Formation and Stability of Bromamide, Bromimide, and Nitrogen Tribromide in Aqueous Solution[1]

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Reaction occurs rapidly between bromine or hypobromite and ammonia in dilute buffered aqueous solutions with the appearance of ultraviolet absorption spectra attributable to NH_2Br, $NHBr_2$, or NBr_3, depending on pH and molar ratio of ammonia to bromine. The product NH_2Br predominates in alkaline solutions at high N/Br ratios, $NHBr_2$ predominates in the pH range 6-9 with N/Br ratios about 5 to 20, and NBr_3 predominates in more acid solutions. Nitrogen tribromide is found in mixtures up to pH 8 when 2 to 3 moles of bromine per mole of ammonia are allowed to react. The existence of NBr_3 has been confirmed by extraction into chloroform and analysis of the chloroform solution. All three bromine derivatives are less stable than the corresponding chlorine compounds, $NHBr_2$ being especially evanescent. In dilute aqueous solutions at pH 4.5, NBr_3 decomposes at a rate of about 5% per hour.

Although both bromamide, NH_2Br, and bromimide, $NHBr_2$, are known to be formed in ether solution at low temperatures,[2,3] there has been little definite evidence until recently for the formation of these substances in aqueous solution. Moldenhauer and Burger had observed that NH_2Br was extractable from ether into water, and other workers had noted on indirect bases that some brominated derivative of ammonia must be formed in aqueous solution.[4]

Beginning in 1955, however, Johannesson,[5] in a series of papers, reported the formation of both NH_2Br and $NHBr_2$ from ammonia and bromine in dilute aqueous solutions and described a number of their properties in this medium.

Johannesson's initial identification of NH_2Br and $NHBr_2$ was based on ultraviolet absorption spectrometry. We have been unable to determine from his papers the bases on which assignments of the observed spectra to these compounds were made, but our results confirm generally his findings.

Ultraviolet spectrophotometry has been used in our studies also as a major tool for following the reactions between aqueous bromine or hypobromite and ammonia and in observing subsequent decomposition reactions of the formed products. The results demonstrate quite clearly that not only NH_2Br or $NHBr_2$ but also NBr_3 may be formed rapidly under suitable conditions.

Identification of NH_2Br and $NHBr_2$ has been based on comparison of the spectra attributed to them with spectra of ether solutions of these compounds prepared according to Coleman and his co-workers,[3] by com-

parison of the spectra with those of the corresponding chlorine compounds, and by differences in absorption spectra obtained with variations in the ratio of reactants. Nitrogen tribromide, NBr_3, has been further identified by elementary analyses after extraction into chloroform.

Although there are old claims of preparation of NBr_3, these have been largely discounted,[6] and so the present observations appear to represent the first modern demonstration of its existence.

Experimental

Reagents.—To ensure the absence of substances reducing bromine, all water used for the preparation of reagents or reaction mixtures was purified in the following manner. Enough saturated bromine solution was added to distilled water to give a positive test for oxidizing bromine, the water was stored for at least 2 days, the remaining oxidizing bromine was removed by boiling the water, and then the water was redistilled in an all-glass distillation apparatus.

Stock bromine solution was prepared by shaking an excess quantity of liquid bromine with purified distilled water until a nearly saturated solution was obtained. The liquid bromine used was reagent grade material which had been purified further by refluxing with solid KBr and subsequent redistillation, according to Bauer and Daniels.[7] Dilutions of the nearly saturated solution were standardized by pipetting suitable volumes beneath the surface of a solution of excess KI in pH 5 acetate buffer and titrating the liberated iodine with standard sodium thiosulfate to a starch end point, the thiosulfate being standardized daily against $KH(IO_3)_2$. Titration at pH 5 was used to avoid inclusion of bromate in the oxidizing titer, particularly in titration of reaction mixtures.

Standard ammonia solutions of appropriate stock concentrations were prepared by dilution of reagent grade concentrated ammonia followed by titration of suitable portions with standard HCl to a methyl red end point.

The reaction mixtures were buffered to minimize changes in pH

(1) Results largely taken from the thesis submitted to the Graduate School, Radcliffe College, by Hend A. Galal in partial fulfillment of requirements for the Ph.D. degree; presented in part before the Division of Water and Wastes Chemistry, American Chemical Society, Atlantic City, N. J., Sept. 1962.

(2) W. Moldenhauer and M. Burger, *Ber.*, **62B**, 1615 (1929).

(3) H. G. Coleman, H. Soroos, and C. B. Yager, *J. Am. Chem. Soc.*, **55**, 2075 (1933); H. G. Coleman, C. B. Yager, and H. Soroos, *ibid.*, **56**, 965 (1934).

(4) See, for example, O. Wyss and J. R. Stockton, *Arch. Biochem.*, **12**, 267 (1947).

(5) (a) J. K. Johannesson, *New Zealand J. Sci. Tech.*, **B36**, 600 (1955); (b) *Chem. Ind.* (London), 97 (1958); (c) *Analyst*, **83**, 155 (1958); (d) *J. Chem. Soc.*, 2998 (1959); (e) *Am. J. Publ. Health*, **50**, 1731 (1960).

