The plot of E *vs.* $\log i/(i_d - i)$ for the polarographic wave in this case gave a straight line from the slope of which the value of n was calculated to be 2.8.

The values of K_d from equation (7) were calculated for the two indium chloride complexes. K_d for the $InCl_4^-$ ion for hydrochloric acid concentrations of 8–11.6 N was calculated to vary between 6 and 13. This would indicate that the $InCl_4^-$ ion is quite unstable in aqueous solution. K_d for the $InCl_2^+$ ion for hydrochloric acid concentrations of 1 to 4 N was calculated to vary between the limits 1.5×10^{-2} and 3.3×10^{-2}, indicating this latter complex to be more stable than the former by a factor of 10^2.

Acknowledgment.—The authors wish to express their appreciation to the Office of Naval Research for their support of the work, part of which is covered in this report.

Summary

Polarographic reduction of indium(III) ion in solutions of varying chloride ion activities has been studied. Evidence has been presented for the possible existence of two indium chloride complex ions in aqueous solution, $InCl_4^-$ and $InCl_2^+$. The $InCl_4^-$ complex is found to be relatively unstable and to exist only in solutions of high chloride ion concentration.

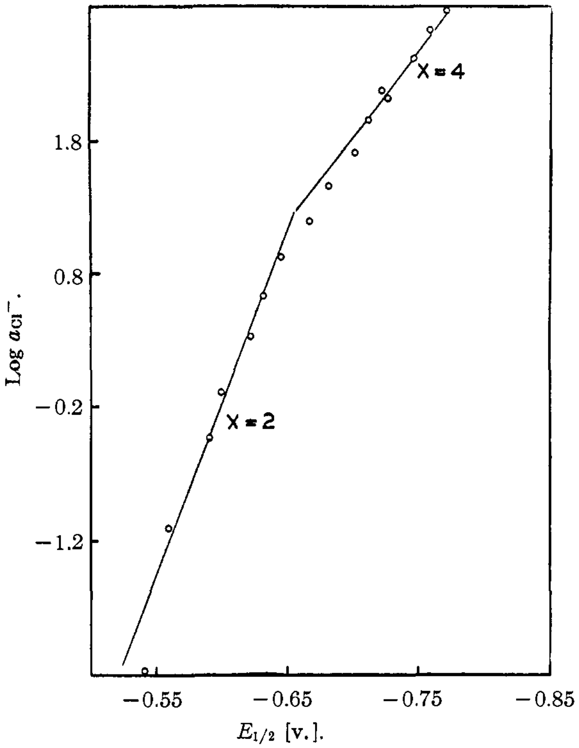

Fig. 1.

SOCORRO, NEW MEXICO RECEIVED JULY 31, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Some Aspects of Reactions between Ammonia and Mercury(I) Compounds

BY SRINATH D. ARORA,[1] WILLIAM N. LIPSCOMB AND M. C. SNEED

The action of excess 0.1 N aqueous ammonia on mercury(I) nitrate and perchlorate is described by the reaction $2Hg_2^{++} + X^- + 4NH_4OH \rightarrow 2Hg + Hg_2NX + 3NH_4^+ + 4H_2O$ where X^- is NO_3^- or ClO_4^-. A similar reaction occurs with mercury(I) chloride $2Hg_2Cl_2 + 4NH_4OH \rightarrow 2Hg + Hg_2NCl{\cdot}H_2O + 3H_2O + 3NH_4^+ + 3Cl^-$. When about 0.7 N ammonia is used, the ratio of Hg_2Cl_2 to solution may be chosen to give the reaction $Hg_2Cl_2 + 2NH_4OH \rightarrow Hg + HgNH_2Cl + NH_4^+ + Cl^- + H_2O$ which proceeds through intermediate formation of $Hg_2NCl{\cdot}H_2O$. The product, $HgNH_2Cl$, may be transformed to $Hg_2NCl{\cdot}H_2O$ by 0.1 N aqueous ammonia. The reaction of gaseous ammonia with Hg_2Cl_2 yields $Hg + Hg(NH_3)_2Cl_2$, while that of liquid ammonia yields Hg plus some $HgNH_2Cl$ and some $Hg(NH_3)_2Cl_2$. The compounds Hg_2NNO_3, Hg_2NClO_4, $Hg_2NOH{\cdot}2H_2O$, $Hg_2NCl{\cdot}H_2O$, $Hg_2NBr{\cdot}H_2O$ and Hg_2NI are shown to be isomorphous by means of X-ray diffraction photographs. The structure of the Hg_2N^+ framework is very similar to that of cristobalite, SiO_2. Bonds from Hg are linear, while those from nitrogen are tetrahedral, and the Hg–N distance is 2.07 Å.

