

[CONTRIBUTION FROM THE ATOMIC ENERGY PROJECT, SCHOOL OF MEDICINE, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Hypobromite and Hypochlorite Oxidation of Ammonium Hydroxide, Hydrazine and Hydroxylamine¹

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The alkaline oxidation of ammonium salts with hypochlorite or hypobromite gives nitrogen containing a small percentage of nitrous oxide. Under these conditions hydrazine gives mainly nitrogen with very little nitrous oxide while hydroxylamine reacts to give an appreciable amount of nitrous oxide. Ammonia containing N¹⁵ was oxidized in the presence of hydrazine or hydroxylamine using insufficient oxidant to complete the reaction. The residual hydrazine or hydroxylamine was isolated and found to contain no excess N¹⁵ suggesting that the paths of formation of N₂ and nitrous oxide from ammonia do not involve hydrazine or hydroxylamine as intermediates.

The recent appearance of reports on the oxidation of ammonium salts with sodium hypobromite,^{1a} on the oxidation of hydrazine with various oxidants² and on the presence of hydroxylamine as an intermediate in the decomposition of chloramine by hydroxide³ prompts us to report a number of related and confirmatory observations made in this Laboratory during the past three years. Our observations were reported in part at the Consolidated Engineering Corporation Mass Spectrometer Group Meeting in Pasadena, Calif., May, 1951.

During the routine determination of N¹⁵ by mass spectrometric measurements of nitrogen samples generated from ammonium salts by oxidation with sodium hypobromite,⁴ we commonly observed inordinately high output voltages for $m/e = 30$. Large 44 backgrounds also are seen. Further, samples with very high N¹⁵ content give substantial peaks at $m/e = 31, 44, 45$ and 46. The output voltages corresponding to these peaks are markedly diminished when such gas samples are suitably trapped with liquid nitrogen. Typical illustrative data are presented in Table I together with mass spectra for tank nitrogen.

These observations suggest the formation of nitrous oxide (44) and possibly nitric oxide (30) during the oxidation of ammonium ions by hypobromite. A comparison of the infrared spectra of nitrous oxide, nitric oxide, and of the condensable gaseous products of the oxidation, Fig. 1, shows that only *nitrous* oxide is formed under the conditions of the reaction. The 30 peak seen in the mass spectrum, therefore, is due solely to cleavage of nitrous oxide during ionization with the formation of NO⁺.

The amount of nitrous oxide formed is markedly increased in the presence of cupric ion as shown in Table I. Smaller increases are noted with added manganous, silver, mercuric or ferric ions. Hydrazine oxidized with hypobromite gives less nitrous oxide than do ammonium salts; hydroxylamine, on the other hand, gives a relatively large amount of nitrous oxide. The formation of nitrite ion

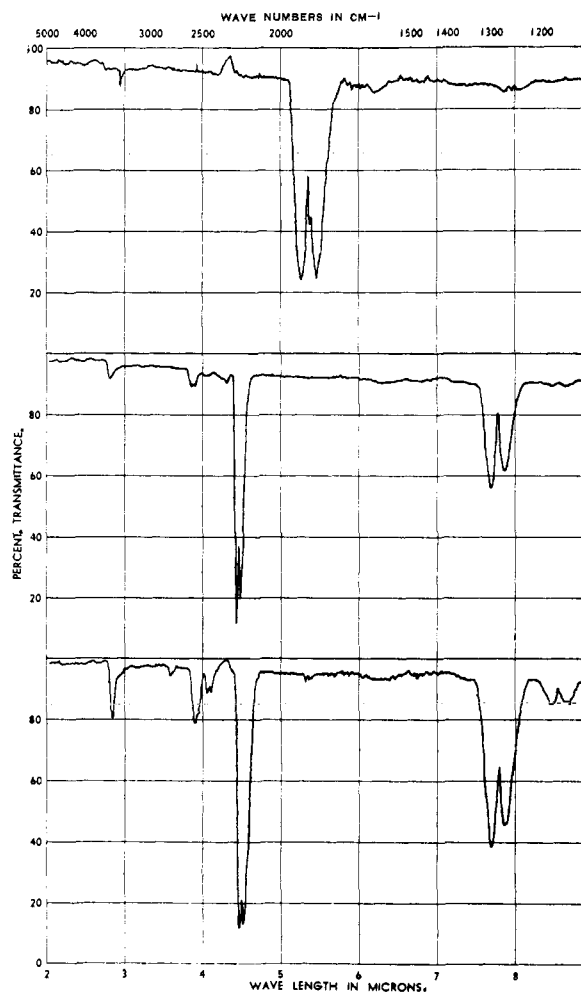


Fig. 1.—Infrared spectra for nitric oxide prepared according to Johnston and Giauque (top) the gases condensable by liquid air, generated by the oxidation of ammonium sulfate with sodium hypobromite (middle), and commercial nitrous oxide (bottom).

