a factor 4.7. Plots of $(sV_\infty a/b)$, the specific reaction rate constant one would expect if anisole enters into the rate equation to the first power, *versus* the dielectric constant $D$, and of $(sV_\infty a/b)$ *versus* molarity of anisole, were linear. Plots of $(sV_\infty a)$ *versus* $D$ or *versus* molarity of anisole were definitely not linear, showing strong curvature. Furthermore, a plot of log $(sV_\infty a/b)$ *versus* $(D - 1)/2D + 1$ was roughly linear. These suggest that the reaction is probably first order in anisole and that the extra order of unity in the observed kinetics arises from an electrostatic solvent effect.

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NEW ORLEANS, LOUISIANA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

# The Synthesis of Unsymmetrically Disubstituted Hydrazines

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Unsymmetrically disubstituted hydrazines, $RRN \cdot NH_2$, can be prepared from the corresponding nitrosamines, $RRN \cdot NO$, by use of the following reducing systems: (a) lithium aluminum hydride in ether, (b) sodium in alcohol and (c) sodium in liquid ammonia in the presence of substances which act as acids in ammonia. The following hydrazines have been prepared, where RR = $(C_2H_5)_2$, $(n\text{-}C_3H_7)_2$, $(\text{iso-}C_8H_7)_2$, $(n\text{-}C_4H_9)_2$, $(\text{iso-}C_4H_9)_2$, $(n\text{-}C_5H_{11})_2$, $[-CH_2(CH_2)_3CH_2-]$ (N-aminopiperidine), $(CH_3)(C_6H_5)$ and $(-CH_2CH_2OCH_2CH_2-)$ (N-aminomorpholine). Various identifying derivatives have been prepared such as the oxalate salt, 1,1-disubstituted semicarbazide, N-dialkylaminourethan, or the N,N-dialkylhydrazones.

## Introduction

In connection with investigations which have had as their objective the extension of the Raschig synthesis to the preparation of N-substituted hydrazines[1] from the corresponding amines and chloramines it became necessary to have available for purposes of comparison a number of unsymmetrically N,N-disubstituted hydrazines of the aliphatic series. The two simplest members, N,N-dimethylhydrazine and N,N-diethylhydrazine, were first prepared by E. Fischer[2] from the corresponding nitrosamines by reduction with zinc and dilute acetic acid. Lithium aluminum hydride has been used more recently for the reduction of nitrosamines by Schueler and Hanna.[3] Although we too have found the lithium aluminum hydride method to be useful it has been our experience that the preparation of N,N-disubstituted hydrazines from the nitrosamines can be accomplished more easily if sodium is employed as the reducing agent either in alcoholic solution or in liquid ammonia in the presence of solutes that are acids in ammonia.

All three methods have been used in the present investigation to accomplish the preparation of a number of typical unsymmetrically disubstituted hydrazines. These are colorless liquids and possess a characteristic ammoniacal odor. All suffer autoxidation and deterioration on exposure to the atmosphere. Difficulties were experienced in attempting to analyze the free bases, even though formation of the desired substances was verified by determination of the neutral equivalents. For this reason all products were converted into appropriate derivatives.

The dimethyl and diethyl derivatives are very soluble in water; the di-*n*-propyl- and diisopropylhydrazines are only somewhat water soluble whereas both of the dibutylhydrazines and di-*n*-amylhydrazine are practically insoluble in water. Prolonged heating on the steam-bath is necessary to effect reduction of Fehling solution. Ethereal solutions react to precipitate salts when treated with anhydrous acids. The hydrochlorides and the sulfates are extremely hygroscopic. The oxalates represent well defined compounds. Crystalline compounds could not be obtained with picric acid and styphnic acid.

The hydrazines react with aldehydes and ketones, but most of the common carbonyl derivatives are liquids. Crystalline 1,1-disubstituted semicarbazides, $R_2NNHCONH_2$, are obtained with potassium cyanate in dilute aqueous acetic acid. No semicarbazide derivative of di-*n*-amylhydrazine could, however, be obtained. The methyl ester of chlorocarbonic acid reacts readily with diethylhydrazine to form N-diethylaminourethan methyl ester hydrochloride.

