hours on a shaking machine. Cellulose samples required from four to five days at 20° with shaking for the same degree of esterification; the hemicelluloses reacted very slowly, a high degree of tosylation requiring from two to three weeks. The esters had nitrogen contents of 0.05% or less.

Thiocyanation and Iodination

Replacement of tosyloxy by thiocyanate was effected by heating a mixture of 2 g. of tosyl ester, 200 ml. of freshly distilled acetonyl acetone, and 6 g. of sodium thiocyanate (dried *in vacuo* at 100°) under anhydrous conditions at 110–112° for periods of time as indicated in Table I. Low values for nitrogen were usually obtained unless the reaction mixture was heated for at least five hours.

The starch and mannogalactan tosylates were almost completely soluble in the hot reaction medium, the cellulose tosylates were partly soluble and the hemicellulose esters swelled without appreciable solution. The thiocyanotosylates were recovered in quantitative yields by pouring into four volumes of ice water. The esters were washed repeatedly with distilled water, 95% ethanol, and finally with ether. For analyses, they were dried *in vacuo* at 70° over phosphorus pentoxide. The thiocyano derivatives when dried were powdery materials, white to a light grey in color. Their solubility behavior was very similar to that of the corresponding iodo compounds.

Iodination was performed under conditions comparable to the thiocyanation procedure. Five grams of sodium iodide was used for each gram of tosyl ester and 100 ml.

of acetonyl acetone. No apparent difference was noted in iodination at 100 and 110°, although thiocyanation at the lower temperature was, in some cases, slightly slower than at 110°.

Summary

The replacement of tosyloxy in the primary position by thiocyanate has been found to be applicable to several polysaccharide tosyl esters. When applied to potato starch, cellulose, and guar mannogalactan, the reaction had approximately the same degree of specificity for replacement of the tosyloxy group in the primary position as the iodination reaction.

Both thiocyanation and iodination of the tosylate of the water-soluble polysaccharide of guar indicate that approximately half of the primary hydroxyl groups are involved in linkages.

Thiocyanation and iodination of a corn-cob hemicellulose tosyl ester and iodination of a lima bean pod hemicellulose tosylate yielded substitution to a greater extent than was expected, from the structure of these materials, indicating that possibly some secondary tosyloxy groups were replaced.


[COMMUNICATION No. 1167 FROM THE KODAK RESEARCH LABORATORIES]

## Oxidation Processes. XXI.[1]   The Autoxidation of the p-Phenylenediamines

BY JAMES E. LuVALLE, DUDLEY B. GLASS AND ARNOLD WEISSBERGER

Introduction

Previous papers of this series discussed the autoxidation of α-ketols, I,[2] enediols, II,[3] hydroquinones, III,[4] and α-aminoketones, IV.[5] The present paper deals with the autoxidation of p-phenylenediamines, VI, and, briefly, of p-aminophenols, V.
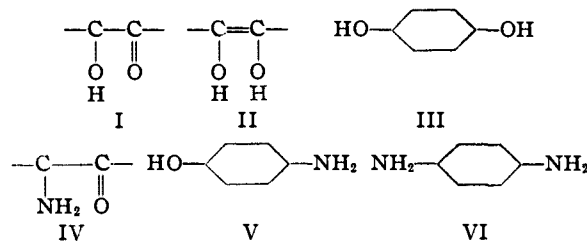
Like the dihydroxy compounds, these substances react with molecular oxygen, and the reaction proceeds in two univalent steps.[6] From the re-

$$R + O_2 \longrightarrow T + H_2O_2 \qquad (1)$$
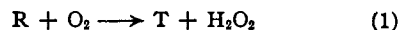
sults of earlier papers of this series,[3,4,5] the rate of the over-all reactions can be expected to depend upon the rate of formation of the semiquinone, upon its concentration in the various equilibria involved, and upon its reactivity with oxygen.

The intensely colored intermediate products of p-phenylenediamines, *Wurster's salts*, exist as free radicals, semiquinones, in dilute solution,[6] and as dimers or higher polymers in higher concentration.[6c] These semiquinones are much more stable than the corresponding fully oxidized quinonediimines,[6b,7] and quinoneimines[7] which are readily hydrolyzed to the corresponding quinones. Moreover, the higher N-methylated diamines undergo a demethylation reaction when oxidized. Thus, N,N'-tetramethyl-p-phenylenediimine loses a methyl group with formation of N,N'-trimethyl-p-phenylenediamine and formaldehyde,[6,7] and N,N'-tetramethyl-, N,N'-trimethyl-, and N-dimethyl-p-phenylenediamine couple in oxidizing solutions with a p-substituted phenol to give an identical indoaniline dye.[8] The latter reaction shows that the trimethyl-p-phenylenedi-

(1) XX. LuValle and Weissberger, THIS JOURNAL, **69**, 1821 (1947).

(2) (a) Weissberger, Mainz and Strasser, *Ber.*, **62**, 1942 (1929); (b) Weissberger and Bach, *J. Chem. Soc.*, 226 (1935).

(3) Weissberger and LuValle, THIS JOURNAL, **66**, 700 (1944).

(4) (a) James and Weissberger, *ibid.*, **60**, 98 (1938); (b) James, Snell and Weissberger, *ibid.*, **60**, 2084 (1938); (c) LuValle and Weissberger, Part XIX, *ibid.*, **69**, 1576 (1947).

(5) James and Weissberger, *ibid.*, **59**, 2040 (1937).

(6) (a) Michaelis and Hill, *ibid.*, **55**, 1487 (1933); (b) Michaelis, Schubert and Granick. *ibid.*, **61**, 1981 (1939); (c) Michaelis and Granick. *ibid.*, **65**, 1747 (1943).

(7) (a) Willstätter and Meyer, *Ber.*, **37**, 1494 (1904); (b) Willstätter and Pfannenstiel, *ibid.*, **37**, 4605 (1904); (c) Willstätter and Kubli, *ibid.*, **42**, 4135 (1909).

(8) W. R. Ruby, of these Laboratories, private communication.

amine also undergoes demethylation upon oxidation in a rapid reaction.

The concentration of *Wurster's salts*, the semiquinones, in the equilibrium

$$R + T \rightleftharpoons 2S \qquad (2)$$

increases with increasing methylation of the amino group.[6b] The *rate of reaction* of the semiquinones with molecular oxygen may also be expected to vary within wide limits, depending on kind and number of substituents.

In a first approximation we consider resonance as the main stabilizing factor for the semiquinones.[6] The principal structures of the semiquinones of *p-phenylenediamine* are given in Fig. 1a. The cationic semiquinone, SH_2^+, has three pairs of equivalent structures, the neutral molecule, SH, has no equivalent structures, and the anionic semiquinone, S^-, has again three equivalent structures. For this reason, SH_2^+ and S^- should be stable and exist in appreciable concentrations in their respective pH ranges, at variance with SH, which is expected to be unstable. When two R groups are on one hydrogen, the negative semiquinone ion will not be stabilized by structures shown in Fig. 1a.

The ionic species for the N-alkylated-*p*-phenylenediamines are given in Fig. 2a. The semiquinones of *monalkyl-p-phenylenediamine*

a', b, b', c and c' and is therefore probably about as unstable as the neutral semiquinone. *Trialkyl-p-phenylenediamines* do not form an anionic semiquinone, and *tetramethyl-p-phenylenediamine* even lacks a neutral semiquinone.

The principal resonance forms of the semiquinones of the *p*-aminophenols are given in Fig. 1b. None of the semiquinones has equivalent resonance states. The neutral semiquinone, SH, is probably represented by group (b) because the hydroxyl group will lose a proton more readily than the amino group. The structures of group (a) under SH are tautomers of the structures of group (b).

The ionic species for the semiquinones of the three types of *p*-aminophenols are given in Fig. 2b. The dimethyl semiquinone exists only as SH_2^+ and SH. The remainder may exist as cation, neutral molecule, or anion depending on the pH.

