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Kinetics of Nitrogen Tribromide Decomposition in Aqueous Solution¹

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Tribromamine decomposes to give nitrogen gas and hypobromous acid according to the overall reaction $2\text{NBr}_3 + 3\text{OH}^- \rightarrow \text{N}_2 + 3\text{Br}^- + 3\text{HOBr}$. Decomposition rates were measured over the pH range 6.00 ± 0.05 to 8.00 ± 0.05 for initial bromine to ammonia molar ratios between 4.00 and 12.0. The experimental rate law was found to be $-d[\text{NBr}_3]/dt = k_a[\text{NBr}_3]^2[\text{OH}^-]/[\text{HOBr}] + k_b[\text{NBr}_3]^2$, where $k_a = 1.07 \times 10^4$ and $k_b = 0.34 \text{ l.}/(\text{mol s})$ at 20°C . The first term in the rate equation is consistent with a mechanism in which the rate-determining step is preceded by equilibria among NBr_3 , NHBr_2 , HOBr , NBr_2^- , and OH^- . Hydroxide may attack either NBr_3 or NHBr_2 to produce NBr_2^- which subsequently reacts with NBr_3 . The second term is a simple second-order alternate pathway, occurring in acid solutions.

Introduction

When bromine or hypobromous acid is added to an aqueous ammonia solution, one or more of the bromamines are rapidly formed with their concentrations being a function of temperature, pH, and the bromine to ammonia ratio. Tribromamine, NBr_3 , predominates at neutral pH when the molar ratio of bromine to ammonia is greater than 1.5.² The decomposition reactions of this compound and the other bromamines are of considerable importance to the field of disinfection whenever bromine, bromine chloride, or hypobromite are added to water containing ammonia.^{3a} In comparison to the bromamines, the chloramines are inferior disinfectants^{3b,4} and their persistence and high fish toxicity⁵ have initiated a search for alternatives to chlorine. Although bromine has had widespread use as a swimming pool disinfectant⁶ and is currently being considered as a waste water and cooling water disinfectant, there has been no thorough study of the decomposition kinetics of the bromamines. For this reason a research program was begun in this laboratory to measure the decomposition rates of tribromamine and dibromamine, the compounds most relevant to disinfection practices.

Tribromamine was first shown to exist in dilute aqueous solution by Galal-Gorchev and Morris,⁷ who also measured its rate of decomposition under a variety of conditions. They obtained pure and relatively stable NBr_3 solutions at low pH

even when the molar ratio of bromine to ammonia was 2.5. They also noted that the distribution of the bromamines should be predictable from the ammonium ion and hypobromous acid equilibria. Further work by Johnson and Overby⁶ showed this to be true, with the relative concentrations of the bromamines being dependent on both ammonia concentration and pH. They observed rapid formation of all of the bromamines in contrast to the slower formation reactions of NHCl_2 and NCl_3 . Unlike the chloramine reactions, an equilibrium allows interconversion of the bromamines by merely changing pH, ammonia, or bromine concentration.

The rate of NBr_3 disappearance was determined by monitoring the ultraviolet absorbance at 258 nm due to NBr_3 and HOBr and the total reducible bromine as determined by amperometric titration. Reaction orders with respect to different species were determined from initial rate data rather than concentration-time data taken over a long period of time. This was done because bromide and hypobromous acid, products of NBr_3 decomposition, respectively catalyze and inhibit the reaction.

Experimental Section

Materials. The following procedure was used to eliminate or oxidize any impurities in the reagent water that might reduce bromine. Tap water was filtered through a 0.1- μ filter and a bed of activated carbon for the removal of organic compounds and then passed through 4 ft

of highly regenerated and aged mixed-bed ion-exchange resin. This water was treated with enough sodium hypochlorite solution to give an initial measured hypochlorite-hypochlorous acid concentration of 2 mg/l.⁸ The water was stored in stoppered 5-gal glass carboys and protected from the atmosphere by 50% sulfuric acid traps. After at least 1 day the $\text{OCl}^- + \text{HOCl}$ content was again measured, and if the concentration had dropped by more than 0.5 mg/l., the water was discarded. Otherwise the water was irradiated with either sunlight or an Ultra Violet Products Model 11 lamp until no OCl^- or HOCl was detectable. This water was used to prepare all ammonia, bromine, chlorine, and buffer solutions.