(6) For example, N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, 1950, Vol. 1, p. 707, states, "NBr_3 is said to be a dark-red, explosive liquid (Millon, 1838) but it is very doubtful whether it has ever been prepared." Millon's preparation [*Ann. Chim. Phys.*, (2) **69**, 75 (1838)] involved treatment of NCl_3 with solid KBr. Failure of others to obtain this product and successful preparation of ammonium tribromide, NH_4Br_3, have apparently been major factors for doubt of the validity of this preparation. It seems possible that tribromide ion, unlike Br_2 and hypobromite, may be inactive toward solutions of ammonium salts.

(7) W. H. Bauer and F. Daniels, *J. Am. Chem. Soc.*, **56**, 378 (1934).

as a result of any reactions. Buffers used were acetic acid–acetate at pH 4.5, phosphate mixtures at pH 5.5, 6, 7, and 10.5, borate mixtures at pH 8 and 9, and KOH at pH 12. The concentration of buffer was normally a few hundredths molar. Separate solutions of the reagent grade buffer ingredients were tested prior to use to make sure that no bromine-reducing impurities were present.

Preparations.—Solutions of HOBr for measurement of its absorption spectrum were prepared by treating strong aqueous bromine solutions with either $AgNO_3$, or Ag_3PO_4 followed by vacuum distillation at room temperature, the distillate being collected in a flask containing a few drops of 0.1 M $HClO_4$.[8] The resulting solutions were diluted to about 10^{-3} M, and their concentrations and absorption spectra were determined at once.

Solutions of NH_2Br and $NHBr_2$ in ether were prepared essentially according to the methods of Coleman and co-workers.[3] To prepare NH_2Br, ammonia gas was passed for 10 min. into 30 ml. of anhydrous ether chilled to $-80°$ with a bath of Dry Ice and acetone, and then 25 ml. of a similarly chilled solution containing 0.2 ml. of liquid bromine was added. After the precipitated NH_4Br had settled, most of the solution was decanted into a separatory funnel and washed twice with small portions of ice-cold water. The remaining ethereal layer was then diluted with additional chilled ether to give solutions 2 to 5 × 10^{-3} M, and the spectra were determined immediately at about $3°$. The NH_2Br content was determined by adding a measured volume of the ether solution to excess cold sodium sulfite solution followed by mercurimetric titration of bromide. For the preparation of $NHBr_2$, 1 ml. of liquid Br_2 was added to 50 ml. of chilled ether and then ammonia gas was passed into the solution slowly for 10 min. Subsequent handling was similar to that for the NH_2Br preparations, except that dilutions to about 5 × 10^{-4} M were made for the spectrophotometric determinations.

Reaction Procedure.—Reactions were initiated by mixing rapidly equal volumes, normally 200 ml., of reactant solutions, one containing the desired amount of bromine, the other containing the ammonia and buffer. When experiments were being conducted at pH values of 8.9 and greater, it was possible to make up the bromine solution in buffer also, but for experiments at lower pH values the formation of bromate was sufficiently rapid that this was not feasible and the entire buffer was added to the ammonia solution. Because it was desirable to have the final oxidizing bromine concentration in the range from 1 to 7 × 10^{-4} M to give suitable absorbance measurements, different ratios of ammonia to bromine were obtained by changing the concentration of the ammonia solution. When the amounts of ammonia used were large, additional acidic buffer component was employed to counteract the basicity of the ammonia.

Immediately after mixing, which required only a few seconds, a portion of the reaction mixture was transferred to a silica cell, usually of 5-cm. light path, and repetitive scanning of the absorption spectrum from 340 to 220 mμ with a Beckman DK-2 spectrophotometer was initiated, the reading being made against a blank containing all of the components except the bromine. Directly thereafter and at subsequent 10–20-min. intervals, 50-ml. portions were pipetted from the remaining reaction mixture and analyzed iodometrically for oxidizing bromine as described previously. Thus, residual concentrations of oxidizing bromine as a function of time could be correlated with the absorption spectra.

Results

Ultraviolet absorption spectra for dilute aqueous solutions of Br_2 (0.5 to 2 × 10^{-3} M bromine in 0.1 M $HClO_4$), HOBr (1 to 5 × 10^{-3} M solutions prepared as described previously), and OBr^- (0.5 to 2.5 × 10^{-3} M bromine in 0.1 M KOH), as measured in silica cells of 2-cm. light path with a Beckman DK-2 spectrophotometer, are shown in Figure 1. The wave
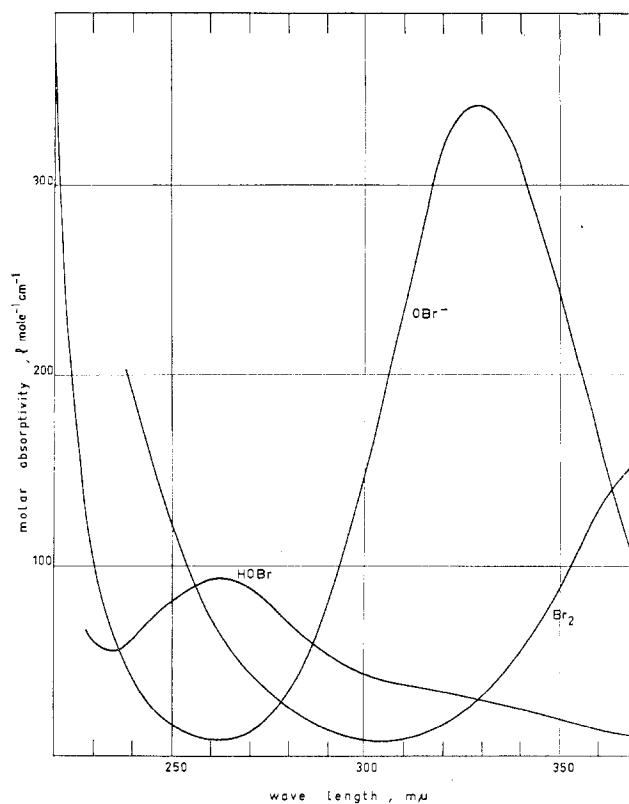
(8) E. A. Shilov, *J. Am. Chem. Soc.*, **78**, 5752 (1950).