Michaelis and Schubert[9] have investigated the dependence of the *concentration of certain semiquinones* upon pH. If the oxidized form, T, is stable, the semiquinone concentration has a maximum when half of the initial quantity of diamine is oxidized, *i. e.*, when R = T. At this point

$$(S/a)_{max.} = \sqrt{K_s}/(2 + \sqrt{K_s}) \qquad (3)$$

where a is the concentration of R + T + S[9] and

A
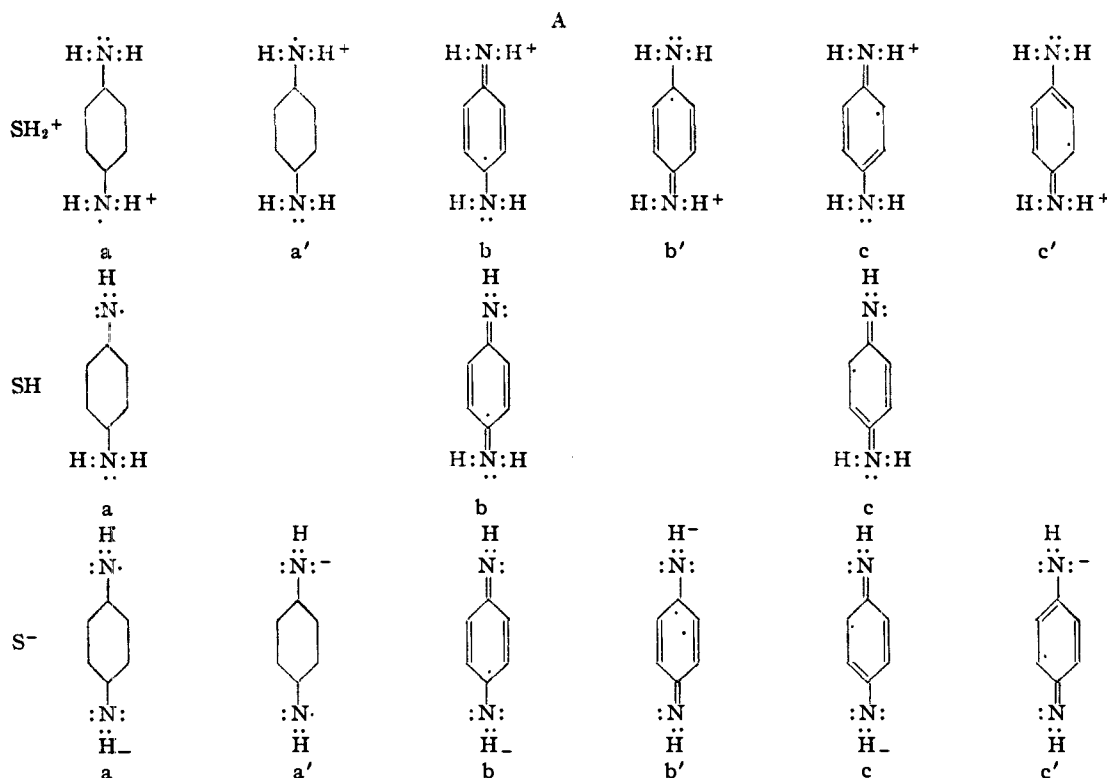
and *s-dialkyl-p-phenylenediamine* resemble *p*-phenylenediamine. The anionic semiquinone of *as-N-dialkyl-p-phenylenediamine* lacks structures

(9) (a) Michaelis and Schubert, *Chem. Rev.*, **22**, 437 (1938); (b) Michaelis, *Annals N. Y. Acad. Sci.*, **40**, 39 (1940); (c) Schubert. *ibid.*, **40**, 111 (1940).
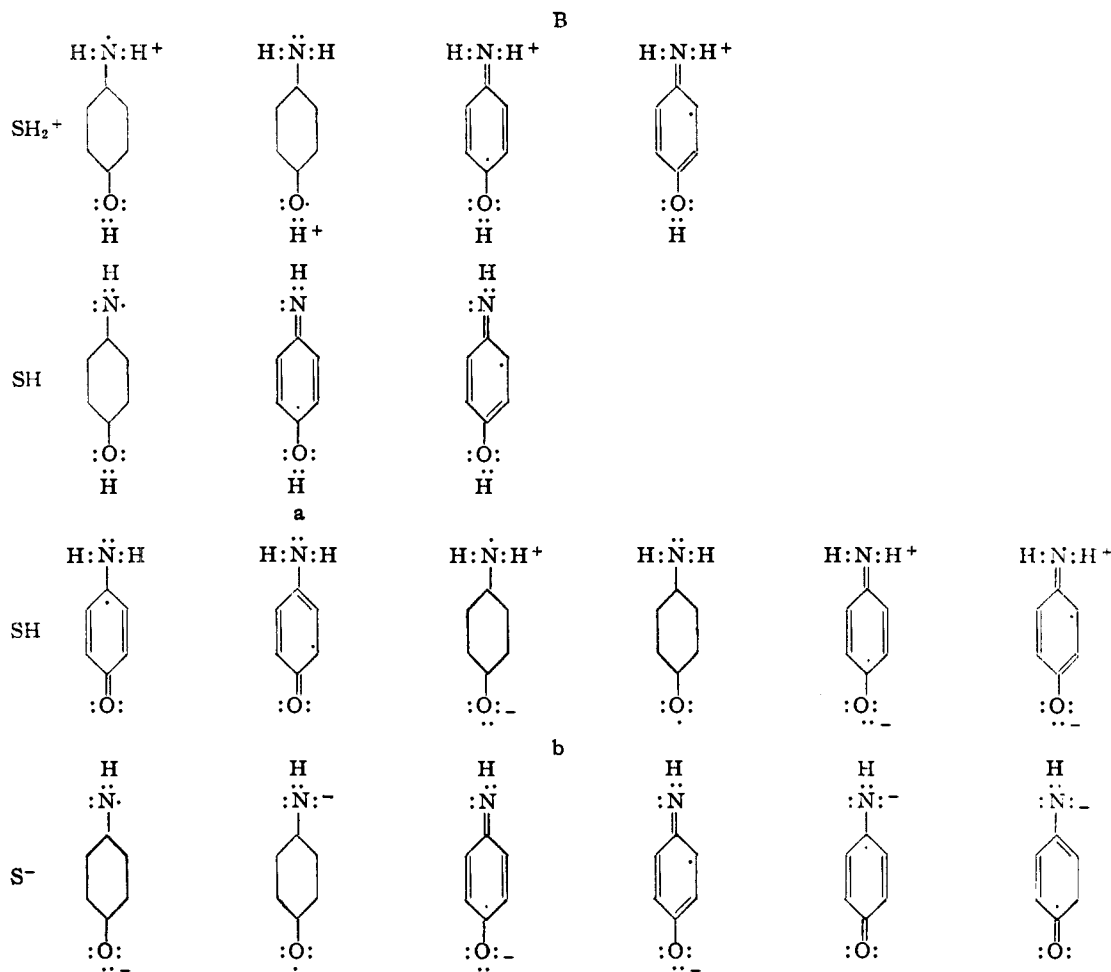
Fig. 1.—(A) Principal structures of the p-phenylenediamine semiquinones. (Note that the anionic semiquinone would only occur for the N-dialkyl-substituted diamine.)   (B) Principal structures of the p-aminophenol semiquinones. (Note that for the neutral semiquinone, structures b are much more likely than structures a.   Structures a are tautomeric with structures b.)

K_s is the semiquinone formation constant of equation (2).

Semiquinone formation constants for oxonine over the pH range −6 to +12 are plotted in Fig. 3 from the data of Table II of Michaelis and Granick.[10] The ionic states of R, S and T are those assigned by these authors. The figure shows that
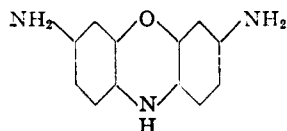
the concentrations of the several *ionic species of S* go through two minima and one maximum between pH 2 and 12.

If the rate of a reaction is determined by the over-all semiquinone concentration, then the rate at 50% completion will vary with pH as $(S/a)_{max}$. However, according to Figs. 1 and 2, SH_2^+, SH and S− cannot be expected to have the same

(10) Michaelis and Granick, THIS JOURNAL, **63**, 1636 (1941).

reactivity. Differences in the reactivity of the ionic species will therefore be superimposed upon the changes in semiquinone concentration with pH. It follows that quite complicated rate–pH curves can be expected for substances such as the p-phenylenediamines.

Experimental

Technique, Materials, Calculations

The techniques and apparatus were the same as in previous investigations of this series.[2,3,4,5] Measurements of pH were made with a Beckman Model G pH meter. The temperature of the thermostat was 19.97 ± 0.02°. Buffers were C. P. or reagent grade chemicals and used at a concentration of 0.200 M. Doubly distilled water was used in all experiments, and absolute alcohol in making the aqueous alcoholic solutions.

All experiments reported in this paper were run in solutions 0.005 M in potassium thiocyanate and potassium cyanide, respectively. Under these conditions, metallic-ion catalysis was negligible, and the data were reproducible. In the absence of these substances, the experiments were very erratic. In some experiments, in absence of potassium cyanide and potassium thiocyanate, cupric ion was added. This eliminated the induction period and increased the total uptake by approximately 50%.