(1) This article is based on work performed under Contract No. AT-04-1-GEN-12 between the Atomic Energy Commission and the University of California at Los Angeles.

(1) (a) K. Clusius and G. Rechnitz, *Helv. Chim. Acta*, **36**, 59 (1953).

(2) (a) W. C. E. Higginson, D. Sutton and P. Wright, *J. Chem. Soc.*, 1380 (1953); (b) W. C. E. Higginson and D. Sutton, *ibid.*, 1402 (1953).

(3) R. E. McCoy, 124th National A.C.S. Meeting, Chicago, Ill., Sept. 6-11, 1953.

(4) D. Rittenberg, "Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Ann Arbor, Mich., 1947.

has also been noted under a wide variety of experimental conditions. The data in Table II show that slightly more nitrous oxide is present in samples generated at 37° than in those generated at 0°. These observations agree with those reported by Clusius and Rechnitz.¹

The possibilities that hydrazine represents an intermediate step in the formation of nitrogen

TABLE I
 MASS SPECTRA FOR NITROGEN SAMPLES FROM VARIOUS SOURCES

The italicized voltages were adjusted to the indicated value by adjusting the pressure in the inlet system and were taken as the points of reference for comparison of the peak size at other values of m/e

N ₂ source Trapping temp. m/e	Commercial tank → 25°	(NH ₄) ₂ SO ₄ + NaOBr -78°	N ¹⁵ H ₄ Cl + NaOBr (63 at. % N ¹⁵) -78°	-196°	(NH ₄) ₂ SO ₄ + NaOBr + Cu ⁺⁺ -78°	NH ₂ OH + NaOBr -78°	H ₂ NNH ₂ + NaOBr -78°	NH ₂ Cl + NaOH -78°
	Volts							
28	20.0	20.0	3.5	3.6	15.0	2.4	20.0	20.0
29	0.15	0.14	10.0	10.0	0.12	0.024	0.15
30	.015	.046	8.0	8.2	0.87	3.3	.005	0.077
31	0.024	0.008	0.012
44	.012	.116	.020	.011	2.72	10.0	.010	.160
45031	.002	0.080
46024	.001

TABLE II

OUTPUT VOLTAGES FOR 28, 30 AND 44 PEAKS IN GAS SAMPLES GENERATED FROM NH₄Cl AND NaOBr AT DIFFERENT TEMPERATURES

All gas samples were cooled to -78° before introduction into the mass spectrometer

Temp., °C.	m/e		
	28	30 Volts	44
0	20.0	0.022	0.085
25	20.0	.033	.121
37	20.0	.041	.144

obtained by the addition of chloramine to hot alkaline aqueous solutions of cyclohexanone.³ However, no N¹⁵ was found in carrier hydroxylamine in oxidations of N¹⁵ ammonia with either sodium hypobromite or hypochlorite, and the nitrous oxide formed must not have originated *via* this intermediate.

Further study of the mechanism of these reactions, as well as the mechanism of oxidation of ammonia and amines by hydrogen peroxide and γ -radiation is in progress.

TABLE III

SUMMARY OF EXPERIMENTS ON THE OXIDATION OF AMMONIA IN THE PRESENCE OF HYDROXYLAMINE OR HYDRAZINE

Oxidant	Carrier	At. % excess N ¹⁵ in NH ₃	Temp., °C.	Solutions conditions	Substance isolated	At. % excess N ¹⁵
NaOBr	H ₂ NNH ₂	1.06	0	6 M NaOH	Benzalazine	0.000
NaOCl	H ₂ NNH ₂	1.05	0	0.2 M H ⁺	Benzalazine	.002
NaOCl	H ₂ NNH ₂	1.05	0	0.2 M H ⁺ + 1% gelatin	Benzalazine	.003
NaOCl	H ₂ NNH ₂	1.05	57	0.2 M H ⁺	Benzalazine	.002
NaOCl	H ₂ NNH ₂	1.05	0	6 M NaOH + 1% gelatin	Benzalazine	.029
NaOCl	H ₂ NNH ₂	1.05	57	6 M NaOH + 1% gelatin	Benzalazine	.033
NaOCl	H ₂ NNH ₂	1.05	0	6 M NaOH	Benzalazine	.000
NaOBr	H ₂ NOH	67.0	0	4 M NaOH	Copper salicylaldoxime	.005
NaOCl	H ₂ NOH	67.0	0	4 M NaOH	Copper salicylaldoxime	.001

from ammonia and that hydroxylamine represents an intermediate in side reactions leading to the formation of nitrous oxide and nitrite were attractive. They were examined with equivocal results using conventional chemical tests.