**Acknowledgment.**—The present investigation was carried out as one phase of a study of the fundamental chemistry of the Raschig synthesis for the preparation of hydrazine, sponsored by the Office of Ordnance Research, Contract DA-11-022-ORD-828. We wish to express our appreciation to Mrs. E. Fett, Mrs. L. Chang and Mr. J. Nemeth for carrying out microanalytical determinations.

## Experimental

The nitrosamines were prepared by reaction of the secondary amine hydrochlorides with sodium nitrite. The preparation of di-*n*-amylnitrosamine is typical of the method employed and is given in detail since this particular compound had not previously been described in the literature.

The hydrazines were prepared by the reduction of the corresponding nitrosamines by use of three reducing systems: lithium aluminum hydride (method A), sodium in alcohol (method B) and sodium in liquid ammonia in the presence of an acidic solute (method C). Examples are presented below and are designed to be illustrative of the methods used specifically for the synthesis of compounds

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(1) L. F. Audrieth and L. H. Diamond, THIS JOURNAL, **76**, 4869 (1954).

(2) E. Fischer, *Ann.*, **199**, 281 (1879).

(3) F. W. Schueler and C. Hanna, THIS JOURNAL, **73**, 4996 (1951); **74**, 3698 (1952).

TABLE I

PREPARATION OF SOME N,N-DISUBSTITUTED HYDRAZINES

| Compound<br>$\begin{matrix}R\\R\end{matrix}\!>\!NNH_2$<br>where RR = | Formula | Starting material Grams | Starting material Mole | Preparative method | Formula | Yield, % | B.p. °C. | B.p. Mm. |
|---|---|---|---|---|---|---|---|---|
| Diethyl | $(C_2H_5)_2NNO$ | 51 | 0.5 | A | $(C_2H_5)_2NNH_2$ | 69 | 96–99 | 760 |
| | $(C_2H_5)_2NNO$ | 20.5 | .2 | C[a] | $(C_2H_5)_2NNH_2$ | 31 | 94–97 | 760 |
| Di-*n*-propyl | $(n\text{-}C_3H_7)_2NNO$ | 65 | .5 | A | $(n\text{-}C_3H_7)_2NNH_2$ | 41 | 43–45 | 16 |
| | $(n\text{-}C_3H_7)_2NNO$ | 26 | .2 | C[b] | $(n\text{-}C_3H_7)_2NNH_2$ | 60 | 36–38 | 12 |
| Diisopropyl | $(i\text{-}C_3H_7)_2NNO$ | 32.5 | .25 | A[c] | $(i\text{-}C_3H_7)_2NNH_2$ | 63 | 41 | 16 |
| Di-*n*-butyl | $(n\text{-}C_4H_9)_2NNO$ | 19.8 | .125 | A | $(n\text{-}C_4H_9)_2NNH_2$ | 72 | 87–90 | 21 |
| | $(n\text{-}C_4H_9)_2NNO$ | 79 | .5 | B | $(n\text{-}C_4H_9)_2NNH_2$ | 39 | 76–77 | 11 |
| Diisobutyl | $(i\text{-}C_4H_9)_2NNO$ | 39.5 | .25 | A | $(i\text{-}C_4H_9)_2NNH_2$ | 48 | 60–61 | 14 |
| | $(i\text{-}C_4H_9)_2NNO$ | 32 | .2 | B | $(i\text{-}C_4H_9)_2NNH_2$ | 44 | 59 | 13 |
| | $(i\text{-}C_4H_9)_2NNO$ | 32 | .2 | C[b] | $(i\text{-}C_4H_9)_2NNH_2$ | 22 | 57–59 | 13 |
| | $(i\text{-}C_4H_9)_2NNO$ | 32 | .2 | B[d] | $(i\text{-}C_4H_9)_2NNH_2$ | 51 | 57–58 | 11 |
| Di-*n*-amyl | $(n\text{-}C_5H_{11})_2NNO$ | 46.5 | .25 | A | $(n\text{-}C_5H_{11})_2NNH_2$ | 55 | 108–110 | 14 |
| | $(n\text{-}C_5H_{11})_2NNO$ | 46.5 | .25 | B | $(n\text{-}C_5H_{11})_2NNH_2$ | 45 | 104–105 | 11 |
| Cyclopentamethylene (N-aminopiperidine) | $\underline{CH_2(CH_2)_3CH_2N}.NO$ | 57 | .5 | A | $\underline{CH_2(CH_2)_3CH_2N}NH_2$[e] | 76 | 54–55 | 18 |
| | | 28.5 | .25 | B | $\underline{CH_2(CH_2)_3CH_2N}NH_2$[e] | 31 | 49 | 12 |
| | | 28 5 | .25 | B[f] | $\underline{CH_2(CH_2)_3CH_2N}NH_2$[2] | 8 | 47–49 | 11 |
| | | 19 | .166 | B[j] | $\underline{CH_2(CH_2)_3CH_2N}NH_2$[e] | 12 | 51 | 16 |
| Methyl phenyl | $CH_3(C_6H_5)NNO$ | 68 | 0.5 | A | $CH_3(C_6H_5)NNH_2$[g,h] | 50 | 108–109 | 15 |
| N-Aminomorpholine | $\underline{CH_2CH_2OCH_2CH_2N}NO$ | 29 | .25 | B | $\underline{CH_2CH_2OCH_2CH_2N}NH_2$[i] | 23 | 163–165 | 760 |