Introduction—The many different conclusions reached by various investigators in studies of the reactions of ammonia with mercury(I) compounds suggest that the reactions and products may vary considerably with the conditions employed for both reactions and analyses. The black solids produced in the reactions have been assigned many different formulas for which the most commonly accepted is $Hg + HgNH_2Cl$, but intermediates such as Hg_2NH_2Cl and Hg_2O have been claimed by the more recent investigators.[2] Under other conditions Egidius[2] has claimed that compounds Hg_4NCl and $Hg_2(NH_3)_2Cl_2$ decompose into $Hg + Hg_2NCl$ and $Hg + Hg(NH_3)_2Cl_2$, respectively.

The present study is intended to elucidate the reactions in dilute aqueous ammonia. Both chemical and physical methods, particularly X-ray diffraction, are used in order to search for possible intermediates or other reactions, and in order to describe more completely the known compounds.

Results and Discussion

1. Action of 0.1 N Aqueous Ammonia.—The black solid, first formed upon reaction with a

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[2] Description of older work may be found in the standard reference books of Inorganic Chemistry. The most recent work is that of E. Gleditsch and T. F. Egidius, *Compt. rend.*, **202**, 574 (1936); *Z. anorg. Chem.*, **226**, 265 (1936); *ibid.*, **228**, 249 (1936). Also T. F. Egidius, *ibid.*, **240**, 97 (1938), and H. Freche and M. C. Sneed, THIS JOURNAL, **60**, 518 (1938).

stoichiometric amount of Hg_2Cl_2, gradually becomes grayish in color, and amalgamates sheet gold before or after drying, at all stages of the reaction, even after 30 seconds. Thus, in disagreement with previous investigators, it seems probable that no mercury(I) intermediate is formed, and that changes in the particle size of Hg cause the color change. The filtrate showed the presence of Cl^- but no Hg_2^{++} or Hg^{++} was detected at any stage. Two series of reactions, at 0 and 25°, were carried out in which accurately weighed samples of 0.4 to 1.0 g. of Hg_2Cl_2 were treated with excess (about 140 ml. per g. of Hg_2Cl_2) 0.1033 *N* ammonia for various times ranging from 30 seconds to 6 days. Although the reaction at 0° is somewhat slower at 25° the percentage of total Cl^- displaced rose from zero to 75.0% after 1 hour and was at 73.6% after 6 days. Chemical analysis of the precipitate gave results in agreement with the assumption of a mixture of $2Hg + Hg_2NCl \cdot H_2O$ as shown in the tabulation.

Substance	Experimental	Theoretical
Hg	91.52	92.24
N	1.84	1.61
Cl	3.77	4.08
H_2O (by difference)	2.87	2.07

Thus the reaction consistent with these results is

$$2Hg_2Cl_2 + 4NH_4OH \longrightarrow 2Hg + Hg_2NCl \cdot H_2O + 3H_2O + 3NH_4^+ + 3Cl^-$$

In order to test for the presence of intermediates in this reaction X-ray diffraction photographs were taken at the various stages. As the reaction proceeded the lines of Hg_2Cl_2 gradually disappeared and only those lines due to $Hg_2NCl \cdot H_2O$ were observed. The final diffraction pattern was identical with that from a separately prepared sample of $Hg_2NCl \cdot H_2O$ prepared by displacement of NO_3^- from Hg_2NNO_3, as described below. Finally, the presence of less than 0.1% of hydrogen as shown by the analysis of the dried precipitate at an intermediate stage also showed that no $HgNH_2Cl$ was present. Thus we believe that no intermediates are formed under these conditions.