Stock sodium hypochlorite solutions were prepared by diluting a 5% analytical reagent grade sodium hypochlorite solution to approximately 0.15 M. Concentrations were determined by a thio-sulfate-iodide amperometric titration as discussed below.

Sodium hypobromite stock solutions of low bromide concentration were prepared according to data obtained by Farkas⁹ and Lewin¹⁰ on the oxidation of bromide ion by hypochlorite ion to form hypobromite and chloride. Kinetic data of Engel,¹¹ Prutton,¹² and Liebhafsky¹³ showed that a pH of 11.0 was high enough to prevent bromate formation but was sufficiently low to give a rapid enough formation of OBr^- when the following procedure was employed. An appropriate amount of Fisher Certified ACS grade potassium bromide was used to prepare a stock hypobromite solution that would be about 0.017 M. A stoichiometric amount of standardized sodium hypochlorite solution was added and the pH was adjusted to 11.0 with 10% NaOH or 6 N HCl. A reaction time of 2-3 days was allowed before the stock was titrated for total halogen by the thiosulfate-iodide amperometric titration. This titration result was compared with the total free bromine content obtained spectrophotometrically from the absorbance of HOBr at 260 nm and OBr^- at 329 nm. The hypobromous acid ($\text{pK}_a = 8.70$) analysis was done by diluting to volume 10 ml of stock in a 100-ml volumetric flask with 10 ml of pH 4.5 sodium acetate buffer. This solution was scanned from 360 to 200 nm on a Cary Model 14 recording spectrophotometer using 4-cm quartz cells and a buffer reference. Hypobromite ion was determined by diluting 4 ml of stock to 100 ml without adding buffer since at pH 10 or above OBr^- is the major species. Agreement of all three results to within 2% was taken as evidence that the hypobromite reaction was essentially complete.

Sodium thiosulfate solutions¹⁴ were prepared by diluting 0.10 N stock and were standardized prior to use by amperometric titration with potassium iodate. Primary standard iodate solutions¹⁵ were prepared by dissolving ACS grade KIO_3 weighed to the nearest 0.1 mg in 1 l. of reagent water followed by a 1:5 dilution.

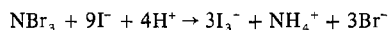
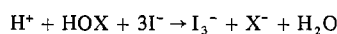
Ammonia stock solutions 0.002 667 M in NH_4Cl were prepared with ACS grade reagent.

Buffers used at pH 6.00 ± 0.05 were prepared from ACS grade dibasic potassium phosphate and monobasic potassium phosphate to give final phosphate concentration of 0.01 M in the reactor. A pH 8 buffer was prepared by adding enough 0.20 M KH_2PO_4 to 1500 ml of 0.0667 M sodium borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) until the pH stabilized at 8.00 ± 0.05 .

The ionic strength of all solutions used in runs was held at 0.100 by 0.0333 M K_2SO_4 .

Methods. Total reducible halogen in all solutions was determined by the thiosulfate-iodide method using an amperometric end point detection.¹⁶ Samples were delivered into 125 ml of solution 0.01 M in potassium iodide and 0.25 M in acetic acid. The titration apparatus consisted of a Sargent XV polarograph used in conjunction with a rotating platinum-saturated calomel electrode system. In order to minimize interferences from the reduction of any dissolved oxygen that might be present, 200 mV was applied across the electrodes and the pH was not allowed to go below 3.0.¹⁶

The following reactions produced triiodide¹⁷



Hypobromous acid solutions were prepared with enough hypobromite stock solution to give the desired initial HOBr concentration plus about 10% excess. After diluting to volume in an amber reaction bottle, a 25-ml aliquot was then removed and titrated amperometrically with 0.016 N sodium thiosulfate to determine total reducible bromine. The concentration was then adjusted to the desired value.

Ammonia solutions were prepared with appropriate amounts of the diluted ammonium chloride stock. After the addition of K_2SO_4 stock, the solution volume was equalized with that of the hypobromous acid. Initial ammonia concentrations in the reactor after mixing were 0.667, 1.33, and 2.67×10^{-4} M. At each concentration three runs were carried out for the initial bromine to ammonia molar ratios of 12.00, 6.00, and 4.00.

