KINETICS OF THE NITRIC ACID OXIDATION OF SULFIDES TO SULFOXIDES

Y. Ogata and T. Kamei

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

(*Received in Japan* 15 *April* 1970; *Received in the UK for publication* 3 *June* 1970)

Abstract—The nitric acid oxidation of *p,p'*-dichlorodiphenyl sulfide under air to give *p,p'*-dichlorodiphenyl sulfoxide is accompanied by autoxidation catalyzed by N_2O_4, but the reaction under nitrogen proceeds according to the stoichiometry: $ArSAr + HNO_3 \rightarrow ArSOAr + HNO_2$. The rate measurement under nitrogen in 90 vol % acetic acid by means of UV spectrophotometry affords the rate law: $v = k'[ArSAr][HNO_3][HNO_2]$. In the presence of excess nitric acid, the k value increases with increasing acidity of the media, the plot of log k vs H_0 giving a straight line with a slope of *ca* -2. This rate behaviour suggests that protonated N_2O_4 is an important attacking agent in the oxidation. The oxidation of other sulfides is discussed.

It is known that organic sulfides react with nitric acid to give organic sulfoxides, sulfones and their nitro compounds. Under suitable conditions, however, nitric acid can be an excellent reagent for the oxidation of sulfides to sulfoxides without concomitant formation of sulfones. It has been reported that the nitric acid oxidation of sulfides gives sulfoxides at *ca* 0°, but sulfones at *ca* 120°,[2–4] but there seems to be no literature on the kinetic and mechanistic study of the reaction.

The present paper describes the results of our study on the effect of oxygen, the stoichiometry and the kinetics concerning the nitric acid oxidation of organic sulfides, especially *p,p'*-dichlorodiphenyl sulfide which affords the corresponding sulfoxide in aqueous acetic acid. The kinetic study was carried out by following the formed sulfoxide by means of UV spectrophotometry. A probable mechanism is discussed on the basis of the data obtained.
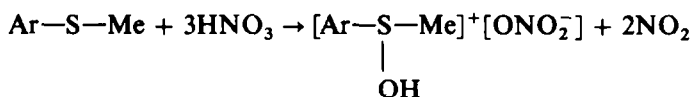
RESULTS

The reaction of diphenyl sulfide with 1·0 M HNO_3 in 70 vol % aqueous acetic acid at 40° for *ca* 3 hr gave diphenyl sulfoxide and 4-nitrodiphenyl sulfide, their yields being *ca* 80% and 20%, respectively. No diphenylsulfone and 4-nitrodiphenyl sulfoxide were detected. Oae *et al.*[5] have reported, on the basis of the dipole moment measurements, that the S atom of diaryl sulfide has the electron-releasing conjugation, while the S atom of diaryl sulfoxide and sulfone have the electron-withdrawing conjugation. These results agree with our findings that the *para*-position of diphenyl sulfide is nitrated, but diphenyl sulfoxide is not. The electron-attracting groups retard the oxidation, since no 4-nitrodiphenyl sulfoxide was obtained in the above oxidation of diphenyl sulfide.
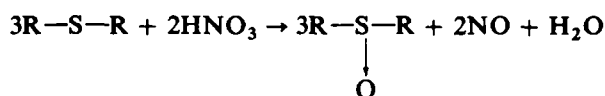
p,p'-Dichlorodiphenyl sulfide was chosen as the substrate which can be oxidized to sulfoxide but resists nitration. *p,p'*-Dichlorodiphenyl sulfide was oxidized with 1·0 M

HNO_3 in 90 vol % aqueous acetic acid at 40°, giving a quantitative yield of p,p'-dichlorodiphenyl sulfoxide. Virtually no nitration and no further oxidation of the product were observed.