Figure 1.—Absorption spectra for Br_2, HOBr, and OBr^-: Br_2, mean of 7 solutions, 0.5 to 2 × 10^{-3} M in 0.1 M $HClO_4$; HOBr, mean of 12 solutions, 1 to 2 × 10^{-3} M, distilled from $AgNO_3$ or Ag_3PO_4, in 10^{-4} M $HClO_4$; OBr^-, mean of 12 solutions, 0.5 to 2.5 × 10^{-3} M in 0.1 M KOH; all measurements in 2-cm. cells.

lengths of maximum absorption and absorptivities at these points for HOBr and OBr^- agree well with the published spectra of Anbar and Dostrovsky.[9] A maximum for Br_2 is exhibited outside the range shown at 390 mμ with a molar absorptivity of 177 l./mole-cm.

The shapes of the spectra for HOBr and OBr^- and the intensities of absorption are very similar to those for HOCl and OCl^- except for a shift to longer wave lengths of 30–35 mμ.

(A) NH_2Br.—When dilute solutions of bromine were mixed with excess ammonia at pH values of 9, 10.5, and 12, absorption spectra measured 2–4 min. after mixing showed none of the features of the spectra of Figure 1, but instead exhibited a maximum absorbance at 278 mμ with an absorptivity based on moles of oxidizing bromine of 390 l./mole-cm. At pH 12 and 10.5 the forms of the absorption spectra and the absorptivities near 278 mμ were independent of the initial molar ratio of ammonia to bromine—varied from 1 to 500—and of the extent of disappearance of oxidizing bromine with time. At wave lengths less than 243 mμ the light absorption increased with time as oxidizing bromine decreased, indicating the formation of a product absorbing at these short wave lengths.

These observations support strongly the idea that a single product containing oxidizing bromine is formed rapidly in all the solutions at pH 12 and 10.5 and de-

(9) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1105 (1954).

composes as oxidizing bromine is lost. In agreement with Johannesson,[5a] the substance absorbing at 278 mμ is believed to be NH_2Br, partly because of its formation even with very high ratios of ammonia to bromine, partly on the similarity of the reaction conditions to those yielding NH_2Cl from hypochlorite and ammonia, and partly on the basis of an observed maximum in absorption at 284 mμ for NH_2Br in ether.
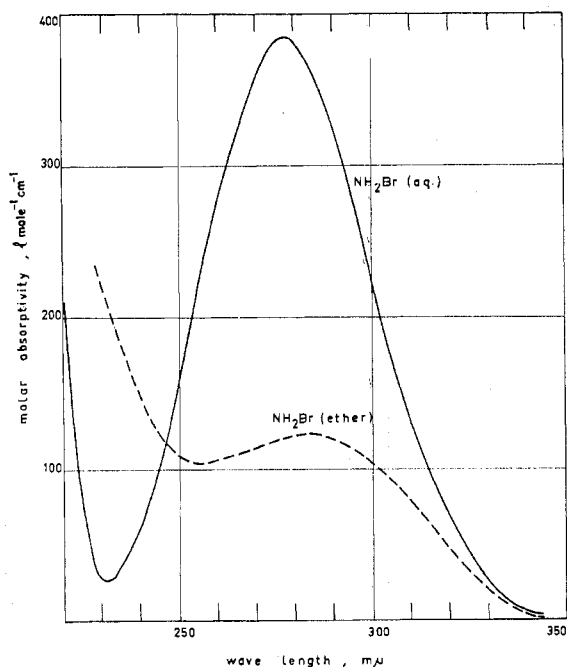
In Figure 2 the absorption spectrum of NH_2Br in

Figure 2.—Absorption spectra for NH_2Br. Aqueous, mean of 9 solutions 1 to 5 × 10^{-4} M, molar ratio N/Br 12 to 500, pH 9, 10.5, 12, a(278) = 386 ± 15; measurements in 5-cm. cells. Ether, 2 to 5 × 10^{-3} M, 3°, 1-cm. cells.

aqueous solutions, derived from measurements on the most nearly stable of the alkaline reaction mixtures, is compared with that measured for NH_2Br in ether, prepared as described previously. Although the spectra appear rather dissimilar, apart from the similar location of the absorption maxima, the differences in absorption in ether at wave lengths less than 240 mμ can be accounted for quite adequately if the NH_2Br in ether was contaminated with considerable $NHBr_2$, as will be seen.

The aqueous NH_2Br solutions were stable enough and the spectrophotometric data concordant enough to regard absorptivity values near the absorption maximum as reliable within 10%.