Kinetic runs to determine the overall stoichiometry were done in the following manner. The ammonia solution was added to a hypobromous acid solution contained in the reactor bottle thermostated at 20.0 ± 0.2 °C by a constant-temperature bath. Stirring was continued only until the end of the mixing process at which time aliquots were withdrawn for spectrophotometric and total reducible bromine analysis. Further aliquots were taken as rapidly as possible (every minute for uv analysis and after 5-10 min for total reducible bromine). The absorbance was measured at 258 nm which, according to Galal-Gorchev and Morris⁷ and as confirmed in this laboratory, is the absorbance maximum of NBr_3 . This value was the sum of the absorbances due to NBr_3 , HOBr , and OBr^- . Molecular bromine, Br_2 , was considered to be unimportant here since even at pH 6 its concentration was only 2.5% of the total reducible bromine, not in the form of an amine, for a bromide concentration of 10^{-4} M. The concentration of NBr_3 was determined by solving the following two simultaneous equations for the two unknowns [NBr_3] and ($[\text{HOBr}] + [\text{OBr}^-]$), given the total absorbance A and the total reducible bromine concentration [Br_T]

$$[\text{HOBr}] + [\text{OBr}^-] = \frac{A - 1/3(\epsilon_1 L [\text{Br}_T])}{\epsilon_2 L - \epsilon_1 L/3} \quad (1)$$

$$[\text{NBr}_3] = \frac{[\text{Br}_T] - ([\text{HOBr}] + [\text{OBr}^-])}{3} \quad (2)$$

The path length of the cell is L and ϵ_1 and ϵ_2 are the respective molar absorptivities of NBr_3 and $\text{HOBr} + \text{OBr}^-$. ϵ_2 is pH dependent and was determined experimentally before each run from the absorbance of a bromine solution of known titer. The molar absorptivity of NBr_3 , $\epsilon_1 = 5000 \pm 200 \text{ l.}/(\text{mol cm})$, was determined from relatively stable aqueous solutions at pH 6 correcting for excess hypobromous acid. This value for ϵ_1 differs from the value of 4600 reported by Galal-Gorchev and Morris.⁷

In order to measure more accurately initial decomposition rates and instantaneous rates in the early stages of reaction, the above procedure was modified. Two 10-ml syringes were charged with equal volumes of initial hypobromous acid and ammonia solutions. The syringes were then clamped to a thermostated aluminum double-syringe holder that would allow injection of both solutions. Intimate mixing was obtained with a T-connector from which the reaction mixture was fed into a quartz cell for rapid uv analysis. The first point could be recorded as soon as 5 s after mixing. The reaction was followed for only 5-15 min as the objective of these runs was to measure only initial rates as accurately as possible. In one series of runs the initial excess of HOBr was held constant while initial ammonia and hence the initial NBr_3 concentration was varied. In another series the initial NBr_3 concentration was held constant while the excess HOBr concentration was varied. Since there was not sufficient time to monitor the total reducible bromine, the $\text{HOBr} + \text{OBr}^-$ concentration was determined using the stoichiometric relationship derived from the first series of experiments. It was necessary to know these values in order to make the proper corrections to the total absorbance at 258 nm.

A Fortran IV computer program was used to compute NBr_3 concentrations as a function of time using eq 1 and 2 with input data of time, absorbance at 258 nm, and total bromine. Data were smoothed by doing linear least-squares analyses on the data with the proper function for first-order, second-order, or 1.5-order behavior. Initial and instantaneous rates were calculated from a linear fit of a known function to a selected portion of the experimental decomposition curve. The best fits in most cases were obtained by plotting $[\text{NBr}_3]^{-1/2}$ with respect to time.

An additional number of kinetic runs were carried out to study the effect of added bromide on the decomposition rate of NBr_3 .

Results

Decomposition Stoichiometry. It has been previously observed⁶ that as NBr_3 decomposes, HOBr is generated. In

Table I. Stoichiometric Results for NBr_3 Decomposition

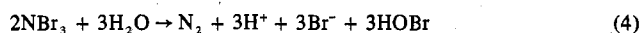
10^4 - $[\text{NH}_3]_0$, M	10^4 [Total bromine] $_0$, M	$R = \Delta[\text{HOBr}]/\Delta[\text{NBr}_3]$		
		pH 6.00 ± 0.05	pH 7.00 ± 0.05	pH 8.00 ± 0.05
0.667	8.00	1.67	1.44	1.71
0.667	4.00	0.98	1.27	1.20
0.667	2.67	1.55	1.25	1.21
1.33	16.00	1.79	1.49	1.11
1.33	8.00	1.43	1.25	1.32
1.33	5.33	1.71	1.44	
2.67	32.00	1.50	1.56	1.26
2.67	16.00	1.32	1.78	1.23
2.67	10.67	1.68	1.36	1.31

order to determine the ratio of HOBr produced to NBr_3 decomposed, a series of runs were carried out under a variety of initial conditions. By use of the procedure described in the Experimental Section, the concentrations of NBr_3 and HOBr were computed as a function of time. A stoichiometric ratio, R , was defined by

$$R = \frac{[\text{HOBr}]_t - [\text{HOBr}]_0}{[\text{NBr}_3]_0 - [\text{NBr}_3]_t} = \frac{\Delta[\text{HOBr}]}{\Delta[\text{NBr}_3]} \quad (3)$$