Bordwell[2] put forward one of the two proposals for the stoichiometry of the nitric acid oxidation of organic sulfides to sulfoxides.

$$Ar—S—Me + 3HNO_3 \rightarrow [Ar—\underset{|}{S}—Me]^+[ONO_2^-] + 2NO_2$$
$$OH$$

Goheen's[3] proposal is:

$$3R—S—R + 2HNO_3 \rightarrow 3R—\underset{\downarrow}{S}—R + 2NO + H_2O$$
$$O$$

Neither proposal is supported by decisive evidence. Firstly, we attempted to establish the stoichiometry by measuring the concentrations of sulfide, sulfoxide and HNO_3. As shown in Table 1, the results obtained under air differ from those under N_2 atmosphere; i.e., in the oxidation under air, p,p'-dichlorodiphenyl sulfide is completely converted to the corresponding sulfoxide even when the ratio of the initial concentration of sulfide to that of nitric acid is 3:1. Nitric acid has only two oxidizable O atoms. Hence, any oxidant other than nitric acid must exist in the reaction system under air, and it must be molecular oxygen. On the other hand, the results obtained under N_2 atmosphere show that the consumption of one mole of nitric acid corresponds to the formation of one mole of the sulfoxide; i.e., the stoichiometry of the nitric acid oxidation is as follows:

$$Ar—S—Ar + HNO_3 \rightarrow Ar—\underset{\downarrow}{S}—Ar + HNO_2 \qquad (1)$$
$$O$$
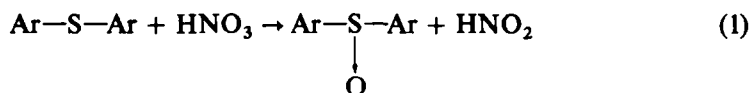
Besides, the concentration of formed nitrous acid was observed to be equal to the initial concentration of sulfide at the end of reaction.

TABLE 1. STOICHIOMETRY OF NITRIC ACID OXIDATION OF p,p'-DICHLORODIPHENYL SULFIDE TO THE SULFOXIDE IN 90 VOL % ACETIC ACID AT 40°. $[H_2SO_4] = 0.56M$

$[(p\text{-}Cl\text{-}C_6H_4\text{-})_2S]$, M		$[HNO_3]$, M	$[(p\text{-}Cl\text{-}C_6H_4\text{-})_2SO]$, M	$[(p\text{-}Cl\text{-}C_6H_4\text{-})_2SO]/[HNO_3]$
	0.06	0.04	0.06	1.5
Under air	0.08	0.04	0.08	2.0
	0.06	0.02	0.06	3.0
Under N_2	0.03	0.02	0.020	1.0
	0.05	0.02	0.023	1.1

Therefore, the kinetic study on the nitric acid oxidation of p,p'-dichlorodiphenyl sulfide to the corresponding sulfoxide was carried out under N_2 atmosphere. The conversion was nearly quantitative under these kinetic conditions as tabulated in Table 2. The rate was measured by following the sulfoxide produced. Unless sulfuric acid or sodium nitrite is added to the reaction mixture at the start, the reaction has a

long induction period. The addition of urea, a scavenger of HNO_2, stops the reaction.

The reaction was carried out with excess nitric acid with preliminary addition of H_2SO_4 and $NaNO_2$ to simplify the rate behavior. The graphical examination of the rate data shows that they fit the second-order equation:

$$v = k[ArSAr][HNO_2] = k(a - x)(b + x) \qquad (2)$$

Here, a is the initial concentration of p,p'-dichlorodiphenyl sulfide, b is that of nitrous acid and x is the concentration of the product. The concentration of HNO_2 is expressed as $(b + x)$, because of its formation as a reaction product according to Eq (1). Another rate equation, e.g., $v = k''[ArSAr]$ or $v = k'''[ArSAr][HNO_2]^{1/2}$, did not agree with the observation.

The effect of the initial concentrations of substrate and HNO_2 was examined and listed in Table 2 which supports the rate Eq (2). The rate is independent of the concentration of nitric acid because of its excess concentration.