Reactions of 0.1 *N* aqueous ammonia with solutions of pure mercury(I) nitrate and perchlorate[3] gave essentially the same results as the chloride but the reactions were comparatively rapid because the chloride dissolved so slowly. Potentiometric titrations of 0.1075 *N* aqueous ammonia with 0.1044 *N* mercury(I) nitrate or with 0.1247 *N* mercury(I) perchlorate showed smooth curves, indicating no intermediate reactions, with equivalence points at exactly the ratio determined by the reaction

$$2Hg_2^{++} + X^- + 4NH_4OH \longrightarrow 2Hg + Hg_2NX + 3NH_4^+ + 4H_2O$$

The residues amalgamated gold at all stages.

Separation of the free Hg from the Hg_2NNO_3 either by distillation (reduced pressure, 25°) or by leaching with nitric acid yielded samples of yellowish powder. The original black material (which was thus shown to contain a ratio of 0.975 of free Hg to 1.000 bound Hg) and the samples of yellowish powder (which was shown on analysis to be $Hg_2N_2O_3$) gave identical X-ray patterns. The presence of nitrate ion in $Hg_2N_2O_3$ was shown by infrared absorption analysis[4]; the sample showed absorption bands at the wave numbers 1330(vs), 1053 (vw), 818(m), 695(vw shoulder) and 680(m). Comparison with wave numbers[5] of NO_3^- at 1390, 1050, 831 and 720 indicates clearly the presence of NO_3^- ions, probably somewhat perturbed. The study of Hg_2NClO_4 was considerably less extensive, the compound being identified by its X-ray diffraction pattern.

2. **Nature of Hg_2NX Compounds.**—Pure solid $Hg_2N_2O_3$ was easily converted to $Hg_2NCl \cdot H_2O$, $Hg_2NBr \cdot H_2O$, Hg_2NI or $Hg_2NOH \cdot 2H_2O$ by treatment, respectively, with 10 to 20% aqueous solutions of KCl, KBr, KI or KOH, which treatment displaced substantial quantities of nitrate ion in each case. Powder diffraction photographs of

TABLE I

X-RAY DIFFRACTION DATA

$Hg_2NOH \cdot 2H_2O$			$HgNH_2Cl$	
Spacing, Å., obsd.	Relative intensity[a] Obsd.	Relative intensity[a] Calcd.	Spacing Å., obsd.	Relative intensity[a] Obsd.
5.518	237	131	5.143	95
2.884	65	71	4.319	67
2.757	131	87	3.303	82
2.395	48	45	2.941	8
2.198	43	35	2.779	40
1.842	24	28	2.627	40
1.693	41	31	2.570	6
1.619	36	26	2.299	38
1.459	8	9	2.202	20
1.443	42	37	2.154	9
1.383	11	10	2.030	19
1.341	15	13	1.987	9
1.247	17	16	1.837	16
1.196	6	4	1.801	4
1.171	5	4	1.702	16
1.106	8	8	1.652	6
1.100	16	13	1.588	6
1.072	14	12	1.478	15
1.053	11	8	1.435	7
1.004	3	5	1.325	4
0.978	13	10	1.274	5
.963	11	7	1.191	5
.926	5	7		
.922	16	13		
.894	4	6		
.865	4	6		
.848	4	6		
.838	16	17		
.812	3	9		
.811	21	29		
.799	14	20		
.790	5	9		

[a] Calculated data are from Hg positions only. Observed data were obtained with CuK_α radiation from samples loosely packed in capillaries about 0.2 mm. in diameter.

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[3] Prepared by the method of E. Newburg, *Trans. Electrochem. Soc.*, **69**, 611 (1936), and W. Pugh, *J. Chem. Soc.*, [2] 1824 (1937).

[4] A nujol mull of finely powdered material was examined in a Perkin-Elmer model 12C spectrometer. See R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948); R. B. Barnes, R. C. Gore, U. Liddel and V. Z. Williams, "Infrared Spectroscopy," Reinhold Publishing Corp., New York, N. Y., 1944.