More definitive results were obtained by oxidizing under various conditions N¹⁵-labeled ammonia in the presence of approximately equimolar amounts of hydrazine or hydroxylamine, with half an equivalent of hypobromite or hypochlorite. The residual hydrazine or hydroxylamine was isolated as benzalazine or copper salicylaldoxime, purified to constant isotopic composition and analyzed for N¹⁵. The results of various experiments are collected in Table III.

Under the conditions tried, significant amounts of N¹⁵ were found in carrier hydrazine only for alkaline hypochlorite oxidations in the presence of gelatin. Under the conditions employed for the preparation of nitrogen for mass analysis, hydrazine does not appear to be an intermediate.

We observed the formation of nitrous oxide in the reaction of sodium hydroxide with chloramine, Table I, and in the reaction of hypochlorite with ammonia. Also, cyclohexanone oxime has been

Experimental

Preparation and Analysis of Samples.—Solutions of sodium hypobromite⁴ and sodium hypochlorite⁵ were prepared by addition of the halogen to cooled solutions of sodium hydroxide. The concentration of the sodium hydroxide was varied depending on the strength and alkalinity desired in the hypohalite solution. Dilute solutions of chloramine⁶ were prepared by reaction of sodium hypochlorite and ammonium hydroxide and distillation under reduced pressure.

Nitrogen samples for mass analysis were generated in evacuated Faraday tubes by mixing the degassed oxidant held in the first limb with the degassed sample held in the second limb. Samples were chosen so as to give 2 to 5 mg. of gas.

Mass analyses were carried out on a model 21-201 Consolidated Isotope Ratio mass spectrometer. Samples of gas were introduced directly into the inlet system from the Faraday tubes *via* an adapter which permitted trapping condensable gas present in the sample at temperatures of -78° or -196°.

The sample of volatile nitrogen oxides for spectroscopic examination in the infrared was generated from ammonium chloride in a closed system consisting of a 500-cc. flask fitted with a nitrogen inlet and separatory funnel connected through a Dry Ice trap to a liquid nitrogen trap. The liquid nitrogen trap, which could be isolated from the rest of the system by stopcocks, was connected in turn to a 5-

(5) R. Adams and B. K. Brown, "Organic Syntheses," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 309.

(6) W. Marckwald and M. Wille, *Ber.*, **56**, 1319 (1923).

cm. gas cell with NaCl windows. This cell could be evacuated independently of the rest of the system. A solution of 3.8 g. of ammonium chloride in 20 cc. of distilled water was placed in the generator, the system swept with tank nitrogen, and with a slow sweep of nitrogen, 100 cc. of sodium hypobromite reagent was added dropwise to the ammonium chloride solution. At the conclusion of the reaction the liquid nitrogen trap was isolated from the rest of the system, the gas cell was evacuated and the condensed sample in the liquid nitrogen trap was allowed to expand by evaporation into the gas cell. The contents were finally brought to atmospheric pressure by the addition of tank nitrogen.

Nitric oxide generated by the addition of 50% sulfuric acid to a 4 M solution of potassium nitrite containing 1 M potassium iodide, was collected and purified as described by Johnston and Giaque.⁷

The redistilled nitric oxide was expanded into the 5-cm. gas cell and diluted with nitrogen for spectroscopic examination. The spectra were obtained with a Baird model B double beam infrared spectrophotometer equipped with a sodium chloride prism. The 5-cm. cell containing the gas to be analyzed was placed in the sample beam and a sodium chloride block was placed in the comparison beam.

Oxidation of Ammonia in the Presence of Hydrazine.—The following example is typical of the procedure used in various experiments: 531 mg. of ammonium sulfate, containing 1.064 at. per cent. excess N¹⁵, and 529 mg. of hydrazine sulfate were dissolved in a minimal amount of water, cooled with ice, and sodium hypobromite solution was added with vigorous stirring. The amount of sodium hypobromite employed was roughly one-half that required to completely oxidize the combined ammonia and hydrazine present in the solution, and was determined independently

(7) H. L. Johnston and W. F. Giaque, *THIS JOURNAL*, **51**, 3194 (1929).

on similar quantities of unlabeled material. After the nitrogen evolution had ceased, 0.5 cc. of benzaldehyde was added, the solution was stirred several hours and allowed to stand for 3 days at room temperature. The benzalazine, which separated as yellow crystalline lumps, was filtered with suction, washed well with water and dried. The total yield of 340 mg. was recrystallized twice from ethanol. The two filtrates from the crystallizations, and the crystals of benzalazine were each refluxed 6 hours with 1.5 g. of zinc dust and 6 cc. of 50% acetic acid in ethanol and finally digested with Kjeldahl acid. The at. per cent. excess N¹⁵ found in the first filtrate, second filtrate and crystals was 0.005, 0.000 and 0.000, respectively.