TABLE 2. EFFECT OF THE INITIAL CONCENTRATIONS OF p,p'-DICHLORODIPHENYL SULFIDE AND NITROUS ACID IN 90 VOL % ACETIC ACID AT 40°: INITIAL CONCENTRATION: $[HNO_3] = 1\cdot2M$; $[H_2SO_4] = 0\cdot3M$

$[(p\text{-}Cl\text{-}C_6H_4\text{-})_2S]$, M	$[NaNO_2]$, M	$k \times 10^2$, $M^{-1} sec^{-1}$
0·00601	0·012	1·75
0·01198	0·012	1·99
0·01797	0·012	1·62
0·02704	0·012	1·59
0·01198	0·004	1·96
0·01198	0·008	1·78
0·01198	0·016	1·92

At the lower concentration of nitric acid, the rate data is consistent with a third-order equation:

$$V = k'[ArSAr][HNO_2][HNO_3] = k'(a - x)(b + x)(c - x) \qquad (3)$$

Here, c is the initial concentration of nitric acid. The effect of the initial concentration of nitric acid on k' at constant concentrations of the substrate (0·012 M), nitrous acid (0·004 M) and sulfuric acid (1·35 M) indicates the constancy of k' value (0·534, 0·503 and 0·480 $M^{-2} sec^{-1}$) at various initial concentrations of nitric acid (0·02, 0·04 and 0·06 M, respectively) in 90 vol % aqueous acetic acid at 40°.

The oxidation is accelerated by increasing the acidity of media. The plot of log k vs acidity function $(-H_0)$ gives a straight line with a slope of 1·8 (Fig 1), which means that two protons may participate in the transition state.

The effect of temperature was measured with initial concentrations of 0·012 M p,p'-dichlorodiphenyl sulfide, 1·2 M HNO_3, 0·004 M $NaNO_2$ and 0·3 M H_2SO_4 at 40°, 45° and 50°, giving the second-order rate constants of 1·96, 3·87 and 7·64 × 10^{-2} $M^{-1} sec^{-1}$, respectively. Arrhenius plot of these data gives a good straight line. The calculated activation energy (27·2 kcal $mole^{-1}$) is large, and the activation entropy $(-20\cdot6$ eu) is a large negative value.

In view of the rate Eq (2) for the nitric acid oxidation, the rate of the nitrous acid oxidation was examined at the concentrations of 0·012 M p,p'-dichlorodiphenyl sulfide, 0·016 M $NaNO_2$ and 1·8 M H_2SO_4 in 90 vol % aqueous acetic acid at 40°,
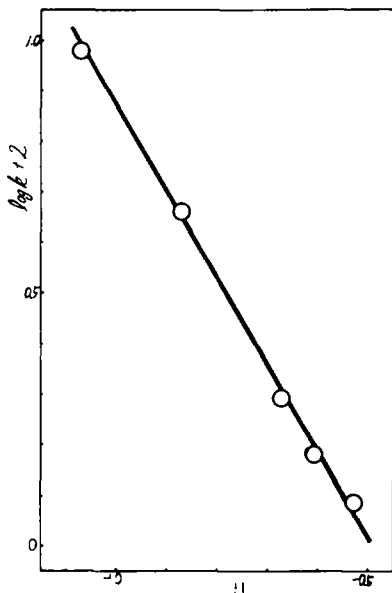
FIG. 1. Plot of log k vs H_0 for the nitric acid oxidation of p,p'-dichlorodiphenyl sulfide to the sulfoxide in 90 vol % acetic acid at 40°. Initial concentration: [Ar-S-Ar] = 0·012M: [HNO$_3$] = 1·2M: [NaNO$_2$] = 0·04M; [H$_2$SO$_4$] = 0·15–0·6M

the second-order rate constant (k) being 4.99×10^{-3} M^{-1} sec^{-1}. The rate constant of 9.55×10^{-2} M^{-1} sec^{-1} for the nitric acid oxidation at $H_0 = -1.07$ corresponds to 7.00 M^{-1} sec^{-1} at $H_0 = -2.00$ which is the acidity function in the nitrous acid oxidation. Therefore, a ratio of rate constant for HNO$_3$ and HNO$_2$ is 1400, which means that the rate of nitrous acid oxidation is so slow that it is negligible in comparison with the rate of the nitric acid oxidation. This observation is consistent with the stoichiometry of Eq (1); i.e., nitrous acid produced in the reaction cannot oxidize sulfide under these conditions.