[a] Ammonium chloride was used as the acid in liquid ammonia. Some diethylamine was isolated during fractionation of the reaction product. [b] Ethanol was used as the acid in liquid ammonia. [c] Difficulty was experienced in attempting to extract the desired hydrazine when method B was employed. [d] Isopropyl alcohol was employed as the solvent. The reaction is very slow at room temperature, but proceeds satisfactorily at 60°. Water was added to dissolve the solid sodium isopropylate resulting in the formation of two phases, the upper phase containing all of the desired hydrazine derivative. [e] Confirmed by preparation of the benzylidene and salicylalidene derivatives, m.p., 69 and 75°, respectively. *Cf.* A. B. Weinhagen, *J. Chem. Soc.*, **113**, 585 (1918). [f] Methanol was used as solvent with a 100% excess of sodium. [g] Confirmed by preparation of benzylidine derivative, m.p. 106–107°. *Cf.* J. Goldstein, *Ber.*. **29**, 813 (1896). [h] Confirmed by preparation of salicylalidene derivative, m.p. 74–75°. *Cf.* F. Bovine and F. Graziani, *Gazz. chim. ital.*, **43**, [II] 674 (1913). [i] Confirmed by conversion to the hydrochloride, m.p. 162–164°. *Cf.* L. Knorr and H. W. Brownsdon, *Ber.*, **35**, 4474 (1902). [j] Ethanol with 100% excess of sodium employed.

listed in Table I in which the amounts of starting materials, percentage yields as well as the boiling points of the respective products are given.

Procedures are also given for typical derivatives of the N,N-disubstituted hydrazines prepared during the course of the present investigation.

**Di-*n*-amylnitrosamine.**—Di-*n*-amylamine (78.5 g., 0.5 mole) was treated with 50 cc. of concentrated hydrochloric acid for conversion to the hydrochloride. The resulting mass was warmed to 70° and allowed to react with a suspension of 42.5 g. of sodium nitrite in 100 cc. of water which was added over a one-hour period with good agitation. The nitrosamine separated on the surface as a yellow oil. After the mixture had been agitated for about 2 hours, it was cooled, the phases separated and the lower aqueous phase extracted with ether. The ether extract and the oily nitrosamine layer were combined, washed with water for the removal of acid and dried over potassium carbonate. Distillation gave 66.5 g. (71.5%) of di-*n*-amylnitrosamine, b.p. 146° at 12 mm., $n^{16}_D$ 1.4497.

*Anal.* Calcd. for $C_{10}H_{22}N_2O$: C, 64.49; H, 11.90; N, 15.04. Found: C, 64.62; H, 11.69; N, 14.81.

