2-} \rightarrow Fe^{3+} + SO_4{}^{2-} + SO_4\cdot^{-} \qquad (12)$$

Ion radicals derived from the salts of these metals of a variable valency may exchange electrons with stable species and thereby form active-ion radicals in, e. g., the reaction of a sulfide with a salt of a trivalent iron. In this case an electron is transferred from the monosulfide ion to the ferric ion, producing the highly-active radical ion; this active-ion radical immediately dimerizes to disulfide, as in Eq. 4.

These reduction-oxidation systems, then, shortened the induction period due to the auto-oxidation of monosulfide to disulfide; the oxidation appeared to proceed even in the dark if traces of these salts were present.

On the other hand, in no case did the addition of these catalysts have any effect on the main reaction. The addition of ferric chloride in the sodium disulfide reduction, in fact, had no effect at all on its reduction rate.

When persulfate is used as a catalyst for a usual reaction, thiosulfate, as well as ferrous or ferric ion, is used as a promoter.¹¹⁾ In the alkaline sulfide reduction of aromatic nitro compounds, thiosulfate, which is an oxidation product of sulfide, is certainly produced; therefore, it may be reasonable to assume that the reduction of persulfate by thiosulfate occurs. However, as disulfide or monosulfide has a far larger reducing power than thiosulfate,* there is no need to consider the effect of thiosulfate.

The Effect of pH.—In an aqueous solution the monosulfide undergoes hydrolysis, as Eq. 1 shows. Therefore, it may be considered that the pH will also have a large effect on the induction period. As is shown in Fig. 7, the addition of neither sodium hydroxide nor sodium hydrogen carbonate had, in fact, any effect on the induction period; rather, each had a large effect on the main reaction. Between the monosulfide ion and the hydrosulfide ion, we could not determine which species is more rapidly oxidized to the disulfide ion.

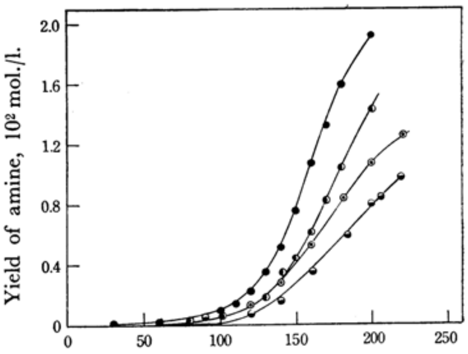

Fig. 7. Effect of pH.
⊙ : Exp. No. 1 in Table I
◒ : Exp. No. 5
◐ : Exp. No. 12
● : Exp. No. 14

Hojyo et al.,³⁾ stated that, in the reduction of nitrobenzene by sodium disulfide in a 70% aqueous methanolic solution, the rate of reaction shows a first-order dependence on the hydroxide ion concentration. They also stated that the reaction mechanism involved an attack by the disulfide ion, which is the kinetically effective species, on the positive nitrogen of the nitro group in conjunction with the hydrolytic equilibrium of the disulfide ion:

$$S_2{}^{2-} + H_2O \rightleftarrows S_2H^{-} + OH^{-} \qquad (13)$$

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10) J. W. L. Fordham and H. L. Williams, *J. Am. Chem. Soc.*, **73**, 4855 (1951).

11) D. Dunn, *Trans. Faraday Soc.*, **42**, 190 (1946).

* Their mercury anodic oxidation potentials clearly show this difference in reducing power.

The effect of the pH on the main reaction in our experiments may be similarly analyzed.

The Irradiation of an Aqueous Sodium Monosulfide Solution.—In order to examine the above hypothesis in detail, the irradiation of an aqueous sodium monosulfide solution was investigated. An aqueous solution of pure sodium monosulfide is colorless, but an aqueous disulfide solution is yellow.[12] When the monosulfide solution was irradiated, it turned yellow. Figure 8 shows that the absorption at 360 mμ, which is not observed before irradiation, appears upon irradiation and thereafter gradually increases in intensity. After a long irradiation its position and the intensity of the maximum absorption of irradiated monosulfide were essentialy identical with those of disulfide which had not been irradiated. The polarograms of the irradiated monosulfide solution support the discussion of the results of spectrophotometry.

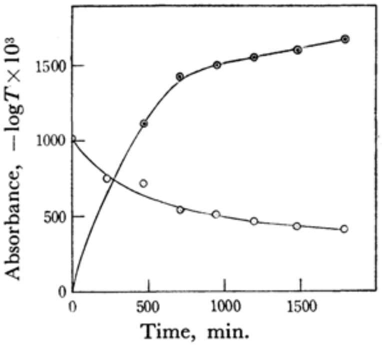

Fig. 8. Irradiation on aqueous sodium monosulfide solution; change of intensity of absorption in visible and ultraviolet region.

Initial concentration of sodium monosulfide aqueous solution: 1.33×10^{-2} mol./l.

Temp.: 37—38°C

⊙ : Intensity of absorption at 360 mμ

○ : Intensity of absorption at 230 mμ

Conclusion

In view of the above facts, the most reasonable conclusion to be drawn from the available data is as follows. In the reduction of aromatic nitro compounds by sodium monosulfide, the reducing power of monosulfide is very small in itself, and the reduction of the nitro compound hardly proceeds at all. However, after the formation of disulfide by the radical oxidation of monosulfide, which involves the dimerization of the sulfide ion radical, the reduction of the nitro group is furthered by the disulfide produced. This step, containing of the formation of the sulfide ion radical and its dimerization, appears as the induction period in the sodium monosulfide reduction of aromatic nitro compounds.

Thanks are due to Mr. Takao Shima for his assistance in some of the experimental work. The authors are also indebted to the Daiwa Dyestuff Co., Ltd., for its gift of materials.

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[12] For example, Gmelins Handbuch d. anorg. chem. syst. No. 21, (1928), pp. 481—494.