A

p-Phenylenediamines

| | NH₂ | HNR | HNR | NR₂ | NR₂ | NR₂ |

$$\begin{array}{cccccc}
\text{NH}_2 & \text{HNR} & \text{HNR} & \text{NR}_2 & \text{NR}_2 & \text{NR}_2 \\
 & & & & & \\
\text{NH}_2 & \text{NR}_2 & \text{HNR} & \text{NH}_2 & \text{HNR} & \text{NH}_2
\end{array}$$

Semiquinones

Cation	SH_2^+	SH_2^+	SH_2^+	SH_2^+	SH_2^+	SH_2^+
Neutral	SH	SH	SH	SH	SH	
Anion	S⁻	S⁻	S⁻	S⁻		

B

p-Aminophenols

$$\begin{array}{ccc}
\text{NH}_2 & \text{RNH} & \text{NR}_2 \\
 & & \\
\text{O} & \text{O} & \text{O} \\
\text{H} & \text{H} & \text{H}
\end{array}$$

Semiquinones

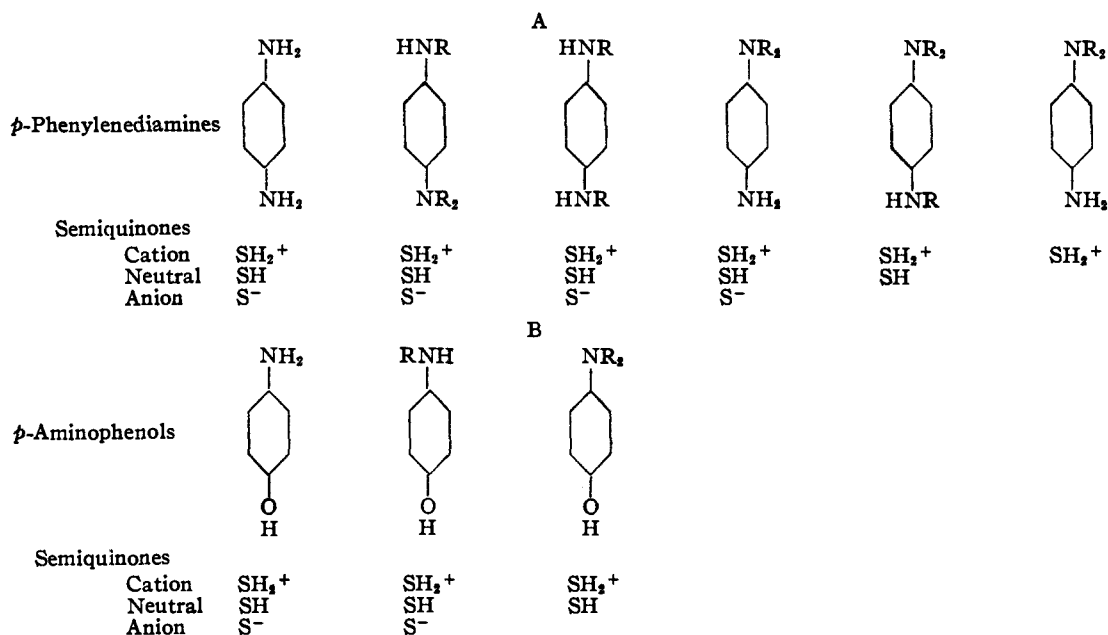|			
Cation	SH_2^+	SH_2^+	SH_2^+
Neutral	SH	SH	SH
Anion	S⁻	S⁻	

Fig. 2.—(A) Ionic species of the p-phenylenediamines; R represents any alkyl group, usually CH_3 or C_2H_5. (B) Ionic species of the p-aminophenols.

The final products of the reaction of diaminodurene were identified as duroquinone by mixed melting point, ammonia by smell, and hydrogen peroxide.[2a] The overall consumption of oxygen indicates a similar course of the oxidation of the other compounds reported in this paper. However, the hydrogen peroxide presumably reacts with the quinonoid products.

Organic Preparations

Eastman Kodak Co. Grade chemicals were used as starting materials for the preparation of all compounds. When working with the free bases, they were kept under an atmosphere of hydrogen or nitrogen to reduce oxidation by the air. All of the products were dried in a vacuum desiccator over sulfuric acid. High-grade filter paper (e. g., Whatman no. 12) was used for all filtrations.

p-Phenylenediamine Dihydrochloride.—Fifty-four grams of p-phenylenediamine was dissolved in a solution of 200 ml. of water and 90 ml. of concentrated hydrochloric acid. The resulting solution was treated with Filtrol and filtered while still hot. The dihydrochloride was precipitated by the addition of 100 ml. of concentrated hydrochloric acid. The product was removed by filtration, dissolved in 200 ml. of hot water, and precipitated with 100 ml. of concentrated hydrochloric acid. The precipitate was removed by filtration, washed with alcohol, and dried.

N-Methyl-p-phenylenediamine Dihydrochloride.—The salt was recrystallized twice from three volumes of methanol which contained a few drops of concentrated hydrochloric acid.

N,N'-Dimethyl-p-phenylenediamine Dioxalate.—The salt .was recrystallized twice from 60% aqueous alcohol. In the first recrystallization the hot solution was treated with Darco and filtered; in the second recrystallization, the hot solution was filtered without the Darco treatment.

N,N-Dimethyl-p-phenylenediamine Hydrochloride.— N,N-Dimethyl-p-phenylenediamine was distilled under reduced pressure. The fraction that boiled at 134–135° at 12 mm. (68 g.) was collected and converted to the hydrochloride by dissolving in 200 ml. of methanol and 43 ml. of concentrated hydrochloric acid. The solution was allowed to stand at 0° until crystallization was complete. The precipitate was removed by filtration and recrystallized from methanol.

N,N,N'-Trimethyl-p-phenylenediamine Dihydrochloride.—This material was prepared satisfactorily in fairly large batches from N,N-dimethyl-p-phenylenediamine by a modification of the method used by Michaelis, Schubert and Granick.[6b]

A mixture of 170 g. of N,N-dimethyl-p-phenylenediamine hydrochloride, 190 g. of p-toluenesulfonyl chloride, and 400 ml. of pyridine was heated on the steam-bath for two hours. At the end of this time, the reaction mixture was poured into 2 liters of water and stirred until crystallization occurred. The precipitate was removed by filtration, washed with water, and recrystallized from 95% alcohol. There resulted 190 g. of 4'-dimethylamino-p-tolylsulfonanilide which melted at 125–126°.

A solution of 11.5 g. of sodium in 500 ml. of absolute alcohol was added to 145 g. of 4'-dimethylamino-p-tolylsulfonanilide in 1 liter of absolute alcohol. After 75 g. of methyl iodide had been added, the mixture was boiled under reflux for twenty hours. At the end of this time, 800 ml. of 5% alkali was added and the alcohol was removed by distillation under reduced pressure. The residue was diluted with 1.5 liters of warm water and the mixture was stirred for thirty minutes. The precipitate was removed by filtration, washed with water, and recrystallized twice from 95% alcohol. The resulting 4'-dimethylamino-N-methyl-p-tolylsulfonanilide (80 g.) melted at 101–101.5°. Anal. Calcd. for $C_{16}H_{20}N_2O_2S$: N, 9.20. Found: N, 9.20.