**N,N-Diisobutylhydrazine by the $LiAlH_4$ Reduction Procedure (Method A).**—The reduction of diisobutylnitrosamine with lithium aluminum hydride in ether was carried out in a 5-liter 3-necked round bottom flask fitted with a reflux condenser, a stirrer, a dropping funnel and a nitrogen inlet tube. The air in the flask was first displaced by nitrogen after which 9.5 g. (0.25 mole) $LiAlH_4$ suspended in 250 cc. of dry ether was introduced into the system and stirred slowly. Approximately one-tenth of the desired quantity of nitrosamine was then added to the solution in the reaction vessel which was immersed in an ice-bath. Some gas evolution was found to take place. After about an hour the major reaction suddenly took place with vigorous foaming and the development of a considerable amount of heat. After the initial reaction had subsided (about ten minutes) the remainder of the nitrosamine was added slowly, the resulting reaction now taking place with considerably less vigor. The mixture was stirred overnight and treated with a 6:1 ether–alcohol mixture. The lithium and aluminum ethylates were removed by filtration and washed with the alcohol until the washings gave a negative reaction with Fehling solution.

Most of the ether and alcohol was removed by distillation; the residue was distilled immediately under reduced pressure, all of the product coming over up to 65° at 14 ml. being collected. The distillate was then fractionated twice under reduced pressure; the principal fraction was collected to give 17.2 g. (48%) of N,N-diisobutylhydrazine, b.p. 58–60° at 14 mm. The identity of the product was verified by conversion to the semicarbazide.

**N,N-Diisobutylhydrazine by the Sodium-Alcohol Reduction Method (Method B).**—A solution of 33 g. (0.25 mole) of diisobutylnitrosamine in 250 cc. of absolute ethanol was cooled to zero and treated over a period of 4 hours with a total of 23 g. of sodium. Since the reduction was found to proceed very slowly toward the end, the solution was allowed to warm to room temperature. Upon completion of the sodium addition petroleum ether was added to the solution and then water until phase separation had occurred. The reaction mixture was then extracted repeatedly with a total of 1.5 liters of low boiling petroleum ether (30–40°) after which the aqueous alcoholic mother liquor showed only a slight test for a reducing agent when treated with Fehling solution. The extract was dried overnight over anhydrous sodium sulfate. The solvent was then removed at atmospheric pressure and the residue fractionated under reduced pressure to give 13.2 g. (36.6%) of the desired product boiling at 58.5–59.5° at 13 mm. Identity of the product with that obtained by lithium aluminum hydride reduction was verified (a) by conversion into 1,1-diisobutylsemicarbazide and (b) by a mixture melting point.

**N,N-Di-*n*-propylhydrazine by Reduction with Sodium in Liquid Ammonia in the Presence of Alcohol (Method C).**—Approximately 750 cc. of liquid ammonia was introduced into a 3-l. Dewar flask to dissolve 18.5 g. (0.8 mole) of sodium. With stirring there was then introduced slowly a solution of 26 g. (0.2 mole) of di-*n*-propylnitrosamine in 50 cc. of alcohol. The ammonia solution was found to have decolorized after the addition of the latter. The liquid ammonia was allowed to evaporate from the reaction mixture overnight. More alcohol was then added to the residue, the insoluble material removed by filtration and the residue extracted with two successive portions of alcohol. The various alcohol extracts were combined and distilled to dryness under reduced pressure. The distillate was fractionated twice to give 13.9 g. (60%) of di-*n*-propylhydrazine, b.p. 36–38° at 12 mm.

**Preparation of 1,1-Disubstituted Semicarbazides.**—Well-defined crystalline semicarbazides, $RRNNHCONH_2$, were obtained by the addition of concentrated aqueous solutions of potassium cyanate to solutions of the hydrazines in acetic acid (*p*H 5 to 6).

(a) **1,1-Di-*n*-propylsemicarbazide,** m.p. 116°. *Anal.* Calcd. for $C_7H_{17}N_3O$: C, 52.80; H, 10.76; N, 26.39. Found: C, 52.92; H, 10.63; N, 26.66.

(b) **1,1-Diisopropylsemicarbazide,** m.p. 163°. *Anal.* Calcd. for $C_7H_{17}N_3O$: C, 52.80; H, 10.76. Found: C, 52.89; H, 10.33.

