BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1207—1211 (1966)

The Alkaline Sulfide Reduction of Aromatic Nitro Compounds. VIII. The Correlation between Sodium Monosulfide and Hydrosulfide in the Reduction of Sodium *m*-Nitrobenzene Sulfonate

By Shizunobu HASHIMOTO and Junzo SUNAMOTO

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

(Received September 14, 1965)

In order to examine the correlation between sodium hydrosulfide and sodium monosulfide, the reduction of sodium *m*-nitrobenzene sulfonate by these aqueous sulfides has been studied kinetically. The rates of the hydrosulfide reduction and the main reaction of the monosulfide reduction were found to be proportional to the concentration of the nitro compound and the square of the concentration of the reducing agent. In the hydrosulfide reduction, the hydroxide ion concentration has a negative effect on the initial state and a positive effect on the final state. The polarographic study on the hydrosulfide reduction confirmed the presence of disulfide ions. From the available data, the correlation among the alkaline sulfides in the reduction was discussed.

The alkaline sulfides may be classified into alkaline hydrosulfide, monosulfide, and polysulfide. In studying the significance of the method of preparation, each stoichiometric equation has been employed for the reduction of aromatic nitro compounds by them, for example:[1]

$$4\,\text{Ar-NO}_2 + 6\,\text{NaSH} + \text{H}_2\text{O} \rightarrow 4\,\text{Ar-NH}_2 + \text{Na}_2\text{S}_2\text{O}_3 \qquad (1)$$

$$4\,\text{Ar-NO}_2 + 6\,\text{Na}_2\text{S} + 7\,\text{H}_2\text{O} \rightarrow 4\,\text{Ar-NH}_2 + 3\,\text{Na}_2\text{S}_2\text{O}_3 + 6\,\text{NaOH} \qquad (2)$$

$$\text{Ar-NO}_2 + \text{Na}_2\text{S}_2 + \text{H}_2\text{O} \rightarrow \text{Ar-NH}_2 + \text{Na}_2\text{S}_2\text{O}_3 \qquad (3)$$

However, it seems reasonable to assume that sodium monosulfide is nothing but sodium hydrosulfide in an aqueous solution, because sodium monosulfide is almost completely hydrolyzed into sodium hydrosulfide and sodium hydroxide in an aqueous solution, as in Eq. 4.[2]

$$\text{Na}_2\text{S} + \text{H}_2\text{O} \rightleftarrows \text{NaSH} + \text{NaOH} \qquad (4)$$

In an earlier paper dealing with the polarographic oxidation of sodium sulfides, the relation of their reducing power has discussed.[3] In the present paper the correlation among the sodium sulfides in the reduction of sodium *m*-nitrobenzene sulfonate will be investigated.

Experimental

Materials.—Sodium monosulfide and disulfide were prepared and purified by the method used in the preceding experiment.[3] Sodium hydrosulfide was prepared and purified according to the method given in the literature.[4] Sodium *m*-nitrobenzene sulfonate was the same as that used in the previous report.[5]

Product Study.—The reduction of sodlum *m*-nitrobenzene sulfonate was carried out under the same conditions as those used in the kinetic experiments, after a reaction of a sufficient duration, the resulting solution was acidified with concentrated hydrochloric acid, boiled on a water bath for about 20 min., and filtered. After it had been washed, the filtrate and the washings were combined and diluted with water to the appropriate voulme. From this solution a sample was taken and submitted to the diazometry according to the usual method. At the same time a part of this solution was submitted to paper chromatography. The reaction gave the corresponding amine in a 92.5% yield by the disulfide reduction, in a 95.5% yield by the monosulfide reduction, and in a 97.3% yield by the hydrosulfide reduction.

The paper chromatography of the resulting solution with several solvents, such as 2% hydrochloric acid,

---

[1] For example, P. H. Groggins, "Unit Processes in Organic Synthesis," John Wiley & Sons, New York (1952), p. 100.

[2] For example, "Gmelins Handbuch der Anorganischen Chemie," Bd. 21 (1928), pp. 481—494.

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

[4] G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart (1954), p. 278; Ed. by Chem. Soc. Japan, "Zikken Kagaku Koza," Vol. 9, Maruzen, Tokyo (1958), p. 56.