The 4'-dimethylamino-N-methyl-p-tolylsulfonanilide (41 g.) was hydrolyzed by heating on the steam-bath for four hours with 40 ml. of acetic acid and 80 ml. of concentrated sulfuric acid. The reaction mixture was dissolved in 800 ml. of water and made alkaline with 275 ml. of 40% sodium hydroxide. The diamine[11] was extracted with ether, the ethereal solution was dried over sodium hydroxide pellets, and the ether was evaporated. The residue was dissolved in 375 ml. of acetone and the salt was precipitated by the addition of 20 ml. of concentrated hydrochloric acid. The precipitate was removed by filtration, washed with acetone, and dissolved in 100 ml. of warm methanol containing 1 ml. of concentrated

(11) Care should be taken to prevent the diamine from coming in contact with the skin. It has a strong irritating and numbing action.
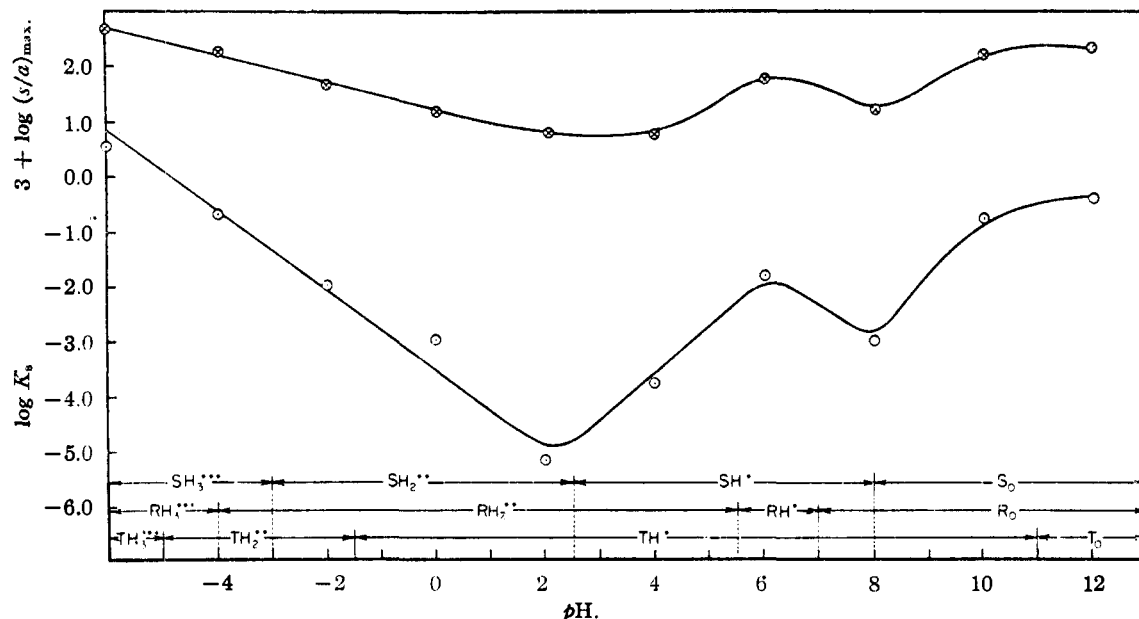
Fig. 3.—Oxonine: -O-O-, log K_s-pH; -⊗-⊗-, 3 + log $(S/a)_{max}$.-pH, S_0 and SH_2^{+++} are quite stable; SH^+ and SH_2^{++} exist only at low concentrations. Data are from Table II of Michaelis and Granick (THIS JOURNAL, **63**, 1636 (1941)).

hydrochloric acid. This solution was diluted slowly with 250 ml. of acetone. The product was removed by filtration, washed with acetone, and dried; yield, 19 g.

N,N,N′,N′-Tetramethyl-p-phenylenediamine Dihydrochloride.—The salt was recrystallized twice from 85% aqueous alcohol which contained a small amount of concentrated hydrochloric acid.

Octamethyl-p-phenylenediamine was prepared from diaminodurene and methyl iodide.[6d] The hydrochloride was recrystallized from 1,2-ethanol acetone.

N,N-Diethyl-p-phenylenediamine Hydrochloride.—The free base was distilled under reduced pressure. The fraction that boiled at 115–116° at 5 mm. (131 g.) was dissolved in 200 ml. of absolute alcohol, and 68 ml. of concentrated hydrochloric acid was added. The salt which crystallized was removed by filtration, washed with alcohol containing a little hydrochloric acid, and dried.

N,N-Di-n-propyl-p-phenylenediamine Sulfate.—A solution of 177 g. of N,N-di-n-propylaniline in a mixture of 1 liter of water and 250 ml. of concentrated hydrochloric acid was cooled to 0° and 70 g. of sodium nitrite in 200 ml. of water was added during a period of five minutes. The solution was stirred at 0–1° for thirty minutes and then made alkaline with 200 ml. of concentrated ammonium hydroxide. The crystals were removed by filtration, washed with water, and recrystallized twice from 95% alcohol. There resulted 85 g. of N,N-di-n-propyl-4-nitrosoaniline which melted at 43–44°. Anal. Calcd. for $C_{12}H_{18}N_2O$: N, 13.58. Found: N, 13.70.

N,N-Di-n-propyl-4-nitrosoaniline (20.6 g.) was placed in the Parr reduction apparatus with 100 ml. of absolute alcohol and 5 g. of Raney nickel, and reduced at a temperature of 60° and a hydrogen pressure of 3 atmospheres. The reaction mixture was filtered and a solution of 5.6 ml. of concentrated sulfuric acid in 25 ml. of absolute alcohol was added. The precipitate was removed by filtration, washed with alcohol, and recrystallized from 125 ml. of absolute alcohol. The product weighed 20 g. Anal. Calcd. for $C_{12}H_{20}N_2 \cdot H_2SO_4$: N, 9.65. Found: N, 9.35.

4-Amino-N,N-dimethyl-o-toluidine Dihydrochloride.—N,N-Dimethyl-4-(p-nitrophenylazo)-o-toluidine was prepared by the method of Fieser and Thompson[12] and recrystallized from acetic acid. The melting point of this

(12) Fieser and Thompson, THIS JOURNAL, **61**, 376 (1939).

material was 121–122°. The azo compound (28.4 g.) was placed in the Parr reduction apparatus with 100 ml. of absolute alcohol and 5 g. of Raney nickel, and reduced at a temperature of 50° and a hydrogen pressure of 3 atmospheres. The catalyst was removed by filtration and the alcohol was distilled under reduced pressure. Acetic anhydride (50 ml.) was added and the mixture was heated on the steam-bath for one hour. The reaction mixture was diluted with 300 ml. of water, neutralized with sodium carbonate, and acidified with 50 ml. of concentrated hydrochloric acid. The mixture was stirred for ten minutes and the precipitate was removed by filtration. The filtrate was made alkaline with 40% sodium hydroxide solution and the product extracted with ether. The ethereal solution was dried over anhydrous magnesium sulfate and the ether was evaporated. The residue (15.6 g.) was dissolved in 100 ml. of 15% hydrochloric acid and the solution was boiled under reflux for one hour. This solution was concentrated to a thick syrup under reduced pressure and the residue was crystallized from 60 ml. of absolute alcohol. The product was removed by filtration, washed with absolute alcohol, and recrystallized from absolute alcohol containing a little concentrated hydrochloric acid. There resulted 12 g. of product. Anal. Calcd. for $C_9H_{14}N_2 \cdot 2HCl$: N, 12.55. Found: N, 12.66.

4-Amino-N,N-diethyl-m-toluidine Hydrochloride.—The salt was recrystallized twice from 95% alcohol which contained 2% concentrated hydrochloric acid.

Diaminodurene Dihydrochloride.—Dinitrodurene (21 g.) was placed in the Parr reduction apparatus with 100 ml. of absolute alcohol and 3 g. of Raney nickel, and reduced at a temperature of 60° and a hydrogen pressure of 3 atmospheres. The catalyst was removed by filtration and 50 ml. of concentrated hydrochloric acid was added, all at once, with vigorous stirring. The precipitate was removed by filtration and dissolved in boiling water. This solution was treated with Darco, filtered, and diluted with 25 ml. of concentrated hydrochloric acid. The precipitate was removed by filtration and recrystallized as before but without the Darco treatment. There resulted 15 g. of diaminodurene dihydrochloride. Anal. Calcd. for $C_{10}H_{16}N_2 \cdot 2HCl$: N, 11.81. Found: N, 11.98.

1-(p-Aminophenyl)-pyrrolidine Hemisulfate Dihydrate.—A mixture of 13.4 g. of p-nitrochlorobenzene and 12.1 g. of pyrrolidine was heated at 95–100° in a sealed tube

for six hours. The reaction mixture was stirred with 100 ml. of water and the product was removed by filtration, washed with water, and recrystallized twice from acetic acid. There resulted 10 g. of 1-(p-nitrophenyl)-pyrrolidine that melted at 167–168°. *Anal.* Calcd. for $C_{10}H_{12}N_2O_2$: N, 14.58. Found: N, 14.62.

The 1-(p-nitrophenyl)-pyrrolidine (10 g.) was placed in 100 ml. of absolute alcohol and reduced to the diamine by the method used to reduce dinitrodurene. The catalyst was removed by filtration and a solution of 2.8 ml. of concentrated sulfuric acid in 10 ml. of water was added to the filtrate. After dilution with 50 ml. of alcohol, the precipitate was removed by filtration, washed with alcohol, and recrystallized from 100 ml. of 75% aqueous alcohol. There resulted 9 g. of product. *Anal.* Calcd. for $C_{10}H_{14}N_2 \cdot 0.5H_2SO_4 \cdot 2H_2O$: N, 11.33. Found: N, 11.65.