The initial concentrations were calculated from the first observed points, since the theoretical initial NBr_3 concentration did not always agree with that observed at all pH's. In order to maximize the differences, R was calculated only for the final few points of a given run. The results summarized in Table I give values of R averaged over the last four points of a run.

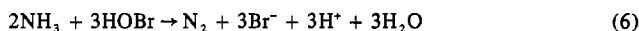
The mean value for R is 1.41 with a standard deviation of 0.22. This is taken as evidence that as 2 mol of NBr_3 decomposes, 3 mol of HOBr is generated according to the overall reactions



in acid solutions and



in basic solutions. This is also in agreement with previous data and the known equation for determining ammonia with an excess of bromine¹⁸



where 3 mol of bromine is required to oxidize 2 mol of ammonia nitrogen.

Decomposition Kinetics. Tribromamine forms in less than 5 s under all conditions used in this study. In kinetics runs where HOBr was present in large excess, the decomposition of NBr_3 was approximately second order for at least 60 min. Beyond this time the rate was more rapid than second-order behavior would predict. Initial rates were measured under conditions of constant initial excess HOBr, constant pH, and a constant ionic strength of 0.100, and the results are shown in Figure 1 for kinetic runs at pH 6.00, 7.00, and 8.00 ± 0.05 . The slopes from the respective plots of $\log \nu_0$ vs. $\log [\text{NBr}_3]_0$ are 1.91 ± 0.12 , 1.97 ± 0.05 , and 1.91 ± 0.03 , where $\nu_0 = -d[\text{NBr}_3]/dt$ at $t = 0$. The reaction order is thus 2 with respect to the concentration of NBr_3 . An order of approximately 1.5 was obtained from least-squares fits to linearized concentration-time data where HOBr was not present in a large excess. This difference was due to a decrease in rate from an inhibitory effect of the additional HOBr generated as NBr_3 decomposed.

In order to quantify the effect of HOBr on the decomposition rate, initial rates were measured under conditions of constant initial ammonia with different concentrations of excess HOBr. The results at pH 7 and 8 are shown in Figure 2 where slopes of -0.90 ± 0.20 and -0.95 ± 0.13 are obtained when $\log \nu_0$ is plotted against $\log [\text{HOBr}]_0$. These slopes show

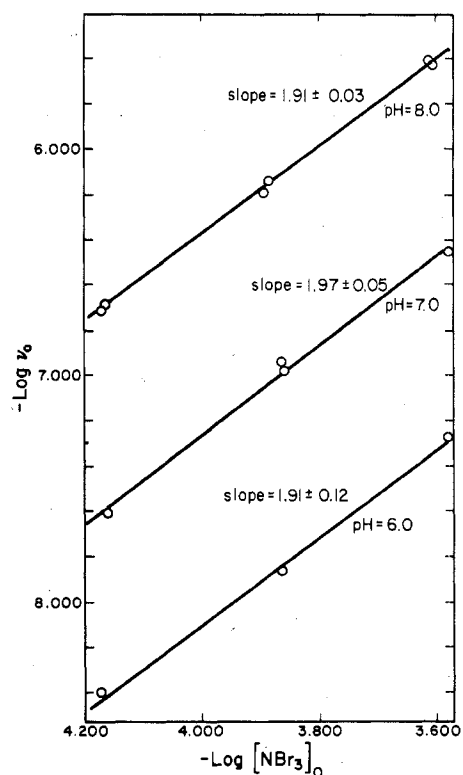


Figure 1. Logarithm of initial rate ($\nu_0 = -d[\text{NBr}_3]/dt$ at $t = 0$) vs. the logarithm of initial NBr_3 concentration. Straight lines are from a least-squares fit to the data. The decomposition order with respect to NBr_3 concentration is given by slopes.