(c) **1,1-Di-*n*-butylsemicarbazide,** m.p. 94°. *Anal.* Calcd. for $C_9H_{21}N_3O$: C, 57.71; H, 11.30; N, 22.44. Found: C, 57.58; H, 11.35; N, 22.32.

(d) **1,1-Diisobutylsemicarbazide,** m.p. 198°. *Anal.* Calcd. for $C_9H_{21}N_3O$: C, 57.71; H, 11.30; N, 22.44. Found: C, 57.90; H, 11.24; N, 21.93.

**N-Diethylaminourethan Methyl Ester Hydrochloride.**—N,N-Diethylhydrazine was treated with the methyl ester of chlorocarbonic acid in ether. The mixture was evaporated to dryness, the residue taken up in alcohol and filtered free from insoluble impurities. The desired product was precipitated from the alcoholic solution by treatment with ether, m.p. 179°.

*Anal.* Calcd. for $C_6H_{15}ClN_2O_2$: C, 39.45; H, 8.13; N, 15.33. Found: C, 39.62; H, 8.30; N, 15.33.

**N,N-Di-*n*-amylhydrazine hydrogen Oxalate.**—One-half gram of N,N-di-*n*-amylhydrazine was dissolved in 6 ml. of 95% ethanol containing 1.2 g. of oxalic acid dihydrate. The oxalate precipitated immediately. It was purified by recrystallization from hot alcohol; m.p. 164° dec.

*Anal.* Calcd. for $C_{12}H_{26}N_2O_4$: N, 10.63. Found: N, 10.52.

**N,N-Pentamethylene-N′-*p*-chlorobenzylidene Hydrazine**: from N-cyclopentamethylene hydrazine (N-aminopiperidine) and *p*-chlorobenzaldehyde in ethanol, m.p. 63°.

*Anal.* Calcd. for $C_{12}H_{15}N_2Cl$: C, 64.72; H, 6.79; N, 12.58. Found: C, 64.93; H, 6.91; N, 12.27.

## Discussion

Reference to the experimental data in Table I indicates that the lithium aluminum hydride procedure is an efficient laboratory method for the reduction of nitrosamines to the corresponding hydrazines. However, difficulties were experienced in initiating the reaction which frequently occurred only after a considerable period of time had elapsed with extraordinary violence and with considerable evolution of heat. It is advisable to initiate the reaction with a small quantity of the desired nitrosamine before the remainder is added. Absolute alcohol should be used to decompose the reaction products instead of water.[3] In many respects, reduction of nitrosamine is accomplished more easily by reaction with sodium either in alcoholic solution or in liquid ammonia. Both speed of the reaction and yields are affected by the reactivity of sodium with the alcohol. Using quantities of ethanol and nitrosamine in a 16:1 mole ratio, it was found that the reaction became slower and slower as more and more of the alkali metal was added to the ethanol–nitrosamine mixture. The reaction proceeds vigorously at first making it necessary to cool the mixture; it is completed by allowing the system to come to room temperature. Reduction using methanol as the solvent was checked for the preparation of N-aminopiperidine. Hydrogen evolution takes place much more rapidly. However, even though a 100% excess of sodium was used, the product yield amounted to only 8% as compared with 31% using ethanol; in addition, 55% of the nitrosamine was recovered unchanged. The methanol–sodium reaction appears to take place so rapidly that hydrogen escapes too quickly to effect hydrogenation of the nitrosamine. It would thus appear that hydrogen in *status nascendi* is responsible for the reaction.

Comparative experiments entailing preparation of N,N-diisobutylhydrazine in ethanol and in isopropyl alcohol revealed that the reaction takes place so slowly at ordinary temperatures in the latter solvent that heating to 60° is necessary. Some increase in yield (from 44 to 51%) was achieved. This is believed, however, to be due in part to the fact that isolation of the product is considerably simplified. Addition of water brings about phase separation. Practically all of the hydrazine separates from the isopropyl alcohol reaction solution.