Spectrophotometric data for reaction mixtures at pH 9 were similar to those at pH 10.5 and 12, with the exception that a minor absorption peak was observed near 230 mμ when the molar ammonia:bromine ratio was less than about 50. There was thus a hint that a second reaction product was being formed under these conditions. As will be shown later, the observations are consistent with the formation of a few per cent of $NHBr_2$.

Reduction of hypobromite was quite rapid in most of these alkaline solutions. Reduction was less pronounced the greater the ammonia:bromine ratio and the lower the pH value. At pH 12 there was a rapid initial loss of oxidizing bromine ranging from about 30% at a molar NH_3/Br_2 ratio of 500 to more than 97% at a molar ratio near unity. Subsequent loss seemed to occur at a first-order rate of about 40% per hour of the remaining oxidizing bromine when the ratio of NH_3/Br_2 was 100 or greater. It appears that a great excess of ammonia is needed at this pH value either to increase the rate of reaction of the OBr^- to form NH_2Br before it can act as an oxidant or is required to displace the equilibrium

$$OBr^- + NH_3 = NH_2Br + OH^-$$
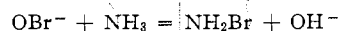
toward complete formation of NH_2Br.

Initial reduction of bromine was less at pH 10.5 and 9 and the subsequent decomposition of NH_2Br was also slower with decreased pH. Although the initial loss was still greater than 85% with an NH_3/Br_2 ratio of unity at pH 10.5, it was negligible when the ratio was 500. Subsequent decomposition at this pH occurred at an apparent first-order rate of 18% per hour and appeared independent of the NH_3/Br_2 ratio when this was greater than 10. At pH 9 there was negligible initial reduction of oxidizing bromine with ratios of NH_3/Br_2 of 46 and 450. However, the subsequent rate of decomposition was now dependent on the NH_3/Br_2 ratio. At a ratio of 46, the rate was about 30% per hour; at a ratio of 450, about 5% per hour; and at a ratio of 640 negligible decomposition was observed over a 1-hr. period.

In Figure 3 some typical data on reduction of hypobromite in the presence of ammonia in these alkaline solutions are summarized.
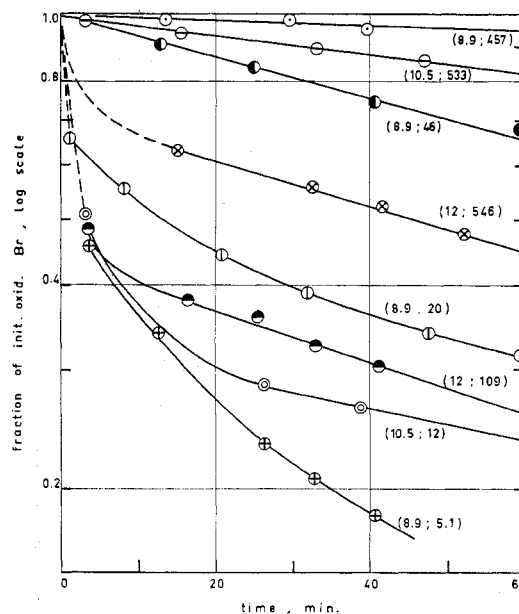

Figure 3.—Loss of oxidizing bromine from alkaline hypobromite–ammonia mixtures. Numbers beside curves indicate pH and initial molar ratio of ammonia to bromine, respectively.

(B) NHBr₂.—There is a marked change in the pattern of the reactions between aqueous bromine and ammonia at pH 8.2 and 7.3 as compared with the reactions at pH 9 and greater. The rapid initial reduction of oxidizing bromine was no longer observed in the same way, but sustained reduction of bromine became more pronounced, particularly so at pH 7.3. At the same time, the spectrophotometric data showed a new absorption band with a maximum absorptivity near 235 mμ, while the absorption band at 278 mμ was much less pronounced. At pH 7.3 no maximum in absorption at 278 mμ was noted even with molar ratios of ammonia to bromine as great as 20.

Examples of the spectra obtained at pH 8.2 are shown in Figure 4 and are there compared with the
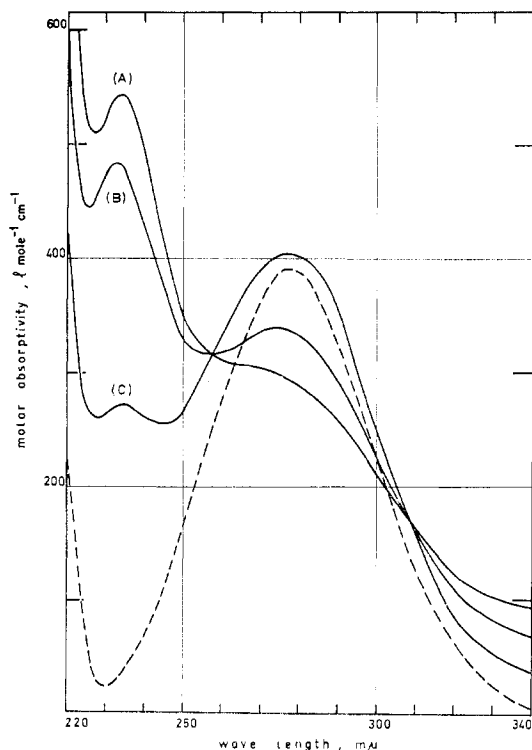

Figure 4.—Absorption spectra of NH₃–HOBr reaction mixtures at pH 8.2. Initial molar ratios of NH₃ to HOBr: (A) 1.02; (B) 2.51; (C) 21.2. Dashed line is previous spectrum for NH₂Br.

spectrum previously attributed to NH₂Br. The decrease in apparent absorptivity at 278 mμ and the corresponding increase near 232 mμ with decreasing NH₃/Br₂ ratio provides strong evidence for the formation of a compound not occurring in the more alkaline solutions, a compound retaining the oxidizing ability toward KI exhibited by bromine and favored by low ratios of ammonia to bromine.