[5] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 178.

these five compounds indicated that the Hg_2N^+ portion of the crystal structure remains essentially constant during these displacements, and that the relative spacings and intensities are so nearly the same that these compounds can be classed as isomorphous. The arrangement of Hg atoms in these structures has been elucidated. The unit cell is cubic with $a = 9.58 \pm 0.01$ Å., with 16 Hg at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$, $\frac{3}{8}\frac{1}{8}\frac{3}{8}$, $\frac{3}{8}\frac{3}{8}\frac{1}{8}$, $\frac{1}{8}\frac{3}{8}\frac{3}{8}$ plus the face centered permutation 000, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$ to be applied to each of these positions. It is therefore inferred that the 8 nitrogen atoms are at 000, and $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, plus the face-centered permutation, in the diamond-type of arrangement. These mercury positions give very good agreement with the intensities (see Table I, where the diffraction pattern of $HgNH_2Cl$ is also included). They permit the Hg to form linear sp bonds, and the nitrogen to form tetrahedral sp^3 bonds in what may be described as an idealized cristobalite type of arrangement with N replacing Si, and Hg replacing O. The Hg–N bond distance is 2.073 ± 0.003 Å. in $Hg_2NOH \cdot 2H_2O$. Very large channels remain after the formation of this Hg_2N^+ three-dimensional framework, and the negative ions and water molecules probably occupy these channels in somewhat disordered positions. It also seems possible that free mercury atoms or aggregates of very few atoms could also be trapped in these channels, a possibility which may explain some of the difficulties concerning the nature of the valence state of mercury in this substance in reactions between mercury(I) compounds and ammonia.

3. **Action of 0.7 *N* Aqueous Ammonia.**—In an attempt to clarify the conditions[6] under which $HgNH_2Cl$ is produced various amounts of Hg_2Cl_2 were treated with aqueous ammonia at 25° as summarized in Table II. It is important to note that exact quantities of all materials as well as the time of reaction are important in the reactions. These experiments are only preliminary, and unfortunately, chemical analyses of the precipitates were not made, but the fact that the chloride in the filtrate falls below 50% is in disagreement with the results of Freche and Sneed, and may suggest that some $Hg(NH_3)_2Cl_2$ is also formed in the reaction. Unfortunately, the three most intense diffraction lines of $Hg(NH_3)_2Cl_2$ coincide exactly with lines of $HgNH_2Cl$ so that detection by this method of fairly large proportions of $Hg(NH_3)_2Cl_2$ would be difficult. However, these results indicate that the $Hg_2NCl \cdot H_2O$ first produced undergoes the further reaction

$$Hg_2NCl \cdot H_2O + NH_4^+ + Cl^- \longrightarrow 2HgNH_2Cl + H_2O$$

TABLE II

ANALYSES FOR CHLORIDE ION AFTER REACTION WITH 0.6 TO 0.7 *N* AMMONIA

Weight of Hg_2Cl_2, g.	Normality of ammonia	Volume of ammonia, ml.	Time of reacn., days	Chloride in filtrate, %	X-Ray diffraction pattern
0.4710	0.685	50	3	69	$Hg_2NCl \cdot H_2O$
.9909	.685	50	1/48	67	not taken
.9915	.685	25	2	34	$HgNH_2Cl$
1.2141	.654	25	35	26	$HgNH_2Cl$

The reverse of this reaction is also well known to occur upon treatment of $HgNH_2Cl$ with dilute aqueous ammonia,[2] as we also confirmed by treatment of 0.5 g. of $HgNH_2Cl$ with 60 ml. of 0.1 *N* aqueous ammonia at 25° for five days. Thus exact concentrations of both ammonia and ammonium chloride are important in the successive transformations $Hg_2NCl \cdot H_2O$, $HgNH_2Cl$, $Hg(NH_3)_2Cl_2$ and the reverse reactions. Except for the question of mercury(I) *versus* mercury(II) compounds, our results compare favorably with those of Egidius[2].

4. **Reactions of Hg_2Cl_2 with Gaseous and Liquid Ammonia.**—The purpose of the following experiments is to test further for possible intermediate compounds or for other reactions. The reaction with gaseous ammonia, dried over barium oxide, was allowed to proceed at room temperature for 15 days in a reaction chamber previously swept out with dry nitrogen. The black product amalgamated sheet gold, and also gave a diffraction pattern[7] identical with that from a separately prepared sample of $Hg(NH_3)_2Cl_2$. These results are summarized by the over-all reaction