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

n-butanol - concentrated hydrochloric acid (4 : 1), 2% aqueous ammonia, and pure water, confirmed only the presence of metanilic acid; the insoluble residue in hydrochloric acid was only sulfur.

Procedure for Rate Measurement.—The procedure for the rate measurement and analysis was the same as the method described earlier.5) The probable error for the determination of the produced amines was ±0.23%.

Procedure for pH Measurement.—A glass electrode and a caromel elelctrode were placed in a reaction flask for the rate measurements; the pH was then followed during the reduction on a Horiba-Hitachi M4-type pH meter.

Polarography on Hydrosulfide Reduction.—Using the same method as in the rate measurements, at appropriate time intervals an aliquot was taken and subjected to a.c. polarography on a Yanagimoto PA-102-type polarography. As the supporting electrolyte, the buffer solution, 0.01 M sodium borate and 0.04 M sodium hydroxide, was used (pH=12.15, as measured by a glass electrode).

Results and Discussion

The differences in the rates of reduction in the initial stage were unexpectedly large when sodium *m*-nitrobenzene sulfonate was reduced by aqueous sodium hydrosulfide, monosulfide, and disulfide. Therefore, these rates could not all be measured under the same reduction conditions; the rates of reduction by monosulfide and hydrosulfide were therefore measured under one set of conditions, while those of reduction by disulfide and hydrosulfide were measured under another set of conditions. These data are compared each other in Fig. 1.

The initial rate of the disulfide reduction was very large and the reaction reached an apparent equilibrium rather early, while in the monosulfide reduction there was an induction period,5) after which the main reaction proceeded at much the same rate as the disulfide reduction. The hydrosulfide reduction showed a medium reaction rate between the rates of the monosulfide and the disulfide reduction. The order of the apparent rates in the initial stage was $S_2^{2-} > SH^- > S^{2-}$, and that at corresponding times after the induction period of the monosulfide reduction was $S^{2-} > SH^- > S_2^{2-}$.

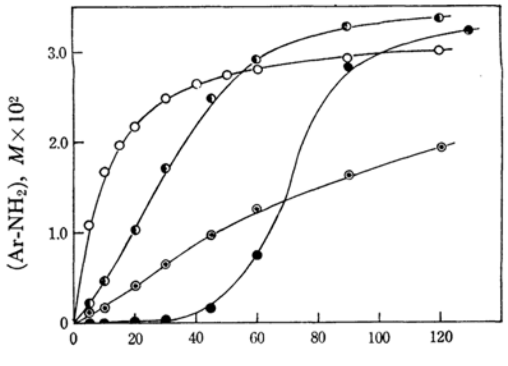

Fig. 1. Reductions of sodium *m*-nitrobenzenesulfonate by sodium hydrosulfide, monosulfide, and disulfide (30°C).
Initial concentrations: (Ar-NO$_2$)=3.50×10^{-2} M
○ (Na_2S_2)=7.19×10^{-2} M
⊙ (NaSH)=7.19×10^{-2} M
◐ (NaSH)=10.9×10^{-2} M
● (Na_2S)=10.9×10^{-2} M

Sodium hydrosulfide undergoes ionic dissociation, but it hardly hydrolyzes at all in an aqueous solution.2) On the other hand, sodium monosulfide undergoes hydrolysis, as has been described above. It may, therefore, be supposed that the difference in the reaction conditions between the monosulfide and the hydrosulfide reductions depends upon the pH of the medium.

A more direct basis for comparison between them is found in the pH dependence of the reaction.