The rate Eq (3) which is first-order in nitric acid and in nitrous acid suggests the preliminary equilibrium (4).

$$HNO_3 + HNO_2 \rightleftharpoons N_2O_4 + H_2O \qquad (4)$$
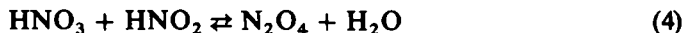
N$_2$O$_4$ produced in (4) may be an attacking species, as reported by Horner et al.[6] for the N$_2$O$_4$ oxidation of phenyl methyl sulfide.

Hence, the N$_2$O$_4$ oxidation of p,p'-dichlorodiphenyl sulfide was examined in glacial acetic acid as shown in Table 3. There is also an apparent difference in the rate data between the oxidations under air and under N$_2$ atmosphere, as observed in Table 1. Since molecular oxygen alone cannot oxidize sulfides to sulfoxides, it may be assumed that the autoxidation catalyzed by N$_2$O$_4$ competes with the oxidation by N$_2$O$_4$ itself. Under N$_2$ atmosphere, the oxidation is accelerated greatly on addition of a very small amount of acid.

The solvent effect on the rate of N$_2$O$_4$ oxidation was examined with chloroform, carbon tetrachloride, acetic anhydride, glacial acetic acid and 1,4-dioxan as solvents, where the acidity functions in their reaction solutions were observed to be nearly

TABLE 3. THE EFFECT OF ATMOSPHERE ON THE CONVERSION (%) IN THE N_2O_4 OXIDATION OF p,p'-DICHLORO-DIPHENYL SULFIDE IN ACETIC ACID AT 40°: INITIAL CONCENTRATION: $[ArSAr] = 0.017M$; $[N_2O_4] = 0.325M$

Reaction time (min)	Atmosphere Air	N_2	N_2^a
30	23.7	17.0	99
90	61.5	38.0	100

 * Addition of a small amount of H_2SO_4.

equal. These solvents apparently affected the rate as shown in Table 4, i.e., the oxidation rate decreases in the order:

$$CHCl_3 > CCl_4 \approx Ac_2O > AcOH \gg Dioxan$$
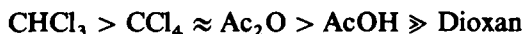
This order seems to show that the solvation for N_2O_4 tends to retard the reaction, but that the polarity of solvent accelerates it as will be described later.

If H_2O is added in the system, nitric acid should be produced according to Eq (4) and the nitric acid oxidation should take place as well. Therefore, the reaction was carried out only in anhydrous solvents.

TABLE 4. SOLVENT EFFECT ON THE CONVERSION (%) OF THE N_2O_4 OXIDATION OF p,p'-DICHLORODIPHENYL SULFIDE AT 40°: INITIAL CONCENTRATION: $[ArSAr] = 0.0134M$; $[N_2O_4] = 0.29M$
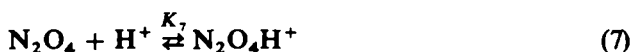
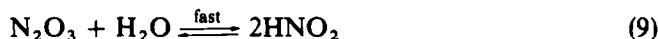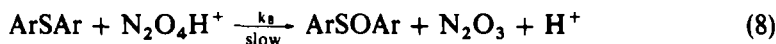| Reaction time (min)	Solvent (Dielectric const. at 20°) CHCl₃ (4.806)	CCl₄ (2.238)	Ac₂O (20.5)	AcOH (6.15)	1,4-dioxan (2.209)ᵃ
10	75	52	49	9	0
30	87	60	56	16	0
90	96	74	74	31	0
180	100	92	91	50	0

 * Dielectric constant at 25°.