$$Hg_2Cl_2 + 2NH_3(g) \longrightarrow Hg + Hg(NH_3)_2Cl_2$$

The reaction with liquid ammonia, dried over sodium, was carried out at −80° in the absence of air. The mercury(I) chloride was converted to a shiny black solid, which became gray when allowed to reach room temperature, and which amalgamated sheet gold and gave a diffraction pattern identical with that of $HgNH_2Cl$. In addition, the portion of the reaction product which dissolved in liquid ammonia was shown to be $Hg(NH_3)_2Cl_2$ by means of an X-ray diffraction photograph. Separate experiments established that pure $HgNH_2Cl$ was not appreciably soluble in pure liquid ammonia, but that solution did take place in the presence of NH_4Cl; when this solution was evaporated a diffraction photograph of the needle-like crystals was identical with that of $Hg(NH_3)_2Cl_2$. Thus it seems likely that the initial reaction is

$$Hg_2Cl_2 + 2NH_3 \longrightarrow Hg + HgNH_2Cl + NH_4Cl$$

and that the NH_4Cl causes a portion of the $HgNH_2Cl$ to dissolve according to the reaction

$$HgNH_2Cl + NH_4Cl \longrightarrow Hg(NH_3)_2Cl_2$$

Acknowledgment.—Financial assistance from the Shevlin Fellowship to S. D. Arora is gratefully acknowledged. We wish to thank Mr. Lewis Katz for his assistance with the aid of a grant from the Graduate School, and Professor B. L. Crawford, Jr., for the infrared analysis.

Experimental

1. **Analysis of Samples.**—Calcd. for Hg_2NNO_3: Hg, 84.07; N, 5.87; O, 10.06; Found: Hg, 84.14; N, 5.7; O (by difference), 10.16; H, < 0.2; H_2O, < 0.1.

Calcd. for $Hg_2NCl \cdot H_2O$: Hg, 85.60; N, 2.99; Cl, 7.57; H_2O, 3.84. Found: Hg, 85.33; N, 3.05; Cl, 7.64; H_2O, 3.90.

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[6] Although Freche and Sneed[2] report that 0.1 *N* ammonia was used, it is clear from Freche's thesis that concentrations as high as 0.6 *N* were employed in experiments with dilute aqueous ammonia.

[7] This pattern is in complete agreement with the structure proposed by C. H. MacGillavry and J. M. Bijvoet, *Z. Kristallographie*, **94**, 231 (1936).

Calcd. for $Hg_2NBr \cdot H_2O$: Hg, 78.19; N, 2.73; Br, 15.57; H_2O, 3.51. Found: Hg, 78.56; N, 2.83; Br, 15.00; H_2O, 3.45.

Calcd. for Hg_2NI: Hg, 74.01; N, 2.58; I, 23.41. Found: Hg, 74.10; N, 2.76; I, 23.00; H_2O, < 0.1.

Calcd. for $Hg_2NOH \cdot 2H_2O$: Hg, 85.68; N, 2.99; H_2O, 7.70; OH, 3.63. Found: Hg, 85.97; N, 3.00; H_2O, 7.39; OH (by difference), 3.64.

Calcd. for $HgNH_2Cl$: Hg, 79.57; N, 5.56; H, 0.80; Cl, 14.07. Found: Hg, 79.56; N, 5.50; H, 0.83; Cl, 13.50.

Mercury content was determined by dissolving the sample in aqua regia, and precipitating as HgS. Nitrogen was determined by a modified Kjeldahl method, H by dry combustion (semimicro) with use of gold to remove free Hg, H_2O by drying for 24 hours over P_2O_5, and halogens by the usual standard methods. Loss and gain of H_2O was very sensitive to treatment of the hydroxide (Millon base), the chloride and bromide. Successive color changes on dehydration over P_2O_5 were: $Hg_2NOH \cdot 2H_2O$, white to yellow to brown; $Hg_2NCl \cdot H_2O$, white to yellow; $Hg_2NBr \cdot H_2O$, yellow to brown. The Hg_2NI dissolved in excess KI solution.

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[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

The Photochemical Reaction between Ozone and Hydrogen Peroxide

BY DAVID H. VOLMAN[1]

The thermal and photochemical gas phase reactions of ozone and hydrogen peroxide in a flow system were studied with the object of elucidating the mechanisms of the reactions. The thermal reaction was found to be heterogeneous and to proceed rapidly in the presence of mercury vapor or mercuric oxide on the walls. For the photochemical reaction, the absence of long chains and the presence of HO radicals was shown. The proposed mechanism postulates an initiation of the reaction by interaction of O atoms formed by ozone light absorption and H_2O_2 with the formation of HO and HO_2 radicals. The kinetic equations developed from the proposed mechanism were in agreement with the experimental results.