A similar procedure was used in oxidations involving NaOCl and in some instances the benzalazine was recrystallized three or four times.

Oxidation of Ammonia in the Presence of Hydroxylamine.—A solution of 100 mg. of ammonium sulfate containing 67 at. per cent. N¹⁵ and 100 mg. of hydroxylamine hydrochloride in 26 cc. of water was cooled with ice, made alkaline with 1 cc. of 6 M sodium hydroxide and with stirring, 0.75 cc. of 0.95 M sodium hypochlorite in 1 M sodium hydroxide was added. After 3–4 minutes the cold solution was acidified with 0.6 ml. of acetic acid and 25 ml. of a 0.25 M solution of acetic acid saturated with salicylaldehyde was added and the mixture warmed. After 10 minutes, 25 ml. of a 3.3% solution of cupric acetate in 0.12 M acetic acid was added and after 15 minutes the solution was cooled and filtered. The copper salicylaldehyde after washing and drying was dissolved in 5 ml. of dioxane and reprecipitated by adding 20 ml. of 0.1 M ammonium acetate in 0.02 M acetic acid. The reprecipitation was repeated three more times. The copper salicylaldehyde was reduced with stannous chloride in 50% acetic acid in ethanol, prior to Kjeldahl digestion.

The procedure employing NaOBr as oxidant was similar.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO AND FROM THE NAVAL RESEARCH LABORATORY]

Preparation of Borazole by the Reduction of Trichloroborazole^{1a}

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Trichloroborazole, prepared by the method of Laubengayer and Brown, may be reduced to borazole by lithium aluminum hydride in ethereal solutions, but the borazole cannot be satisfactorily recovered from the reaction product for reasons which are discussed. The difficulty may be overcome by use of lithium borohydride as the reducing agent. The diborane, formed as a by-product in the latter reaction, may be absorbed by sodium trimethoxyborohydride. A satisfactory procedure for preparing borazole by the reduction reaction is described. Reduction of tribromoborazole, prepared as described in the text, offered no advantages. Attention is called to the fact that borazole undergoes slow decomposition even at room temperatures.

A number of inquiries about sources of supply for borazole, B₃N₃H₆, and about satisfactory methods for its preparation recently have been received by us. It seems desirable, therefore, to describe newly developed preparative methods, even though we are not certain that we have as yet discovered the most favorable conditions for carrying out the method to be described. Originally borazole was obtained by pyrolysis of either the compounds B₂H₆·2NH₃ or B₃H₁₀·4NH₃,^{2a} or of mixtures of am-

monia and diborane.^{2b} More recently it has been prepared by pyrolysis of mixtures of solid lithium borohydride and solid ammonium chloride.³ The latter method avoids the use of diborane and is rapid, but the yields are no better than obtained by the older methods, and the procedure is not readily adaptable to the preparation of more than small quantities.

A new approach to the problem was suggested by the discovery by Laubengayer and Brown⁴ that B-trichloroborazole may be prepared by the action of boron trichloride on ammonium chloride

(1) (a) The subject matter of this paper is taken from Final Reports on Contract N6ori-20 during the period 1950–1952 and from NRL Memorandum Report 209 (September 15, 1953). The reason for the joint publication and the contribution of each laboratory are explained in the text. (b) University of Chicago; (c) Iowa State College, Ames, Iowa; (d) Argonne National Laboratory, Lemont, Ill.; (e) Naval Research Laboratory.

(2) (a) A. Stock and E. Poland, *Ber.*, **59**, 2215 (1926); A. Stock, E. Wiberg, H. Martini and A. Nicklas, *ibid.*, **63**, 2927 (1930); (b) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *THIS JOURNAL*, **60**, 1296 (1938); E. Wiberg and A. Bolz, *Ber.*, **73**, 209 (1940); E. Wiberg, *Naturwiss.*, **35**, 184 (1948).

(3) G. W. Schaeffer, Riley Schaeffer and H. I. Schlesinger, *THIS JOURNAL*, **73**, 1612 (1951). It is not unlikely that lithium borohydride could be replaced by sodium borohydride, which is now commercially available.

(4) A. W. Laubengayer and C. A. Brown, Abstracts of Papers presented at the September Meeting of the American Chemical Society, p. 10, P (1949). A detailed description is found in the thesis, "A Study of the Compound B-Trichloroborazole" by Charles A. Brown, Cornell University, 1948.