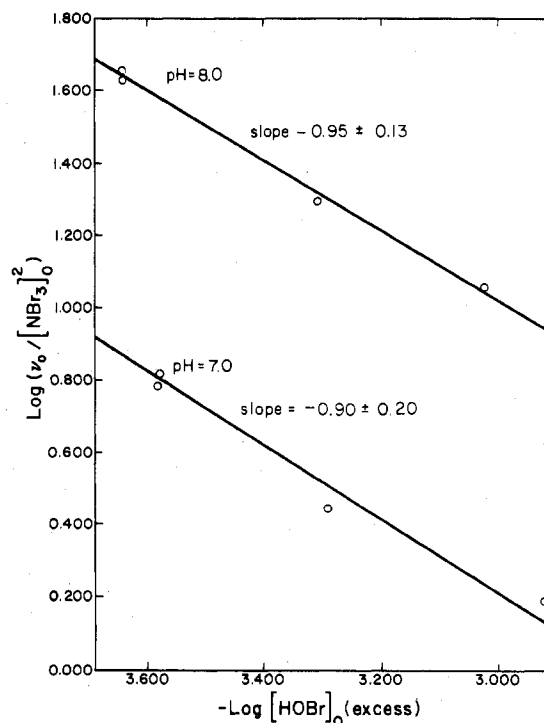


Figure 2. Logarithm of the experimental rate constant, $\nu_0/[\text{NBr}_3]_0^2$, vs. the logarithm of initial excess hypobromous acid.

that HOBr appears in the rate equation with an order of approximately -1. However, at pH 6 the plot is nonlinear with a slope of about -0.5. A plot of $\nu_0/[\text{NBr}_3]_0^2$ vs. $1/[\text{HOBr}]_0$ as shown in Figure 3 at pH 6 gives a nonzero intercept indicating the presence of an additional bromine-independent pathway for NBr_3 decomposition. The HOBr-independent

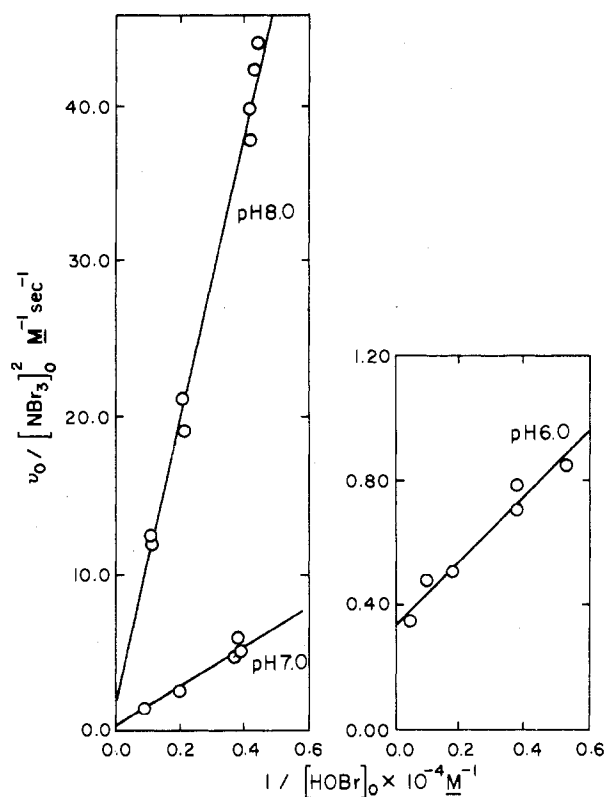


Figure 3. Plot of $\nu_0/[\text{NBr}_3]_0^2$ vs. the reciprocal concentration of initial excess hypobromous acid. The slopes at pH 7 and 8 are equal to the rate constant k' for the bromine-dependent pathway of NBr_3 decomposition. A rate constant for the pH- and bromine-independent pathway is equal to the intercept at pH 6.

portion of the rate is insignificant at pH 7 and 8 where the intercepts in Figure 3 are zero within experimental error. At pH 6 the bromine-independent term comprises 30–90% of the overall initial rate.

The rate of NBr_3 disappearance increases rapidly with increasing pH. This effect is presented graphically in Figure 4 where $\log \nu_0$ is plotted against pH. The slopes in Figure 4 are 0.91 ± 0.16 indicating that the rate is either first order with respect to hydroxide ion or negative first order with respect to hydrogen ion.