Because of the rapid loss of oxidizing bromine from all these solutions and because of the intrusion of a third compound, believed to be NBr₃, it was difficult to find conditions suitable for the measurement of its spectrum uncontaminated by those of other brominated derivatives. Reaction conditions that seemed to lead to the best yield were at pH 6.3 and 5.5 with a molar ratio of ammonia to bromine of about 20.

The estimated spectrum of the compound derived from data on these reaction mixtures is shown in Figure 5, where it is compared with the spectrum for the preparation of NHBr₂ in ether. Although quantitative agreement is not very close, the coincidence be-
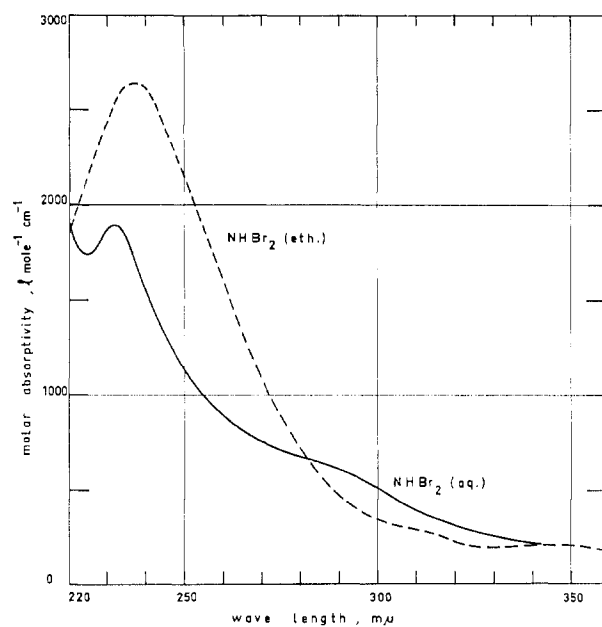

Figure 5.—Absorption spectra for NHBr₂. Aqueous, mean of three solutions with pH values and initial N/B rratios as follows: 6.2, 21.4; 6.3, 5.34; 5.5, 20.4. Concentrations, 1 to 3 × 10⁻⁴ *M*, 5-cm. cells. Ether, mean of three solutions 1 to 6 × 10⁻⁴ *M*, 3°, 1-cm. cells.

tween the absorption peaks at 232 mμ in water and 238 mμ in ether of about the same intensity (the 30% difference is probably within the range of analytical uncertainty in these unstable solutions) and the absence of conflicting features make it likely that the spectra are to be attributed to the same compound.

Consequently, in accord with Johannesson again,[5b] the compound exhibiting an absorption maximum at 232 mμ is believed to be NHBr₂.

Rates of loss of oxidizing bromine for some reaction mixtures in which NHBr₂ appeared to be the predominant compound formed are shown in Figure 6. More than 90% reduction of bromine occurred in less than 30 min. in all but one of these reaction mixtures; in the mixtures at pH 7.2 in less than 10 min. Disappearance of the absorption peak at 232 mμ accompanied the loss of oxidizing bromine, indicating that NHBr₂ is very unstable in these aqueous solutions.

(C) NBr₃.—One of the noteworthy features of the reactions between aqueous bromine and ammonia at pH 8.2 and 7.3 was that when a molar excess of bromine was used, two to three times the ammonia, the reduction of bromine was decreased as compared with equimolar reactants. This was in sharp contrast with observations in more alkaline solutions in which the presence of excess bromine led to substantially complete oxidation of ammonia to nitrogen and higher oxidation products. In these mixtures, a strong ab-
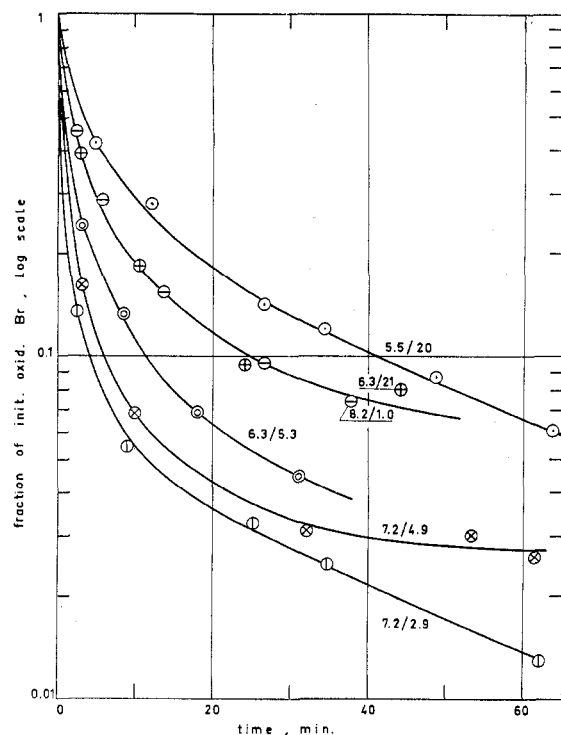
Figure 6.—Loss of oxidizing bromine from neutral and mildly acid $HOBr-NH_4^+$ mixtures. Numbers beside curves indicate pH and initial molar ratio of ammonia to bromine, respectively.