The thermal reaction between ozone and hydrogen peroxide in acid aqueous solution has been most recently studied by Taube and Bray.[2] A chain mechanism was postulated. In a study of the photo-sensitized reaction of hydrogen and oxygen,[3] where the major product is hydrogen peroxide with some ozone formation, it was postulated that the thermal reaction between ozone and hydrogen peroxide accounted for some of the water formed in the reaction. Subsequent experiments in which ozone and hydrogen peroxide were mixed in the gas phase showed that the reaction was rapid. However, in these experiments, mercury vapor and hydrogen were present in the reaction vessel. In this paper it will be shown that the rapidity of the reaction is attributable to these components of the reaction system.

The present work had as its original object the investigation of the ozone–hydrogen peroxide gas phase thermal reaction. However, for reasons developed below this was abandoned after some preliminary experiments, and the emphasis has been placed on the photochemical reaction. It is believed that this is the first report of this light reaction.

The following equations pertinent to the discussion of the reaction mechanism are given for convenience in reference.

$$O_3 + 2537\ \text{Å.} = O_3^*,\ I_a \tag{1}$$

$$O_3^* + M = O_3 + M,\ k_1 \tag{2}$$

$$O_3^* = O_2 + O,\ k_2 \tag{3}$$

$$O + O_2 + M = O_3 + M,\ k_3 \tag{4}$$

$$O + O_3 = 2O_2,\ k_4 \tag{5}$$

$$O + H_2O_2 = HO_2 + HO,\ k_5 \tag{6}$$

$$HO + H_2O_2 = HO_2 + H_2O,\ k_6 \tag{7}$$

$$HO + O_3 = HO_2 + O_2,\ k_7 \tag{8}$$

$$HO_2 + HO_2 = H_2O_2 + O_2,\ k_8 \tag{9}$$

Of these reactions, the first five are those used in explaining the photo-decomposition of ozone, modified to the extent that the production of O atom is represented not by the initial absorption act but by the more rigorous set (1), (2), (3). The work on ozone has been reviewed extensively by Schumacher.[4,5] At low concentrations of ozone in oxygen, in addition to an O atom formation step, equations (4) and (5) must be added to explain the experimental data.

Equation (7), first proposed by Haber and Weiss,[6] was used by Taube and Bray[2] in their mechanism of the thermal solution reaction and by Volman[7] in connection with the gas phase photochemistry of hydrogen peroxide. Equation (8) is also used by Taube and Bray. Equation (9) is discussed in connection with the reaction of H atom and oxygen[3] and in connection with the photochemistry of hydrogen peroxide.[7]

The proposed mechanism is unique in its main features, since it includes all the elementary steps likely in ozone photolysis, in hydrogen peroxide photolysis and in the thermal reaction of ozone and hydrogen peroxide. It remains then, primarily, to establish that the set (1), (2), (3) is more logical than

$$O_3 + 2537\ \text{Å.} = O_2 + O \tag{10}$$

and that the reaction of O atom with hydrogen peroxide does occur and proceeds *via* (6) rather than *via*

$$O + H_2O_2 = H_2O + O_2 \tag{11}$$

which appears to be the only other possibility, and finally that HO_2 radicals do not react under the conditions of the experiment with either ozone or hydrogen peroxide.

Experimental

Apparatus.—The apparatus is shown in Fig. 1. The gas flows were measured by calibrated flowmeters F_1, F_2, F_3,

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[1] On leave 1949–1950 from University of California, Davis, California.

[2] Taube and Bray, THIS JOURNAL, **62**, 3357 (1940).

[3] Volman, *J. Chem. Phys.*, **14**, 707 (1946).

[4] Schumacher, THIS JOURNAL, **52**, 2377 (1930).

[5] Beretta and Schumacher, *Z. physik. Chem.*, **B17**, 417 (1932).

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

[7] Volman, *J. Chem. Phys.*, **17**, 947 (1949).