1-(4-Amino-m-tolyl)-pyrrolidine Hemisulfate.—A mixture of 22.4 g. of 2-nitro-5-iodotoluene and 12 g. of pyrrolidine was heated at 95–100° in a sealed tube for one hour and the reaction mixture was stirred with 100 ml. of water. The precipitate was removed by filtration and recrystallized twice from acetic acid. There resulted 8 g. of 1-(4-nitro-m-tolyl)-pyrrolidine that melted at 86–88°. This nitro compound was reduced by the method used for dinitrodurene. The catalyst was removed and a solution of 1.2 ml. of concentrated sulfuric acid in 15 ml. of absolute alcohol was added. The precipitate was removed by filtration, washed with alcohol, and recrystallized twice from 80% aqueous alcohol. There resulted 5 g. of product. *Anal.* Calcd. for $C_{11}H_{16}N_2 \cdot 0.5H_2SO_4$: N, 12.43. Found: N, 12.29.

1-(p-Aminophenyl)-piperidine Hemisulfate.—A mixture of 79 g. of p-nitrochlorobenzene and 100 ml. of piperidine was heated at 95° for four hours in a flask attached to an air condenser. At the end of this time, the reaction mixture was diluted with 200 ml. of water and stirred thoroughly. The precipitate was removed by filtration, washed with water, and recrystallized twice from 200 ml. of 95% alcohol. There resulted 70 g. of 1-(p-nitrophenyl)-piperidine that melted at 103–103.5°. *Anal.* Calcd. for $C_{11}H_{14}N_2O_2$: N, 13.58. Found: N, 13.69.

The 1-(p-nitrophenyl)-piperidine (20.6 g.) was reduced by the method used for dinitrodurene. The catalyst was removed and a solution of 2.8 ml. of concentrated sulfuric acid in 150 ml. of alcohol was added to the filtrate. The precipitate was removed and recrystallized twice from 300 ml. of 75% aqueous alcohol. There resulted 10 g. of 1-(p-aminophenyl)-piperidine hemisulfate. *Anal.* Calcd. for $C_{11}H_{16}N_2 \cdot 0.5H_2SO_4$: N, 12.43. Found: N, 12.34.

1-(4-Amino-m-tolyl)-piperidine Sulfate.—A mixture of 26.3 g. of 2-nitro-5-iodotoluene and 20 ml. of piperidine was heated in an oil-bath at 110° for four hours. The oily reaction mixture was washed with water and crystallized from 50 ml. of methanol. The crystals were stirred with 80 ml. of 15% hydrochloric acid, the insoluble material was filtered off (unreacted 2-nitro-5-iodotoluene), and the filtrate was poured into water containing an excess ammonium hydroxide. The precipitate was removed by filtration, washed with water, and recrystallized from 50 ml. of methanol. There resulted 12.5 g. of 1-(4-nitro-m-tolyl)-piperidine that melted at 53–54°. This nitro compound was reduced by the method used for dinitrodurene. The catalyst was removed and a solution of 3.2 ml. of concentrated sulfuric acid in 5 ml. of water was added. The precipitate was removed by filtration, washed with alcohol, and recrystallized twice from 75 ml. of 75% aqueous alcohol. There resulted 14 g. of 1-(4-amino-m-tolyl)-piperidine sulfate. *Anal.* Calcd. for $C_{12}H_{18}N_2 \cdot H_2SO_4$: N, 9.72. Found: N, 9.69.

1-(p-Aminophenyl)-morpholine Hemisulfate Hydrate.—A mixture of 80 g. of p-nitrochlorobenzene and 100 g. of morpholine was heated at 115–120° for three and one-half hours. The reaction mixture was ground in a mortar with 300 ml. of warm water. The solid was removed by filtration, washed with water, and the product recrystal-

lized twice from 150 ml. of acetic acid. There resulted 85 g. of 1-(p-nitrophenyl)-morpholine that melted at 150–151°. A portion of this nitro compound (20.8 g.) was mixed with 200 ml. of absolute alcohol and reduced by the method used for dinitrodurene. The catalyst was removed and a solution of 2.8 ml. of concentrated sulfuric acid in 40 ml. of water was added. The mixture was heated to a boil, filtered, and allowed to cool. The product was removed and recrystallized from 75% aqueous alcohol. There resulted 15 g. of 1-(p-aminophenyl)-morpholine hemisulfate hydrate. *Anal.* Calcd. for $C_{10}H_{14}N_2O \cdot 0.5H_2SO_4 \cdot H_2O$: N, 11.42. Found: N, 11.43.

1-(4-Amino-m-tolyl)-morpholine Sulfate.—A mixture of 80 g. of 2-nitro-5-iodotoluene and 61 g. of morpholine was heated at 95–100° for four hours. The reaction mixture was ground in a mortar with 500 ml. of water and the solid was separated. The solid was added to 800 ml. of 15% hydrochloric acid. The mixture was stirred and heated at 70–80° for twenty minutes. After cooling, the mixture was filtered and the filtrate made alkaline with concentrated ammonium hydroxide. The precipitate was removed by filtration and recrystallized twice from acetic acid. There resulted 33 g. of 1-(4-nitro-m-tolyl)-morpholine that melted at 142–143°. The nitro compound (22.2 g.) was mixed with 200 ml. of absolute alcohol and reduced by the method used for dinitrodurene. The catalyst was removed and a solution of 5.6 ml. of concentrated sulfuric acid in 100 ml. of water was added. The mixture was warmed until solution took place and then was allowed to cool. The product was separated and recrystallized from 75% aqueous alcohol. There resulted 20 g. of 1-(4-amino-m-tolyl)-morpholine sulfate. *Anal.* Calcd. for $C_{11}H_{16}N_2O \cdot H_2SO_4$: N, 9.65. Found: N, 9.67.

p-Aminophenol Hydrochloride.—A boiling solution of 100 g. of the salt in 150 ml. of water containing 1 ml. of concentrated hydrochloric acid was treated with Darco, filtered, and allowed to cool. The precipitate was removed by filtration and recrystallized from water.

p-Methylaminophenol Hemisulfate.—The salt was recrystallized twice from water which contained 0.1% sulfuric acid.

p-Dimethylaminophenol Hemisulfate.—The salt was dissolved in boiling 75% aqueous alcohol, treated with Darco, filtered, and cooled. The solid was separated and recrystallized from 75% aqueous alcohol.

Calculations and Results

All calculations of $\log(V'_i - V_i)$–time curves were made by Guggenheim's method,[13] as outlined in a previous paper.[4c] The oxygen uptake–time curves represent several types: (1) first-order reactions, denoted by (1st), (2) autocatalytic reactions, denoted by (α), and (3) reactions which are initially autocatalytic, reach saturation and then follow the first-order law, denoted by (β).

The mean values for the reaction-rate constants, k, of (1) and (3) are taken in the first-order part of the reactions. This part always includes the point at which the reaction is 50% complete. For comparison, the k values of the autocatalytic reactions (2) were therefore taken at 50% completion of the reactions. Figure 4 shows Guggenheim curves of 1st, α-, and β-type reactions of various p-phenylenediamines. The β-curves may remain first-order up to the end or drop off near the end of the reaction.

In addition, there are several curves which can be dissected and allotted to consecutive reactions. In the autoxidation of *N,N'-dimethyl-*

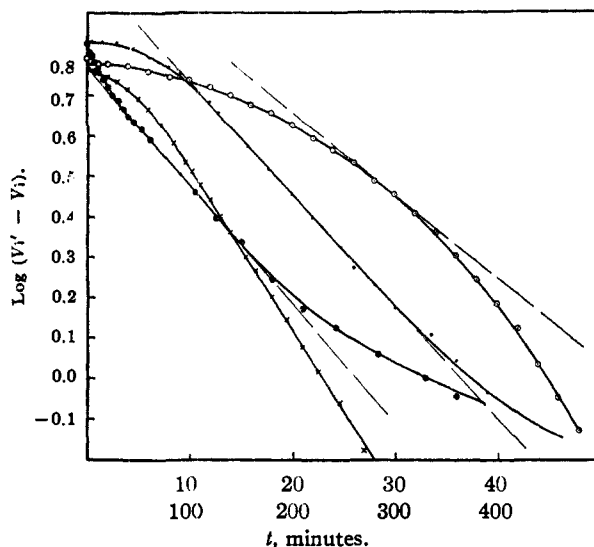(13) Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

Fig. 4.—Types of Guggenheim curves: -⊙-⊙-, diaminodurene, α-curve, upper time scale; -⊗-⊗- N-dimethyl-p-phenylenediamine in presence of 6.00×10^{-4} M benzoquinone at pH 7.57. Composite curve with rapid initial reaction, lower time scale; ·×-×- N-dimethyl-p-phenylenediamine at pH 7.88, β-curve, lower time scale; -●-●- N-dimethyl-p-phenylenediamine at pH 7.56, β-curve, lower time scale.

p-phenylenediamine at pH 11.33, a rapid autocatalytic reaction is followed by a slower first-order reaction. The uptake–time curves are given in Fig. 5. The upper curve shows the total uptake–time curve, and the lower curve gives the uptake of the first six milliliters of oxygen on an expanded time scale. The theoretical uptake for the oxidation of the diamine to the diimine according to equation (1) is 6.0 ml. Hence, the autoxidation of the diamine takes place in the autocatalytic reaction, and the following first-order reaction represents the autoxidation of some secondary product of the diimine, presumably the quinone.