sorption band appeared with a maximum near 260 mμ, close to the absorption maximum for HOBr, but with an apparent absorptivity per mole of oxidizing bromine about 20 times as great as that of HOBr. Johannesson, who also observed such an absorption band in some of his experiments, attributed it to Br_3^-, which has an absorption maximum at 265 mμ with a molar absorptivity of 3.8×10^4. Calculations based on a hydrolysis constant for Br_2 of 5×10^{-9},[10] and a formation constant for Br_3^- equal to 18,[11] show that the maximum apparent absorptivity per mole of oxidizing bromine that could be contributed by Br_3^- in these reaction mixtures was less than 10, and less than 100 in any of the more acid reaction mixtures used, whereas the observed apparent absorptivities near 260 mμ were as great as 1500.

When mixtures of the reactants were allowed to react in more acidic solutions, at pH 6.4, 5.5, and 4.5, the peak near 260 mμ became prominent even in solutions with a molar ratio of ammonia to bromine greater than 1, being more pronounced the lower this molar ratio and the lower the pH. At pH 4.5 it, and an accompanying minor maximum at about 320 mμ, were the major features of all the spectra for NH_3/Br_2 ratios up to 10. Moreover, rates of reduction of oxidizing bromine were considerably slowed at this pH value and became relatively independent of the initial ratio of ammonia to bromine. Results with some of these mixtures at pH 4.5 are shown in Figure 7.

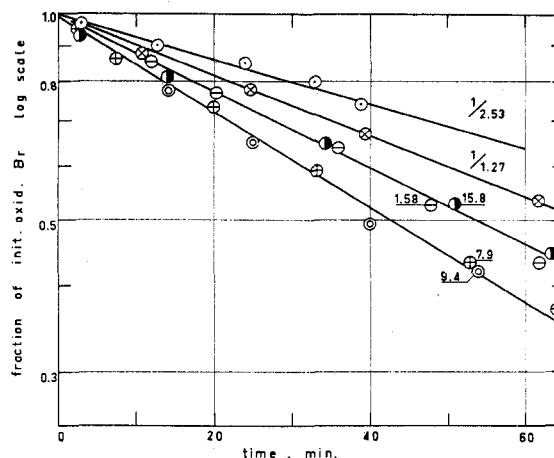It seemed likely that the third of the brominated

(10) H. A. Liebhafsky, *J. Am. Chem. Soc.*, **61**, 3513 (1939).
(11) R. G. Griffith, A. McKeown, and A. C. Winn, *Trans. Faraday Soc.* **28**, 101 (1932).

Figure 7.—Loss of oxidizing bromine from Br_2–NH_4^+ reaction mixtures at pH 4.5. Numbers beside curves indicate initial molar ratio of ammonia to bromine.

derivatives of ammonia, NBr_3, was being formed in these mildly acid solutions and that it had a stability considerably greater than that of $NHBr_2$.

The compound showed best stability and proximity to purity within the range of these experiments in reaction mixtures at pH 4.5 with a molar ratio of bromine to ammonia of about 2.5. It was found that the oxidizing bromine was completely removed from such mixtures by a single extraction with either CCl_4 or $CHCl_3$; the resulting organic solutions had spectra similar to that of the aqueous solution, showing an absorption maximum at 265 mμ with an absorptivity per mole of NBr_3 equal to 5×10^3 and a minor band at 342 mμ with an absorptivity equal to 10^3. Bromine in CCl_4 or $CHCl_3$ has an absorption maximum at 415 mμ with an absorptivity equal to 150 and has negligible absorbance near 265 mμ. In the related series of chlorine compounds, only Cl_2 and NCl_3 are readily extracted from aqueous solutions by CCl_4.

In Figure 8 the absorption spectra of this NBr_3 for aqueous solution and for solution in $CHCl_3$ are shown.

Additional confirmation that the compound is NBr_3 was obtained by analysis. A chilled reaction mixture (1 l.) at pH 4.5 was prepared and extracted as rapidly as possible into 200 ml. of cold chloroform. As soon as the layers had separated sufficiently, the chloroform layer was discharged into excess of sodium bisulfite solution with vigorous stirring. The bisulfite layer was then separated from the chloroform, diluted to 200 ml., and separated into two 100-ml. portions. Ammonia was determined in one portion by alkaline distillation into boric acid and titration with standard HCl; bromide was determined in the other portion by mercurimetric titration. Analysis of three different preparations in this way gave a mean Br:N ratio of 3.3. Although this is somewhat greater than the theoretical 3.0 value for NBr_3, it should be noted that any decomposition to N_2 or other oxidized nitrogenous products during the extraction procedures would have left the bromide value unchanged while lessening the ammonia.