DISCUSSION

The observed facts are summarized as follows: (i) The rate is expressed as $v = k'[Ar\text{–}S\text{–}Ar][HNO_3][HNO_2]$. (ii) The rate is proportional to h_0^2, where $-\log h_0 \ (= H_0)$ is acidity function. (iii) Nitrous acid is an excellent initiator for the reaction, and the reaction is stopped by addition of urea, a scavenger of nitrous acid. (iv) The rate of the nitric acid oxidation is much faster than the rate of the nitrous acid oxidation. (v) The reaction is retarded by electron-attracting groups in benzene rings of the sulfide. (vi) The N_2O_4 oxidation is accelerated by increasing the polarity of solvent and retarded by the solvation of N_2O_4.

The findings suggest a following mechanism as a most probable one.

$$H^+ + NO_3^- \overset{K_5}{\rightleftharpoons} HNO_3 \tag{5}$$

$$HNO_3 + HNO_2 \overset{K_6}{\rightleftharpoons} N_2O_4 + H_2O \tag{6}$$

$$N_2O_4 + H^+ \overset{K_7}{\rightleftharpoons} N_2O_4H^+ \tag{7}$$

$$ArSAr + N_2O_4H^+ \xrightarrow[\text{slow}]{k_8} ArSOAr + N_2O_3 + H^+ \qquad (8)$$

$$N_2O_3 + H_2O \underset{\text{}}{\overset{\text{fast}}{\rightleftharpoons}} 2HNO_2 \qquad (9)$$

This mechanism, where the rate is determined by step 8, leads to the rate equation:

$$v = k_8[ArSAr][N_2O_4H^+] = k_8 K_5 K_6 K_7[H^+]^2[NO_3^-][HNO_2][ArSAr]/[H_2O]$$

because equilibria 5–7 seem to be much shifted to the left side. This rate equation is consistent with the observed one.

The mechanism also explains above observations (iii)–(v), i.e., the need of nitrous acid for the initiation, the slow oxidation with nitrous acid alone, and the electrophilic nature of attacking species because of the retardation of the reaction with electron-attracting groups in the sulfide.

There is still a problem whether N_2O_4 attacks homolytically or heterolytically. It is well known that N_2O_4 in the media of a high dielectric constant almost completely dissociates mainly by heterolysis,[7, 8] but it dissociates homolytically in non-polar solvents.[8]

$$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad (10)$$

The oxidation proceeded much faster in chloroform or carbon tetrachloride than in acetic acid or acetic anhydride or dioxan as shown in Table 4. Therefore, the homolytic dissociation of N_2O_4 to NO_2 may be important in this reaction. But the rate should depend on half order of the concentrations of nitric and nitrous acids, if NO_2 were an attacking species; also it has been reported that dioxan,[9] acetic anhydride[10] and acetic acid[10] can form stable complexes (II–IV) with N_2O_4, but chloroform and carbon tetrachloride cannot.
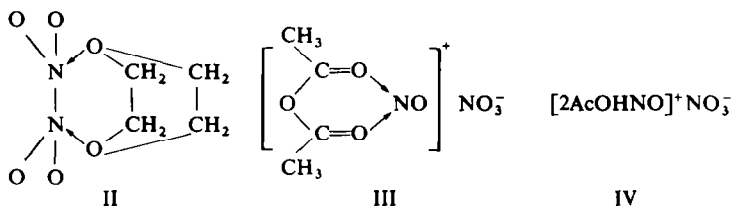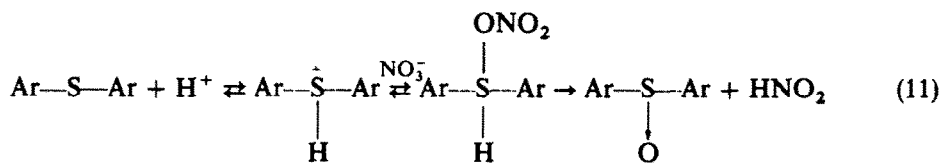

Therefore, it is probable that the rate is affected by the solvation of N_2O_4.