The uptake–time curves for the autoxidation of N,N'-tetramethyl-p-phenylenediamine at pH 6.65 and pH 13.20 are given in Fig. 6. There is a definite break in each curve after approximately three milliliters of oxygen have been absorbed, and the Guggenheim curve for the total reaction (Fig. 7) shows two distinct sections with a transition period. The theoretical uptake for the autoxidation of the diamine to the semiquinone is 3.0 ml., and the inspection of the reaction mixture shows that Wurster's Blue accumulates to a high concentration. The rate constant for the first three milliliters of oxygen uptake belongs, therefore, to

the autoxidation of the diamine to the semiquinone, while the latter portion of the uptake represents the autoxidation of the semiquinone to the diimine. Inasmuch as the latter portion of the uptake exceeds three milliliters, the diimine again undergoes secondary reactions.

The tabulated rate data for p-phenylenediamine and some of its alkyl derivatives, and for the p-aminophenols, may be obtained in the form of an American Documentation Institute Document.[14]

The rates are all in such a region that, from the point of view of accuracy of measurement, the data are of equal significance. However, the measurement on tetramethyl-p-phenylenediamine at pH 13.2, though it is also in an easily observed region of rate, may be less reliable because of the possibility of demethylation and the possibility of higher solubility of oxygen at very high pH.

Discussion

Type of Curve and Mechanism.—An α-curve, exemplified by dihydroxydurene,[4a,15] is again found on the autoxidation of diaminodurene. The recoverable product from the autoxidation of diaminodurene is duroquinone. In some experiments, however, the autoxidation was completed about a half hour before the precipitation of the duroquinone, which probably is formed by hydrolysis of the duroquinonediimine. Thus, diaminodurene autoxidizes by the mechanism of Classes I-A-3[15] or I-C.[15] With the exception of diaminodurene, all of the p-phenylenediamines
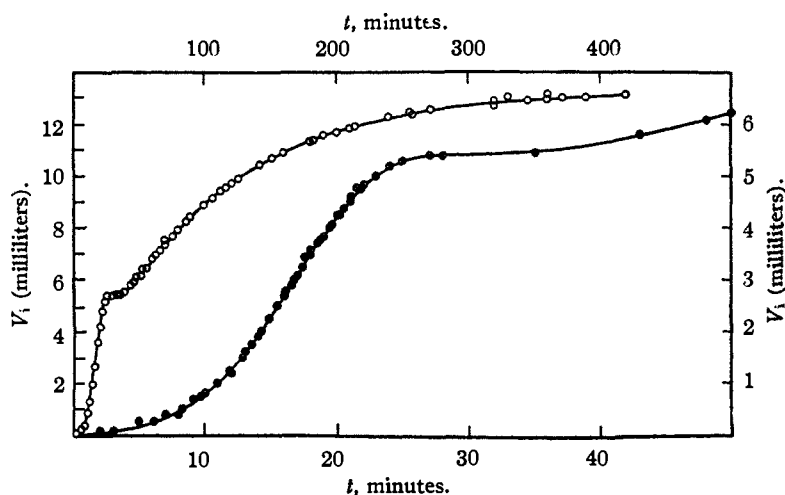

Fig. 5.—Uptake–time curves for N,N'-dimethyl-p-phenylenediamine at pH 11.33: -⊗-⊗-, first six milliliters, bottom abscissa, right-hand ordinate; -O-O-, total uptake, top, abscissa, left-hand ordinate.

autoxidize by a mechanism giving a β-type curve. Only occasionally, at low pH or high pH, will a compound give an α-type curve. The β-curves

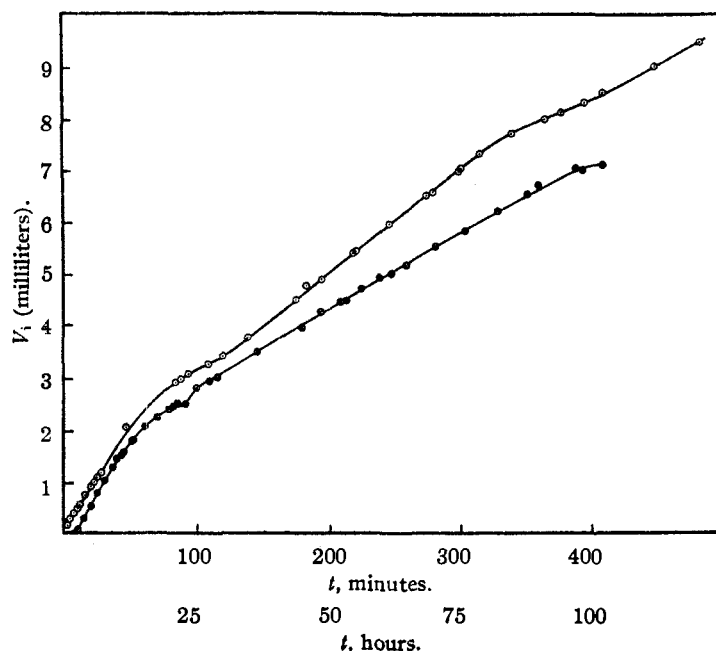(15) LuValle and Weissberger, THIS JOURNAL, **69**, 1567 (1947).

Fig. 6.—Uptake–time curves for N,N'-tetramethyl-*p*-phenylenediamine: - ⊙-⊙-, *p*H 6.65, upper time scale; -⊗-⊗-, *p*H 13.20, lower time scale.

added, a very rapid initial uptake of 10–20% of the total oxygen consumption during thirty to sixty seconds is followed by the normal first-order reaction. The elimination of the induction period appears to be caused by the poised equilibrium

$$R + Q \rightleftharpoons S_{diamine} + S_{quinone}$$

Effect of Solvents.—Experiments with diaminodurene and *p*-diethyl-*o*-toluidine show that the rate in 20% ethanol solutions is lower than in water. Since the semiquinones are more stable in alcoholic solution than in water,[6b] the lower rate may be due to the increased stability of the semiquinone.

Rate Dependency upon the Concentrations of Substrate and Oxygen.—Experiments with N-dimethyl-*p*-phenylenediamine, N,N'-trimethyl-*p*-phenylenediamine, and diaminodurene show that the rate is first-order with respect to the *initial concentration* of the *diamine*. The rate

correspond to the mechanism of Class II-A-3 which was assigned to the *p*-phenylenediamines in an earlier paper of this series.[16] Kinetically, it is difficult to distinguish Class II-A-3 from Class I-E.[16] The rate of autoxidation for the latter mechanism is determined by the rate of *formation* of the semiquinone, but, for the former mechanism, the rate of *autoxidation* of the semiquinone enters into the rate equation. Class II-A-3 is differentiated from Class I-E by the appearance of intensely colored fairly stable semiquinones during the course of the reaction. These latter were observed with all of the *p*-phenylenediamines investigated in the present study.

If the rate of autoxidation of the semiquinone is high compared with the rate of formation of the semiquinone, the latter is rate-determining, and the concentration of semiquinone is low. Insofar as the rate of autoxidation of the semiquinone drops, it becomes more and more rate-determining, and the concentration of the semiquinone increases until eventually the mechanism becomes that found with tetramethyl-*p*-phenylenediamine.