It may be possible to prepare more concentrated or
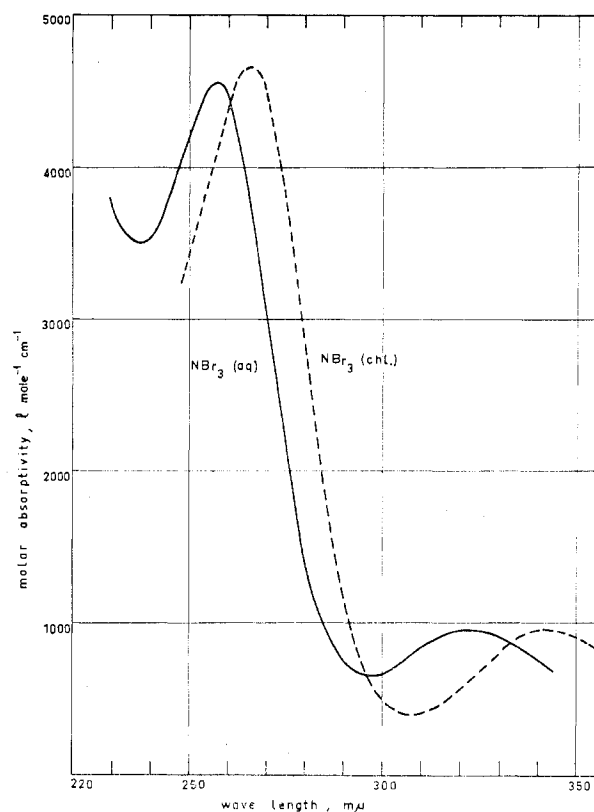
Figure 8.—Absorption spectra for NBr$_3$. Aqueous, mean of 2 solutions: (a) 3 × 10^{-4} M Br, pH 6.3, Br/N = 2.94; (b) 1.6 × 10^{-4} M Br, pH 4.5, Br/N = 2.50. Chloroform, extract from pH 4.5 reaction mixture with Br/N = 2.50, concentration in CHCl$_3$ 2 × 10^{-4} M, 5-cm. cells.

stable solutions of NBr$_3$ by working in still more acid solutions, but they have not been investigated in connection with this work because the stronger tendency for Br$_3^-$ formation would have made spectrophotometric observations ambiguous.

(D) General Comparison of Bromo and Chloro Derivatives of Ammonia.—In Table I the ultraviolet absorption data for brominated derivatives of ammonia derived from the observations in this study are sum-

TABLE I

SUMMARY OF ABSORPTION DATA FOR COMPOUNDS OF
BROMINE AND CHLORINE IN THE +1 OXIDATION STATE

	Cl[a]		Br		
Type of compd.	Absorption max., mμ	Molar absorptivity	Absorption max., mμ	Molar absorptivity	Δmμ (Br − Cl)
HOX	233	100	261	93	28
OX$^-$	292	350	329	343	37
NH$_2$X	245	455	278	390	33
NHX$_2$	206	2100	232	1900(?)	26
	295	300	290(?)	. . .	. .
NX$_3$	220	8100	258	4600	38
	340	260	323	940	−17
(CH$_3$)$_2$NX	264	360	300	490	36
(C$_2$H$_5$)$_2$NX	262	310	297	450	35

[a] The data for the chlorine derivatives have been taken from results of previous studies in these laboratories. See particularly I. Weil and J. C. Morris, *J. Am. Chem. Soc.*, **71**, 1664, 3123 (1949); M. L. Granstrom, Ph.D. Thesis, Harvard University, 1954; W. R. Samples, Ph.D. Thesis, Harvard University, 1959.

marized together with data for a number of other compounds containing bromine in the +1 oxidation state and are compared there with data for analogous chlorine derivatives. In all instances, except for the weaker secondary bands of molecules of the types NHX$_2$ and NX$_3$, the absorption maxima for the bromine derivatives occur at wave lengths about 30 mμ greater, and the absorptivities of the corresponding bands are approximately equal.

Although theoretical justification of the observed constancy of shift is not possible without a knowledge that similar transitions are producing the absorption, the analogies noted do give added confidence with regard to the occurrence and spectrophotometric identification of NH$_2$Br, NHBr$_2$, and NBr$_3$.

There is also parallel behavior in the conditions of formation of the chloro and bromo derivatives of ammonia. The compound NH$_2$Cl is observed as the predominating species in solutions at pH values greater than 6 or 7 depending on the ammonia:chlorine ratio; NHCl$_2$ is important in the pH range 4–6; and NCl$_3$ dominates in more acid solutions, although with an excess of chlorine it can be observed at pH values up to about 8.[12]

Except for a shift to somewhat higher pH values, indicating greater ease of multiple substitution with bromine, the pattern of formation of the brominated derivatives is very much the same. The patterns of formation can be predicted from a consideration of ionization equilibria for ammonium ion and hypohalous acids and thus provide additional support for the assigned occurrence of the brominated compounds. Moreover, NHCl$_2$ is the least stable of the chlorine derivatives in aqueous solution; similarly, NHBr$_2$ exhibits the least stability of the brominated compounds.

(E) Chlorination of Ammonium Bromide.—Farkas, Lewin, and Bloch,[13] in a study of the oxidation of bromide by hypochlorite, found the rate-determining step to be

$$HOCl + Br^- \longrightarrow HOBr + Cl^-$$
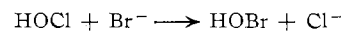
with a rate constant, k_o = 2.95 × 10^3 l. mole^{-1} sec.$^{-1}$ at 25°.