Watt[4] has pointed out that either electron reduction or hydrogenation may occur when metal–ammonia solutions are used as reducing agents. Hydrogenation usually takes place when there is present in liquid ammonia a solute (acid) that will undergo reaction with the dissolved metal to give hydrogen *in situ*. Thus, for instance, G. B. L. Smith and co-workers[5] have shown that nitroguanidine can be reduced to aminoguanidine if reaction with sodium is carried out in the presence of ammonium chloride; extensive decomposition occurs in the absence of ammonium salt. Nitrosamines react very slowly with metal–ammonia solutions, but more rapidly in the presence of acidic solutes to yield the corresponding hydrazines. Two proton donors were employed in the present study; (a) ethanol. whose acidic nature is enhanced by solution in the basic solvent ammonia and (b) ammonium chloride which furnishes the ammonium ion, the acid analog species in liquid ammonia. Ethanol, presumably a weak acid in liquid ammonia, was found to give better yields than ammonium chloride, a comparatively strong acid. Not only did appreciable quantities of nitrosamine escape hydrogenation, but some cleavage of the nitrogen–nitrogen bond to the amine was found to occur when ammonium chloride was used. It is interesting to note in this connection that Emil Fischer[2] succeeded in effecting the reduction of nitrosamines to the hydrazine in aqueous solution by use of zinc and acetic acid, but obtained no product when stronger acids such as hydrochloric acid and sulfuric acid were employed.

Use of liquid ammonia as a non-aqueous solvent

[4] G. W. Watt, *Chem. Revs.*, **46**, 317 (1950).

[5] P. Fuller, E. Lieber and G. B. L. Smith, This Journal, **59**, 1150 (1937).

for effecting reduction of nitrosamines to the hydrazines is preferred. First, the reactions can be carried out in a completely homogeneous system. Secondly, recovery of the product involves only removal of the solvent by evaporation after which the residue is subjected to either an extraction or a distillation procedure.

URBANA, ILLINOIS

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[CONTRIBUTION NO. 1940 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

# The Kinetics of the Oxygenation of Ferrous Iron in Phosphoric Acid Solution

BY MARK CHER AND NORMAN DAVIDSON

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The rate of the $Fe^{++}$, $O_2$ reaction in $H_3PO_4$, $NaH_2PO_4$ solutions at an ionic strength of 1.0–1.1 $M$ ($NaClO_4$) has been studied by a manometric technique. The rate law is $-d(Fe^{++})/dt = k(Fe^{++})p_{O_2}(H_2PO_4^-)^2$, where $k = 4.5(\pm 0.3)$ atm.$^{-1}$ mole$^{-2}$ liter$^2$ hr.$^{-1}$ at 30°. The activation energy is 20(±2) kcal. There is some heterogeneous reaction on a glass wool surface, but it is believed that the above rate data apply to the homogeneous reaction. There is no inhibition by added $Fe^{+++}$. A one-electron reaction mechanism with the rate-determining step, $Fe^{++} + O_2 \rightarrow Fe^{+++} + HO_2$, is consistent with the results. The marked catalytic effect of added $Cu^{++}$ can be explained by the reactions (unbalanced with respect to $H^+$): $Fe^{++} + Cu^{++} \underset{k_8}{\overset{k_7}{\rightleftarrows}} Fe^{+++} + Cu^+$; $Cu^+ + O_2 \underset{k_{10}}{\overset{k_9}{\rightleftarrows}} Cu^{++} + HO_2$; $HO_2 + Fe^{++} \xrightarrow{k_3} Fe^{+++} + H_2O_2$. At 30°, $\mu = 1$ $M$, $(H_3PO_4) = 0.434$ $F$, $(H_2PO_4^-) = 0.302$ $F$, $p_{O_2} = 150$ mm., $k_7 = 1.0 \times 10^3$ $M^{-1}$ hr.$^{-1}$, $k_9/k_8 = 5.1 \times 10^{-2} M^1$ atm.$^{-1}$, and $k_{10}/k_3 = 23$.