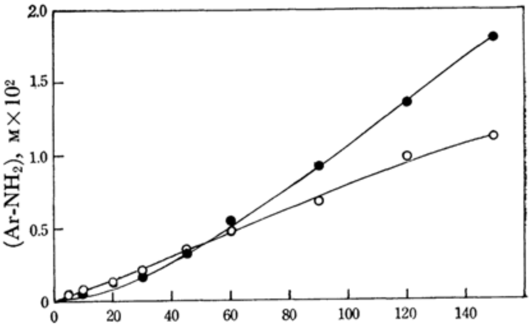

Fig. 2. The effect of sodium hydroxide on the sodium hydrosulfide reduction (30°C).
Initial concentrations: (Ar-NO$_2$)=3.49×10^{-2} M
(NaSH)=6.99×10^{-2} M
● (NaOH)=8.10×10^{-3} M ○ None

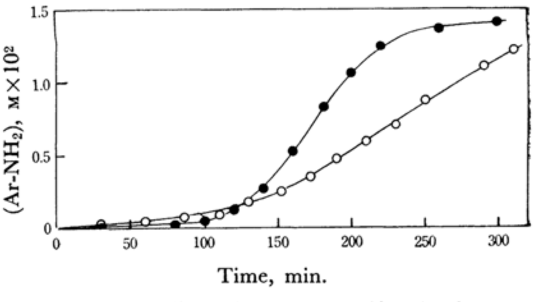

Fig. 3. The effect of hydrogen sulfide in the sodium monosulfide reduction (35°C).
Initial concentrations: (Ar-NO$_2$)=1.56×10^{-2} M
● (Na_2S)=5.63×10^{-2} M
○ (Na_2S)*=2.81×10^{-2} M

* Gaseous hydrogen sulfide was introduced into the aqueous sodium monosulfide solution till the color of phenolphthalein disappears and excess hydrogen sulfide was removed by nitrogen till the removed gas shows negativity on a lead acetate paper.

The addition of sodium hydroxide in the hydrosulfide reduction made the initial rate slower, while it accelerated the rate of the subsequent reaction. In the reduction by the aqueous monosulfide solution, which absorbed hydrogen sulfide, the induction period disappeared and the rate of the overall reaction became slower, approaching that of the hydrosulfide reduction. The correlation between them is shown in Figs. 2 and 3.

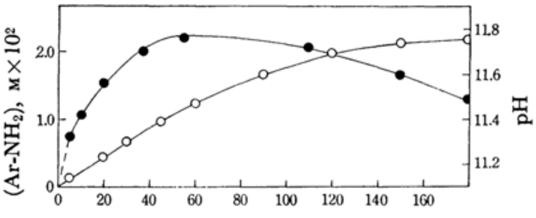

Fig. 4. pH change during the course of the hydrosulfide reduction (30°C).
Initial concentrations: $(\text{Ar-NO}_2)=3.49\times10^{-2}$ M
$(\text{NaSH})=7.19\times10^{-2}$ M
● pH ○ Yield of amine

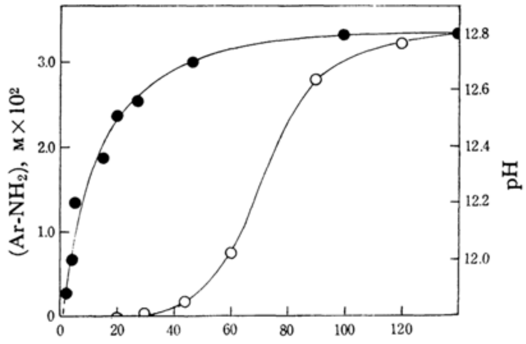

Fig. 5. pH change during the course of the monosulfide reduction (30°C).
Initial concentrations: $(\text{Ar-NO}_2)=3.49\times10^{-2}$ M
$(\text{Na}_2\text{S})=7.19\times10^{-2}$ M
● pH ○ Yield of amine

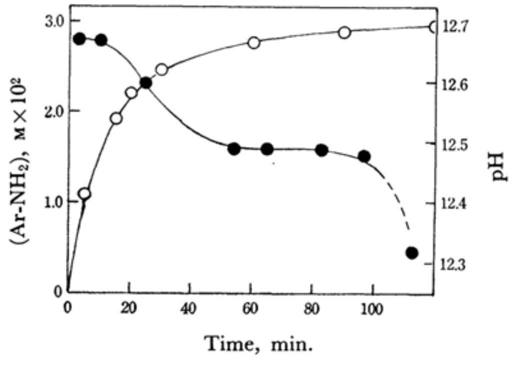

Fig. 6. pH change during the course of the disulfide reduction (30°C).
Initial concentrations: $(\text{Ar-NO}_2)=3.49\times10^{-2}$ M
$(\text{Na}_2\text{S}_2)=7.19\times10^{-2}$ M
● pH ○ Yield of amine

pH Change During Reduction.—In the alkaline sulfide reduction, the pH changes during the course of the reduction. On the hydrosulfide reduction, the monosulfide reduction, and the disulfide reduction, therefore, the pH values were followed under the conditions indicated in Figs. 4, 5, and 6 respectively.