Weil and Morris,[14] in a study of the reaction between hypochlorite and ammonia, found the rate-determining step to be

$$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O$$
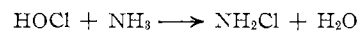
with a rate constant, k_n = 6.2 × 10^6 l. mole^{-1} sec.$^{-1}$ at 25°.

The relative rates of reaction of hypochlorite with ammonia and bromide should then be given by the expression

$$R_n/R_o = \frac{k_n}{k_o} \frac{(N)}{(Br^-)} \frac{1}{(1 + (H^+)/K_a)}$$

(12) A. T. Palin, *J. Inst. Water Engrs.*, **4**, 565 (1950).

(13) L. Farkas, M. Lewin, and R. Bloch, *J. Am. Chem. Soc.*, **71**, 1988 (1949).

(14) I. Weil and J. C. Morris, *ibid.*, **71**, 1664 (1949).

in which (N) is the total concentration of ammonia plus ammonium ion and the term in parentheses is to take account of the ammonium ion equilibrium, K_a being the acid dissociation constant of NH_4^+, equal to 5.5×10^{-10} at 25°.

Evaluation of the ratio, R_n/R_o, for equal concentrations of bromide and ammonia nitrogen gives values of 750 at pH 9, 110 at pH 8, 11 at pH 7, and 1.1 at pH 6.

In qualitative agreement with these calculations we have found that when hypochlorite and ammonium bromide are mixed at concentrations of 2.3×10^{-4} and 4.6×10^{-4} M, respectively, only NH_2Cl is formed when the reaction occurs at pH 8 or greater, some bromamides are formed when the reaction occurs at pH 7, NBr_3 being the one chiefly detected, and predominant formation of bromamides accompanied by very rapid loss of oxidizing halogen (90% within 7 min.) takes place at pH 6.

The Difluorochlorate(I) Anion, ClF₂⁻
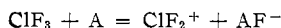
BY K. O. CHRISTE AND J. P. GUERTIN

The difluorochlorate(I) anion, ClF_2^-, a new oxidizing species based on chlorine fluorides, has successfully been prepared in the form of its nitrosyl salt. Nitrosyl fluoride reacts with chlorine monofluoride in a 1:1 mole ratio, forming a white solid at −78°, which is completely dissociated in the gas phase at 25°. A pressure–temperature curve gives a heat of reaction, 15.5 kcal. mole⁻¹, for the dissociation process: complex(s) = NOF(g) + ClF(g). Conductivity and infrared measurements indicate that the complex is ionic in solution and in the solid state, respectively. From these results, the structure $NO^+ClF_2^-$ is assigned to the solid complex, the ClF_2^- anion (point group $D_{\infty h}$) having a probable trigonal bipyramidal structure (sp³d-hybrid) with the chlorine atom at the center, the two fluorine atoms at the apexes, and the three free electron pairs at the remaining corners.

Introduction

Self-ionization has been postulated for certain halogen fluorides, such as BrF_3,[1] in addition to their ability to behave as strong ionizing solvents. However, in the case of chlorine trifluoride, the self-ionization of the pure compound must be considered to be very small, as shown by its low conductivity.[1] Association through fluorine bridging seems to be preferred over self-ionization.[2] In addition, there is n.m.r. evidence[3] that the fluorine exchange in ClF_3 might be caused by trace quantities of HF present as impurity. Yet, ClF_3 can act as an ionizing solvent toward strong Lewis acids, such as AsF_5, SbF_5,[4-6] BF_3,[7] PF_5,[6] and PtF_5,[8] forming the ClF_2^+ cation, or toward Lewis bases, such as NOF,[9] KF, RbF, and CsF,[10-12] forming the ClF_4^- anion, as shown by the equations

$$ClF_3 + A = ClF_2^+ + AF^-$$

$$ClF_3 + ZF = Z^+ + ClF_4^-$$

where A and ZF are a Lewis acid and a Lewis base, respectively.

In the case of chlorine monofluoride, the existence of the corresponding Lewis acid, Cl^+,[13] is known; however, the existence of the Lewis base, ClF_2^-, has not been reported. With the object of similarly establishing ClF as an ionizing solvent represented by the equations

$$ClF + A = Cl^+ + AF^-$$

$$ClF + ZF = Z^+ + ClF_2^-$$
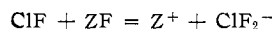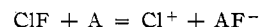
we have investigated the interaction of ClF with NOF. This research is part of a general investigation of complexes based on chlorine fluorides.

Experimental

Materials.—The materials used in this work were manipulated in a standard Pyrex glass high-vacuum system which had stopcocks and joints lubricated with Halocarbon grease (high-temperature grade). Chlorine monofluoride and NOF (both from Ozark-Mahoning Co.) were purified by several low-temperature vacuum distillations. Little etching could be observed in the vacuum line. The purity of the volatile compounds was determined by measurements of their vapor pressures, molecular weights, and infrared spectra.

Infrared Spectra.—All infrared spectra were recorded on a Beckman Model IR-9 grating spectrophotometer in the range 4000–420 cm.⁻¹. Pyrex glass cells equipped with AgCl windows were used for all spectra. The infrared spectrum of solid NO⁺-

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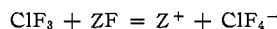(7) H. Selig and J. Shamir, *Inorg. Chem.*, **3**, 294 (1964).

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