Addition of quinone to a diamine in the proper concentration before autoxidation eliminates the induction period and causes a (β) reaction to become first-order throughout its course. The necessary concentration of quinone varies with the diamine between one-twentieth of the concentration of the diamine and less. The rate constant is identical with that derived from the autoxidation of the diamine alone. If less than the critical concentration of quinone is added, the induction period is not completely eliminated. If more than this critical concentration of quinone is
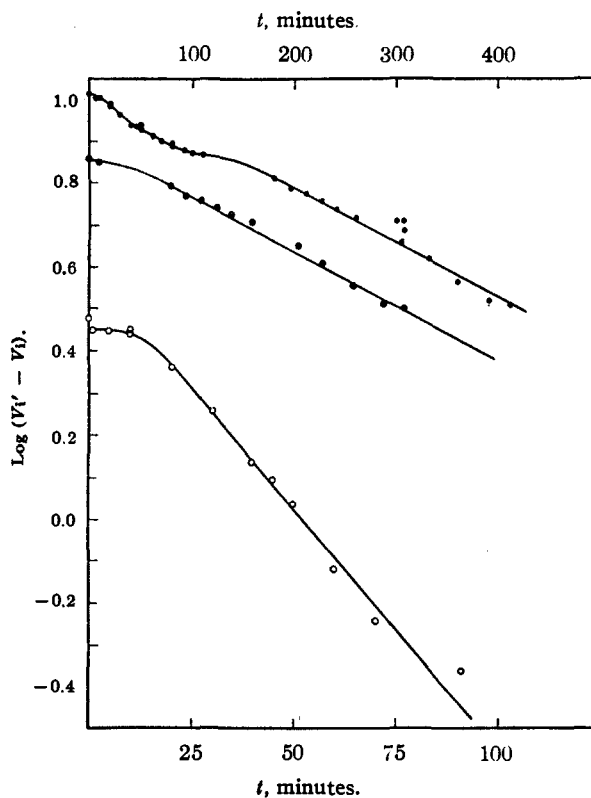

Fig. 7.—Guggenheim curves for N,N'-tetramethyl-*p*-phenylenediamine at *p*H 6.65: -●-●-, total uptake, top abscissa; -O-O-, first three milliliters of uptake, bottom abscissa; -⊗-⊗-, latter seven milliliters of uptake, top abscissa.
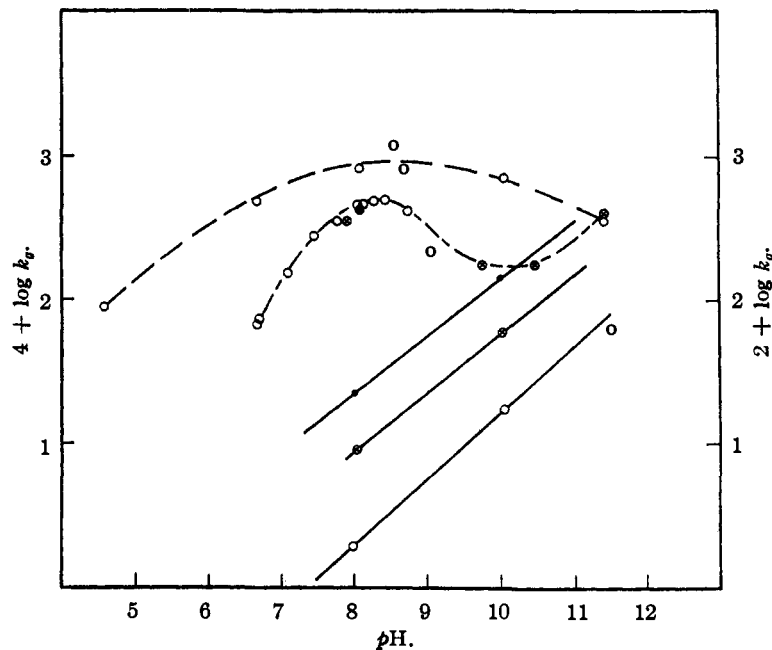
Fig. 8.—Straight lines refer to right-hand ordinate, $2 + \log k_g$: -O-O-, p-aminophenol; -●-●-, p-methylaminophenol; -⊗-⊗-, p-dimethylaminophenol. Curves refer to left-hand ordinate, $4 + \log k_g$: — — —, p-diethylamino-o-toluidine; O, in presence of 2.00×10^{-4} M benzoquinone; ⊗, in absence of benzoquinone; -⊖- -⊖-, diaminodurene.

At pH 7.8 and 11.3, the rate is about of order 0.8 with respect to oxygen, while at pH 9.8 the rate appears to be first-order with respect to oxygen. These data indicate that the mechanism of Class I-E[15] may also occur with the p-phenylenediamines. The effect of added quantities of the diimines was not investigated because of the instability of these compounds in aqueous solution.[7]

Dependency of Rate on pH.— The data for p-aminophenol and the N-methylated p-aminophenols (Fig. 8) are not sufficient to warrant a detailed discussion. However, from the points measured it appears that the change of the rate of autoxidation of p-aminophenol itself with pH is not far from linear in the range investigated. It is known that the salts of p-aminophenol are stable, while the free base reacts with oxygen, and the anion of the base might be expected to have an even higher autoxidation rate in line with the results on desylamine and on dihydroxy compounds. The low slope (about 0.4) of the curves may suggest that the reactivity of the anions is not very much higher than that of the neutral molecules.

laws observed give no reason to assume a more complicated dependency for any of the other compounds in the range of concentration investigated.

A few experiments with N,N'-trimethyl-p-phenylenediamine indicate that the *rate dependency with respect to oxygen varies* with the pH.

The rate–pH relation of p-phenylenediamine and of the N-alkylated p-phenylenediamines shown in Fig. 9 is rather complicated. For N-tetramethyl-p-phenylenediamine, the figure gives

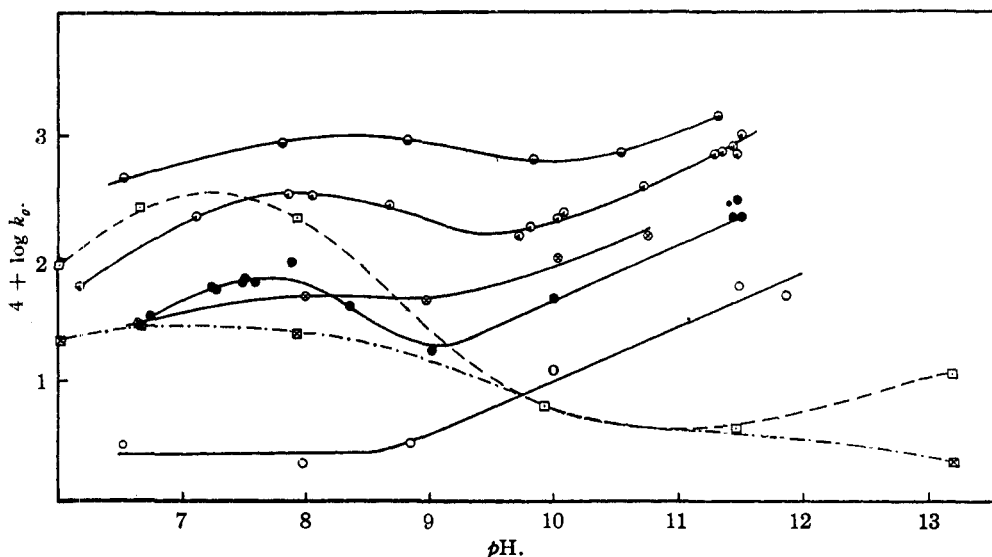Fig. 9.—p-Phenylenediamines, $4 + \log k_g - p$H: -O-O-, p-phenylenediamine; -⊗-⊗-, N-methy -p-phenylenediamine; -●-●-, N-dimethyl-p-phenylenediamine; -⊖-⊖-, N,N'-dimethyl-p-phenylenediamine; N-methyl, N'-dimethyl-p-phenylenediamine; -□-□-, N,N'-tetramethyl-p-phenylenediamine, semiquinone formation; -⊠--⊠--, N,N'-tetramethyl-p-phenylenediamine, semiquinone autoxidation.

the data for the oxidation to the semiquinone and for the oxidation of the semiquinone. The salts of these compounds with strong acids are known to be stable, while the free bases are oxidized by air. Accordingly, all curves may be extrapolated to reaction rates close to zero at very low pH. Our measurements begin between pH 6 and 7, in most cases in a distinctly ascending part of the rate-pH curve. However, between pH 7 and 9, maxima are reached, and the rates begin to drop. The drop of the curves is not steady but leads to minima at pH about 10 and from there on the rates increase again sharply. For p-phenylenediamine itself and N-methyl-p-phenylenediamine, the maximum and minimum are very flat, almost fused into a region of inflection.