In the hydrosulfide reduction the pH first increased with the progress of the reduction, but after a while it decreased a little. In the monosulfide reduction the pH continuously increased with the progress of the reaction; indeed, the pH in the induction-period intervals of the reduction increased remarkably. In the disulfide reduction, unlike the monosulfide reduction, the pH only decreased during the course of the reduction.

The rate of the main step in the monosulfide reduction of sodium *m*-nitrobenzene sulfonate depends upon the pH, as we previously reported.[5] Hojyo et al. also presented evidence that the rate of the disulfide reduction of nitrobenzene in an aqueous methanolic solution shows a first-order dependence on the hydroxide ion concentration.[6] On the basis of these data, it is clear that the alkaline-sulfide reductions are always closely connected with the pH of the medium.

In spite of the foregoing results, which show the pH dependence of the rate of alkaline-sulfide reductions, there remains the interesting question of why no induction period appears in the reduction by a hydrosulfide that shows a lower pH value than the monosulfide in an aqueous solution.

The Rate of the Hydrosulfide Reduction.—Since the hydrosulfide hardly hydrolyzes at all in an aqueous solution, it may be assumed that its stoichiometric concentration is almost equal to the kinetically-available concentration. The rate of the hydrosulfide reduction is given by runs in

TABLE I. THE EFFECT OF THE INITIAL CONCENTRATION OF THE NITRO COMPOUND AND SODIUM HYDROSULFIDE ON THE APPARENT THIRD ORDER RATE CONSTANTS (30°C)

Initial concn.		Apparent rate const.
(Ar-NO_2) M×10^2	(NaSH) M×10^2	k, l^{2}mol^{-2} min^{-1}
2.00	4.12	1.74±0.12
2.55	7.19	1.32±0.09
2.79	5.73	2.13±0.08
2.86	7.19	1.59±0.08
3.50	3.60	1.20±0.08
3.50	7.19	1.62±0.08
3.50	10.8	2.95±0.33
6.99	7.19	2.59±0.23

---

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

which the initial concentrations of the nitro compound and of sodium hydrosulfide have been interchanged. The rate of the reduction is found to be proportional to the concentration of the nitro compound and to the square of the concentration of sodium hydrosulfide:

$$\frac{d(\text{Ar-NH}_2)}{dt} = k(\text{Ar-NO}_2)(\text{NaSH})^2 \qquad (5)$$

The apparent third-order rate constants as calculated by Eq. 5 and the initial concentrations of both reactants are shown in Table I.

The temperature effect obeys the Arrhenius equation, as is shown in Fig. 7; the activation energy was thereby estimated graphically to be $E=$ 9.38 kcal. mol^{-1}.

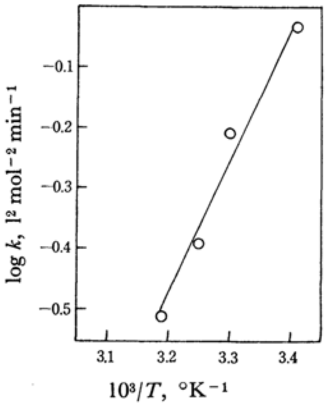

Fig. 7. The temperature dependence of the apparent third order rate constants.

Sodium monosulfide and sodium hydrosulfide are in a hydrolytic equilibrium, as has been described above. If these reducing agents, therefore, are used in the same stoichiometric concentration and compared with each other, the difference in their reduction conditions will be due to the pH in their medium; if the pH change which occurs during the course of the reduction is not considered, the two reactions must be essentially identical in their kinetics. The rate equation in the main step of the monosulfide reduction[5] is, in fact, the same as that given for the hydrosulfide reduction:

$$\frac{d(\text{Ar-NH}_2)}{dt} = k(\text{Ar-NO}_2)(\text{Na}_2\text{S})^2 \qquad (6)$$

A comparison of the apparent third-order rate constants of the hydrosulfide reduction with those of the main step of the monosulfide reduction is shown in Table II. It seems most reasonable to assume that the differences in the rate constants on the two sulfide reductions are due to the hydroxide ion concentration in the medium.