In 1935, Weiss[1] suggested that the oxygenation of dipositive iron, $Fe^{II}$, in aqueous solution proceeds *via* the sequence of one-electron oxidations.

$$Fe^{II} + O_2 \underset{2}{\overset{1}{\rightleftarrows}} Fe^{III} + HO_2 \qquad (1,2)$$

$$Fe^{II} + HO_2 \longrightarrow Fe^{III} + H_2O_2 \qquad (3)$$

$$Fe^{II} + H_2O_2 \longrightarrow Fe^{III} + OH + H_2O \qquad (4)$$

$$Fe^{II} + OH \longrightarrow Fe^{III} + H_2O \qquad (5)$$

The reactions as written are not balanced with respect to hydrogen ion and are not intended to specify the dependence of reaction rate on this variable nor to distinguish between the acid, $HO_2$ and its anion, $O_2^-$. Reactions 4 and 5 are fast and not rate determining and have been independently investigated.[2,3] Until very recently, there has been no strong experimental evidence for reactions 1 and 2, but the mechanism has been widely accepted because of the evidence for the occurrence of $HO_2$ in other reaction systems.

The most reliable and extensive of the early studies of the oxygenation of $Fe^{++}$ in *homogeneous* systems appear to be those by Lamb and Elder[4] and McBain[5] in which it was found that in sufficiently acid (>0.1 $M$) $H_2SO_4$ solution, $-d(Fe^{++})/dt = k(Fe^{++})^2(O_2)(H^+)^0$, suggesting that the rate-determining step is the termolecular, two-electron oxidation

$$2Fe^{II} + O_2 \longrightarrow 2Fe^{III} + H_2O_2 \qquad (6)$$

There is a preliminary announcement of a recent confirmation of this rate law.[6] The interpretation of these experiments appears to us to be valid; nevertheless, some skepticism is permissible because rather concentrated solutions ($(FeSO_4) > 0.1$ $M$) were used in order to get a measurably fast reaction rate, so that the inference of kinetic order from concentration dependence is possibly uncertain because of uncertain activity effects. A brief and not entirely conclusive study in this Laboratory of the same system at higher temperatures will be reported in a following paper.[7]

It is to be expected that the rate of oxygenation of $Fe^{II}$ can be increased by the presence of reagents that complex $Fe^{III}$ strongly. The present paper describes a study of the $Fe^{II}$, $O_2$ reaction in $H_3PO_4$, $H_2PO_4^-$ solutions, in which it has been found that the reaction is much faster than in $H_2SO_4$ solution and apparently proceeds according to the Weiss mechanism. The catalytic effect of $Cu^{++}$ has also been elucidated.

While our investigation was in progress, it has been announced that in concentrated hydrochloric acid[8] and in the presence of fluoride ion,[6] the $Fe^{++}$, $O_2$ reaction rate is first order in each component.

It should also be noted that, some time ago, it was discovered that the $Fe^{II}$ oxygenation is rapid in pyrophosphate solution,[9] although the claim that the reaction is first order[9] in $Fe^{II}$ has been criticized[4] on the grounds that the reaction rate was actually diffusion controlled under the conditions used.

## Experimental

The rate of $O_2$ uptake was measured with a Warburg manometer apparatus (American Instrument Co. no. 5-134). The apparatus was well thermostated and had provision for vigorous shaking of the reaction mixture. The manometric technique has several advantages for reactions that do not proceed too rapidly (> *ca.* 30 minute half time); it is easy to run a large number of samples concurrently, and the method is sensitive to small amounts of reaction. The sensitivity of the manometers was

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[1] J. Weiss, *Naturwissenschaften*, **23**, 64 (1935).

[2] F. Haber and J. Weiss, *Proc. Roy. Soc.* (*London*), **A147**, 332 (1934).

[3] W. G. Barb. J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951).

[4] A. B. Lamb and L. W. Elder, THIS JOURNAL, **53**, 137 (1931).

[5] J. W. McBain, *ibid.*, **5**, 623 (1901).

[6] J. Weiss, *Experientia*, **IX**, 61 (1953).

[7] R. E. Huffman, N. Davidson and J. Andelin, manuscript to be submitted to THIS JOURNAL.

[8] A. M. Posner, *Trans. Faraday Soc.*, **49**, 382 (1953).

[9] J. H. C. Smith and H. A. Spoehr, THIS JOURNAL, **48**, 107 (1926).