The increase in k in the lower pH region can be ascribed to a predominance of the liberation of the free base, *i. e.*, to a formation of R from RH$^+$. The drop from the maximum to the minimum may be ascribed either to a decrease in the total concentration of the semiquinone or to a shift in the ionic equilibrium of the semiquinone in favor of less reactive ionic species, or to both. A definitive discussion is not possible with the present information, but some suggestions are offered in the following:

Table I gives the number of equivalent structures of the semiquinones of p-phenylenediamine and of its N-alkyl derivatives. The lack of any entry indicates that the compound in question does not exist. We learn from the table that of all semiquinones listed, SH$_2$$^+$ can be expected to be the predominant ionic species of the semiquinones at low and medium pH. It is noteworthy in this connection that the more or less steep drop in rate constant, k, with increasing pH is common to all p-phenylenediamine compounds investigated. Michaelis has stated that SH$_2$$^+$ in equilibrium with other ionic species of the semiquinones of p-phenylenediamines has a maximum concentration at about pH 4, and from this its concentration drops with increasing pH. We are therefore inclined to believe that the drop in the rate of autoxidation of the p-phenylenediamine compounds between pH 7 and 10 is due to a decrease in concentration of the semiquinone species, SH$_2$$^+$.

TABLE I

NUMBER OF EQUIVALENT STRUCTURES FOR THE SEMI-
QUINONE SPECIES OF p-PHENYLENEDIAMINE AND ITS
N-ALKYL DERIVATIVES

No. of N-Alkyl groups	SH$_2$$^+$	SH	S$^-$
0	3	0	3
1	3	0	3
2 sym.	3	0	3
2 asym.	2	0	0
3	3	0	
4	3		

The steep rise in k above a pH of about 10 remains to be explained. Two alternative sugges-

tions are offered. The increase may be due to an increased concentration of SH, provided that SH is more reactive than SH$_2$$^+$; the latter can be safely assumed because of the instability of SH to be expected from Table I and Fig. 2. The other reason for the increase of k with pH above 10 would be an increase in the concentration of S$^-$; this explanation cannot be completely excluded. However, the uniformly steep gradient of k *versus* pH at a pH higher than 10 for p-phenylenediamine, methyl-p-phenylenediamine, the dimethyl-p-phenylenediamines and trimethyl-p-phenylenediamine, as contrasted with the retarded and questionable (see Fig. 9) flat increase in k of tetramethyl-p-phenylenediamine, favors the former explanation; Fig. 2 and Table I show that SH can be formed by all the compounds listed except by tetramethyl-p-phenylenediamine, while S$^-$ would also not be formed by the trimethyl compound. Inasmuch as the first acid ionization constant for the p-phenylenediamines occurs at extremely high pK values, the increase in rate above $pH_{min.}$ cannot be attributed to the formation of R$^-$. As the slopes above $pH_{min.}$ are the same for all the N-alkyl-p-phenylenediamines except the N-tetramethyl compound, Table II, it appears that the increase in rate may be attributed to the increase in the concentration of SH.

TABLE II

COMPARISON OF SLOPES OF k_g-pH CURVES

Compound	Slope of k_g-pH curve above $pH_{min.}$	$pH_{min.}$
p-Phenylenediamine	0.44	8.5 (inflection)
N-Methyl-p-phenylenediamine	.41	8.5 (inflection)
N,N'-Dimethyl-p-phenylene-diamine	.32	10
N-Dimethyl-p-phenylenedi-amine	.43	9.1
N,N'-Trimethyl-p-phenylene-diamine	.44	9.5
N,N'-Tetramethyl-p-phenylenediamine	.27(?)	11-12(?)
p-Diethylamino-o-toluidine hydrochloride	.38	10.1
p-Aminophenol	.46 straight line	
N-Methyl-p-aminophenol	.40 probable straight line	
N-Dimethyl-p-aminophenol	.39 probable straight line	

Figure 8 shows that the *addition of benzoquinone* to a concentration of 2×10^{-4} M merely changes the reaction from β to first-order but does not affect the pH dependency.

Effect of Substituent on Rate.—N-Methylation increases the rate of autoxidation of p-aminophenol; the rate of the dimethyl compound was between that of the monomethyl derivative and the parent substance. Figure 9 affords a comparison of the effect of N-methylation upon the rate of autoxidation of p-phenylene-

diamine. The dimethyl derivative autoxidizes most readily at all pH values investigated; next ranks the trimethyl derivative, and the rates of the asymmetrical dimethyl and the monomethyl compounds lie between the higher methylated products and the parent substance. N-Tetramethyl-p-phenylenediamine autoxidizes relatively fast at low pH but more slowly than the parent substance at high pH values.

A comparison of rates for different substances which have not been studied over a considerable pH range requires caution because it is not known whether at an arbitrarily chosen pH value one substance may not be close to its maximum autoxidation rate while any other substance is measured in a relatively slow part of the rate–pH curve. However, a comparison at pH 8 of closely related compounds should furnish some information because at this pH the k–pH curve for most substances is either close to a maximum or flat. The comparison at pH 8 and 11.5 is given in Table III. It is obvious that asymmetrical dialkylation has an effect of about the same order of magnitude, irrespective of whether methyl, ethyl, or propyl

TABLE III

EFFECT OF SUBSTITUENTS UPON THE RATE OF AUTOXIDATION (RELATIVE RATES)

Compound	$\dfrac{k_g \ (p\text{H} \ 11.5)}{k_g \ (p\text{H} \ 8)}$
p-Phenylenediamine	29
N-Methyl-p-phenylenediamine	3
N-Dimethyl-p-phenylenediamine	3.2
N,N'-Dimethyl-p-phenylenediamine	1.6
N,N'-Trimethyl-p-phenylenediamine	2.3
N,N'-Tetramethyl-p-phenylenediamine	0.018
N-Diethyl-p-phenylenediamine	5.4
N-Di-n-propyl-p-phenylenediamine	....
Diaminodurene	0.44
N-Diethylamino-o-toluidine	0.93
4-Amino-N,N'-dimethyl-m-toluidine	10
N-(4-Aminophenyl)-piperidine	11
N-(4-Aminophenyl)-morpholine	....
N-(4-Aminophenyl)-pyrrolidine	22
N-(4'-Amino-3'-methylphenyl)-piperidine	0.61
N-(4'-Amino-3'-methylphenyl)-morpholine	4
N-(4'-Amino-3'-methylphenyl)-pyrrolidine	11
Octomethyl-p-phenylenediamine	No measurable rate

groups are introduced. However, it may be significant that the diethyl compound has the highest rate of autoxidation.

The effect of ring alkylation is illustrated by a comparison of N-diethyl-p-phenylenediamine with N-diethylamino-o-toluidine and of N,N'-dimethyl-p-phenylenediamine with 4-amino-N,N'-dimethyl-m-toluidine. The introduction of a methyl group into the ring in the *meta*-position to the diethylamino group causes a considerable increase in the reaction rate. This can be expected in view of the electron-releasing effect of the methyl group upon the neighboring amino group. However, if the methyl group is present in the *ortho*-position to the dimethylamino group of N-dimethyl-p-phenylenediamine, the reaction rate is cut down considerably. Presumably, a steric interference of the ring methyl group with the N-methyl groups makes less probable a configuration necessary for the formation of the semiquinone.

Diaminodurene exhibits a reaction rate close to that of N,N'-dimethyl-p-phenylenediamine. Figure 8 gives the rate–pH dependency for diaminodurene. In the pH range investigated it shows a broad flat maximum, but no minimum, $i.\ e.$, no rise in oxidation rate at pH higher than 10.

If the two alkyl groups in N-dialkyl-p-phenylenediamine are fused to form a ring, compounds result, some of which are listed in Table III. The *piperidine* derivatives autoxidize considerably more slowly than N-diethyl-p-phenylenediamine and N-diethylamino-o-toluidine, respectively. Substitution of a *morpholone* ring for the piperidine ring further diminishes the autoxidation rate. However, a remarkable effect is obtained when the six-membered ring of piperidine is shrunk to the five-membered ring of *pyrrolidine*. Table III shows that the resulting pyrrolidine derivatives autoxidize at surprisingly high rates, particularly at pH 11. It is difficult to explain this effect. However, we are inclined to believe that the strain upon the C–N–C angle in the five-membered ring favors the π nature of the remaining nitrogen bonds and thus the formation of the semiquinone.

Summary

The autoxidation of p-phenylenediamine and of several of its derivatives has been investigated over a wide pH range.