The effect of molecular oxygen in the nitric acid oxidation may be explained in view of the conversion of N_2O_3 to N_2O_4 by molecular oxygen (Eq (9)). But it has been reported[8] that this conversion is so slow. Therefore, it seems to be probable that molecular oxygen attacks homolytically an intermediate produced from p,p'-dichlorodiphenyl sulfide and N_2O_4. Hence, it is possible that N_2O_4 itself attacks sulfide homolytically. A nucleophilic attack of N_2O_4 or NO_3^- on the S atom is excluded, since more electrophilic p-nitrodiphenyl sulfide could not be oxidized to the corresponding sulfoxide.

Steps 5 and 7 are proposed in view of the acidity effect which suggests the participation of two protons. Since nitric acid is a strong acid, it should dissociate completely under these conditions.[10]

The other schemes, e.g., (11) or (12) might also explain the participation of two protons.

$$Ar\!-\!S\!-\!Ar + H^+ \rightleftharpoons Ar\!-\!\overset{+}{\underset{H}{S}}\!-\!Ar \overset{NO_3^-}{\rightleftharpoons} Ar\!-\!\overset{\overset{\displaystyle ONO_2}{|}}{\underset{H}{S}}\!-\!Ar \rightarrow Ar\!-\!\overset{}{\underset{O}{S}}\!-\!Ar + HNO_2 \qquad (11)$$

$$N_2O_4 + H^+ \rightleftharpoons NO^+ + HNO_3 \qquad (12)$$

These schemes, however, do not fit the observed rate equation; i.e., according to (11), the rate must be independent of the concentration of nitrous acid, and in the case of (12), the rate must be independent of the concentration of nitric acid.

Our previous papers have reported on the nitric acid oxidation in an open vessel,[11-14] where the concentration of N_2O_4 or NO_2 was kept constant at the stationary state, but most of the present reactions were conducted in a closed system, hence, we can see the dependence of rate on the concentrations of nitric and nitrous acids.

An attempted kinetic study on the nitric acid oxidation of dimethyl sulfide was unsuccessful because of the difficulty in determining the concentrations of reactant and product by the UV spectrophotometry (similar absorption peaks for the sulfide and sulfoxide) and chemical analysis (iodometry of produced sulfoxide[15]).

EXPERIMENTAL

Materials. Diphenyl sulfide was prepared by the Friedel–Crafts reaction of benzene with sulfur dichloride,[16] b.p. 99–101° (1 mm) [lit. b.p. 162–163° (18 mm)]. Diphenyl sulfoxide was prepared by the Friedel–Crafts reaction of benzene with thionyl chloride,[17] m.p. 70–71° (lit. m.p. 70–71°). *p,p'*-Dichlorodiphenyl sulfide, m.p. 93–94° (lit.[18] m.p. 95–96°), and *p,p'*-dichlorodiphenyl sulfoxide. m.p. 143–144° (lit.[19] m.p. 143–145), were prepared similarly. The products were identified by means of IR, UV and TLC. Dinitrogen tetroxide was prepared by the pyrolysis of dinitrogen pentoxide.[20] Nitric acid was of guaranteed
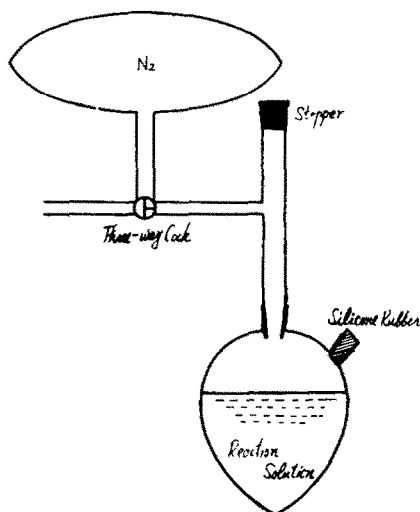

FIG. 2. Apparatus for the nitric acid oxidation of sulphide to sulfoxide

grade. Commercial glacial acetic acid (b.p. 118°), dioxan (b.p. 101°), carbon tetrachloride (b.p. 77°), chloroform (b.p. 61°) and acetic anhydride (b.p. 139°) were purified by ordinary methods and rectified.