TABLE II. THE COMPARISON OF THE APPARENT THIRD ORDER RATE CONSTANTS OF THE HYDROSULFIDE REDUCTION WITH THOSE OF THE MAIN REACTION OF THE MONOSULFIDE REDUCTION

Initial concn.		Apparent rate const.	Temp.
(Ar-NO$_2$) M×10^2	(Reducing agent) M×10^2	k l^{2}mol^{-2} min^{-1}	°C
3.50	7.19*	2.47	35
1.56	5.63**	2.79	
3.50	7.19*	1.62	30
2.18	6.51**	2.11	

* Sodium hydrosulfide ** Sodium monosulfide

It was previously suggested that the induction period observed in the monosulfide reduction was due to the formation of the sulfide ion radical and its dimerization, as follows:[5]

$$(\text{S}^{2-}\text{-H}_2\text{O}) \xrightarrow[\text{Fe}^{3+},\ \text{or}\ \text{S}_2\text{O}_3{}^{2-},\ \text{etc.}]{h\nu,\ \text{O}_2} \text{S}^-\cdot + \text{H}\cdot + \text{OH}^- \qquad (7)$$

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

In view of the above correlation between monosulfide and hydrosulfide, it may similarly be reasonable to assume that the following processes are also involved in the initial stage of the hydrosulfide reduction:

$$\text{SH}^- \xrightarrow{h\nu,\ \text{O}_2,\ \text{etc.}} \text{S}^-\cdot + \text{H}\cdot \qquad (9)$$

$$\text{S}^-\cdot + \text{H}_2 \rightarrow \text{SH}^- + \cdot\text{OH} \qquad (10)$$

$$\text{H}\cdot + \cdot\text{OH} \rightarrow \text{H}_2\text{O} \qquad (11)$$

$$\text{H}\cdot + \cdot\text{H} \rightarrow \text{H}_2 \qquad (12)$$

It appears that the hydrosulfide ion readily gives a sulfide ion radical and a hydrogen radical in the presence of light or oxygen, and that the sulfide ion radical produced immediately dimerizes to give the disulfide ion, as in Eq. 8. The hydrogen radical may couple with the hydroxide radical produced according to Eq. 10 to give water, or dimerize to hydrogen gas. It may be supposed that the hydrogen radical or hydrogen gas produced here is not directly concerned with the reduction of the nitro compound, but further work is in progress on this point and will be reported on at a later date.

On the basis of the results which show that the initial stages in the hydrosulfide reduction and in the monosulfide reduction depend upon the pH of the medium, it may be supposed that this auto-oxidation process of the hydrosulfide ion to the disulfide ion is also affected by the pH and that the rate of the auto-oxidation becomes in accordance with the pH increment.* That is to say, the rate of the formation of the disulfide ion in the aqueous hydrosulfide solution is rapid, but that in the aqueous

---

* When an aqueous monosulfide solution was irradiated with ultraviolet light, the rate of the formation of the disulfide ion became lower with an increase in the hydroxide ion concentration in the medium.[7]

[7] S. Hashimoto and J. Sunamoto and K. Sato, Presented at the Local Meeting of the Chemical Society of Japan, Fukuoka, July 17th, 1965.

TABLE III. A. C. POLAROGRAPHY ON THE HYDROSULFIDE REDUCTION OF SODIUM *m*-NITROBENZENESULFONATE IN AQUEOUS SOLUTION (30°C)

Initial concn.: $(\text{Ar-NO}_2)=5.8\times10^{-2}$ M
$(\text{NaSH})=6.8\times10^{-2}$ M

Reaction time min.	Peak potentials (V. vs. SCE) and wave heights (μ℧)							
	E_1	h_1	E_2	h_2	E_4	h_4	E_5	h_5
0	—		−0.44	160	−0.72	160	−0.80	115
10	—		−0.43	180	−0.70	180	−0.79	120
40	−0.15	120	−0.43	180	−0.70	180	−0.80	180
60	−0.18	140	−0.43	190	−0.70	190	−0.81	190
90	−0.20	190	−0.44	180	−0.70	200	−0.80	190
180	−0.17	195	−0.43	160	−0.70	190	−0.79	200
1620	−0.20	325	—		−0.70	200	—	
Ar-NO$_2$	—		—		−0.70	130	—	
NaSH	—		—		−0.68	130	−0.80	140

monosulfide solution is very slow, because of the high concentration of hydroxide ions. An induction period, therefore, appears only in the monosulfide reduction.

The Polarographic Study of the Hydrosulfide Reduction.—In order to examine the above hypothesis that the disulfide ion will be formed in the hydrosulfide reduction, a. c. polarography was applied to the hydrosulfide reduction of sodium *m*-nitrobenzene sulfonate. As is shown in Table III, the heights of the first, the fourth, and the fifth waves all increased as the reduction proceeded. The increase in the height of the first wave shows the formation of the oxide of sulfide, that is, thiosulfate.[3] The fourth wave was overlapped with the wave of the nitro compound. However, the increase in the height of this wave clearly shows the formation of the polysulfide ions, as is true also with the fifth wave.[3] The polarography of the hydrosulfide reduction confirmed the formation of the disulfide ion and supported the above hypothesis.

Conclusion

Sodium monosulfide and sodium hydrosulfide are in a hydrolytic equilibrium. The reductions by both sulfides, therefore, must be essentially identical in their kinetics. The rate equation in the main reaction of the monosulfide reduction was, in fact, identical with that of the hydrosulfide reduction (cf. Eqs. 5 and 6).

It may be reasonable to assume that the reduction of aromatic nitro compounds by the aqueous monosulfide or the aqueous hydrosulfide proceeds as follows. First, the hydrosulfide ion, as well as the one produced by the hydrolysis of the monosulfide ion in an aqueous solution, gives the sulfide ion radical with light or oxygen and dimerized to the disulfide ion. Secondly, the disulfide ion produced attacks the positively-charged nitrogen atom of the nitro group, because the reducing power of the monosulfide ion or of the hydrosulfide ion is very small in itself.

The hydroxide ion has a negative effect on the first process, involving the formation of the sulfide ion radical and its dimerization, and a positive effect on the second process, which involves the reduction of the nitro group. From these relationships, it is clear that no induction period appears in the hydrosulfide reduction as a result of its low concentration of hydroxide ions at the initial stage.

Hojyo et al. presented evidence that the disulfide reduction of nitrobenzene in an aqueous methanolic solution is given by Eq. 13, in conjunction with the hydrolytic equilibrium of the disulfide ion:[6]

$$-\frac{\mathrm{d}(\text{Ar-NO}_2)}{\mathrm{d}t}=k(\text{Ar-NO}_2)(\text{S}_2{}^{2-}) \qquad (13)$$

On the basis of the assumptions that the rate of the auto-oxidation of the hydrosulfide ion is rather rapid compared with the rate of the reduction of the nitro group, and that the reduction of the nitro group takes place not by the way of the action of the hydrosulfide ion or the monosulfide ion, but by way of that of the disulfide ion,

i) the auto-oxidation of the sulfide ion;

$$\text{S}^{2-}\xrightarrow{\text{H}_2\text{O}}\text{SH}^-\xrightarrow[\text{oxygen, etc.}]{\text{light or}}\text{S}_2{}^{2-}$$

(rather rapidly)

ii) the reduction of the nitro group;

$$\text{S}_2{}^{2-}\xrightarrow{\text{Ar-NO}_2}\text{S}_2\text{O}_3{}^{2-} \qquad \text{(slowly)}$$

it is clear that the rate can be expressed by a third-order equation, second order with respect to the hydrosulfide or the monosulfide, and first order with respect to the nitro compound. In this way the relationship between the disulfide reduction and the hydrosulfide (or the monosulfide) reduction can also be explained.

Thanks are due to Mr. Miyoshi Oshima 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.