Preparation of the reaction solution. Fig 2 shows the apparatus (a 100-ml flask) for the study of stoichiometry and kinetics. The following method was used for the elimination of oxygen out of the reaction soln. After addition of all reagents into the flask cooled by Dry Ice–MeOH or liquid N_2, one neck of the flask is stoppered with a silicone rubber, and another neck is connected with a 3-way cock. One way of the cock was connected with a balloon filled with N_2 gas. After freezing of the reaction mixture, the air in the flask was removed by evacuation through another way of the cock. Then N_2 gas was introduced through the cock, and the mixture frozen again. This procedure was repeated four times and finally the flask is filled with N_2 gas at atmospheric press.

Kinetics. The reaction was started in a thermostat. Aliquots (2 ml) were taken out at appropriate intervals of time by an injector through the rubber stopper, neutralized with alkali, and then extracted with chloroform. The extract was diluted to *ca* 1/625 with MeOH, and the concentration of sulfoxide was measured by means of UV spectrophotometry at 252 and 256·5 mμ. This analytical method of the produced sulfoxide gave good results.

Measurement of the acidity function: The Hammett acidity function[21] was measured spectrophotometrically using 4-chloro-2-nitroaniline as an indicator.

Measurement of the nitrous acid concentration. Nitrous acid was reacted with sulfanilic acid. The formed diazonium salt was reacted with α-naphthylamine to give an azo dye. The content of HNO_2 was estimated by measuring the absorbance of the azo dye at 535 mμ.

REFERENCES

[1] Contribution No. 151
[2] F. G. Bordwell and P. J. Bontan, *J. Am. Chem. Soc.* **79**, 717 (1957)
[3] D. W. Goheen and C. F. Bennett, *J. Org. Chem.* **26**, 1331 (1961)
[4] A. Compagnini, P. Fiandata, N. Marziano and R. Passerini, *Ann. Chim. Rome* **57**, (6), 732 (1967)
[5] Y. Yoshiyasu, Y. Taniguchi, K. Kimura, R. Fujishiro, M. Yoshihara, W. Tagaki and S. Oae, *Bull. Chem. Soc. Japan* **42**, 1878 (1969)
[6] L. Horner and F. Hübenett, *Liebigs Ann.* **579**, 193 (1953)
[7] J. D. S. Goulden and D. J. Millen, *J. Chem. Soc.* 2620 (1950)
[8] P. Gray and A. D. Yoffe, *Chem. Rev.* **55**, 1069 (1955)
[9] H. H. Sisler, *J. Chem. Educ.* **34**, 555 (1957)
[10] C. C. Addison and J. Lewis, *Quart. Rev.* **9**, 115 (1955)
[11] Y. Ogata, Y. Sawaki, F. Matsunaga and H. Tezuka, *Tetrahedron* **22**, 2655 (1966)
[12] Y. Ogata and Y. Sawaki, *J. Am. Chem. Soc.* **88**, 5832 (1966)
[13] Y. Ogata, H. Tezuka and Y. Sawaki, *Tetrahedron* **23**, 1007 (1967)
[14] Y. Ogata, H. Tezuka and T. Kamei, *J. Org. Chem.* **34**, 845 (1969)
[15] S. Allenmark, *Acta Chem. Scand.* **20**, 910 (1966)
[16] W. W. Hartman and R. Phillips, *Organic Syntheses* Coll. Vol. 2, p. 242. Wiley, New York, N.Y. (1950)
[17] R. L. Shriner, H. C. Struck and W. J. Jorison, *J. Am. Chem. Soc.* **52**, 2060 (1930)
[18] E. Bergmann and M. Tschudnowsky, *Z. phsik. Chem.* (B) **17**, 107, 111 (1932)
[19] E. Bergmann and M. Tschudnowsky, *Ber. Dtsch. Chem. Ges.* **65**, 457, 461 (1932)
[20] A. Pedlerand and F. H. Pollard, *Inorganic Syntheses* Vol. 5, p. 87. McGraw-Hill, New York, N. Y. (1957)
[21] M. A. Paul and F. A. Long, *Chem. Rev.* **57**, 1 (1957)