Figure 5 shows the effect of different concentrations of potassium bromide on the decomposition rate of NBr_3 in a system very low in initial bromide. When the added bromide is 10^{-4} M, the rate of increase is slight, which may indicate a threshold effect or that the amount of Br^- initially present is this order of magnitude. Further increases of up to 5×10^{-3} M Br^- markedly enhanced the rate. Plots of $\log \nu_0$ vs. $\log [\text{Br}^-]$ were not linear, but least-squares fits yielded slopes of about 0.4. The effect was considerably reduced at pH 8 where the order was 0.2. This pH dependence may be evidence for an additive term or terms in the rate equation for Br^- . However, the exact bromide dependence for the rate of NBr_3 disappearance has not been determined. The formation of Br_3^- and its interference in the absorbance at 258 nm prevented the addition of a large excess of Br^- to reaction solutions.

Bromate, BrO_3^- , was regarded as a possible interference in the initial rate data at pH 8 and those runs involving high concentrations of bromide, since the available kinetic data^{11,12,13} suggest that bromate formation is bromide catalyzed and most rapid near pH 9. In order to minimize this interference all hypobromous acid solutions were prepared and used as quickly as possible, usually within 1 h. The absorbance at 258 nm was also measured prior to each run. Since BrO_3^- has a negligible absorptivity at that wavelength, any significant

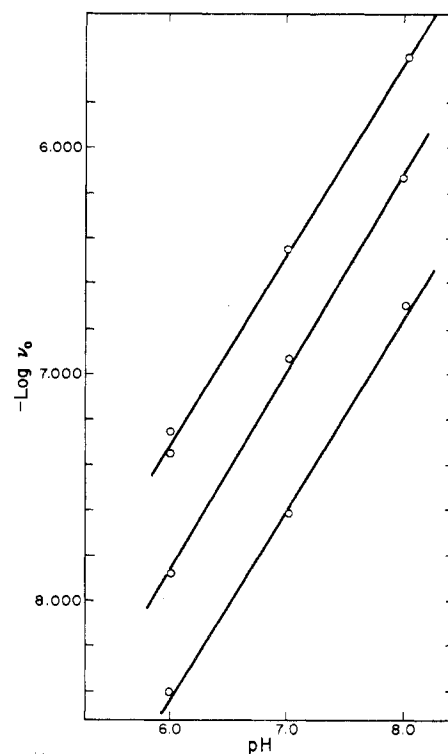


Figure 4. Logarithm of initial rate, ν_0 , vs. pH, where the mean slope is 0.90 ± 0.16 .

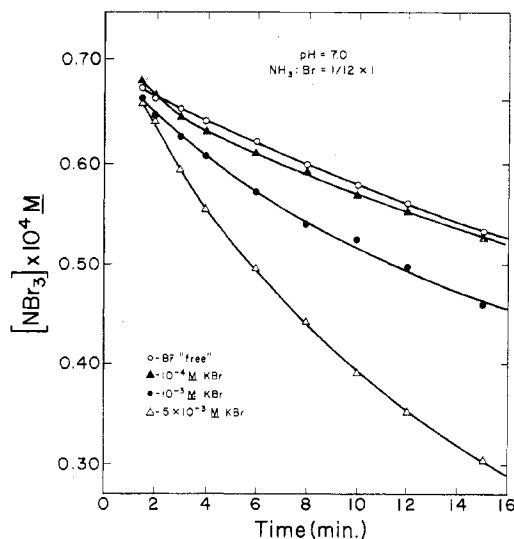


Figure 5. Tribromamine concentration vs. time showing the effect of bromide on the decomposition rate at pH 7 in the presence of a large excess (6.00×10^{-4} M) of hypobromous acid; $[\text{NBr}_3]_0 = 0.667 \times 10^{-4}$ M.

portion of the HOBr and OBr^- oxidized to BrO_3^- would have been detectable as an unusually low absorbance.

Discussion

The Rate Equation. The initial rate data obtained at pH 7 and 8 under conditions of constant ionic strength and low initial bromide are most consistent with the rate equation

$$\nu = -\frac{d[\text{NBr}_3]}{dt} = k_a \frac{[\text{NBr}_3]_0^2 [\text{OH}^-]}{[\text{HOBr}]} \quad (7)$$

When $-\log \nu_0$ is plotted against $-\log ([\text{NBr}_3]_0^2 [\text{OH}^-] / [\text{HOBr}])$, the average k is 1.18×10^4 l./mol s) calculated from the quotient $\nu_0 [\text{HOBr}]_0 / [\text{NBr}_3]_0^2 [\text{OH}^-]$.

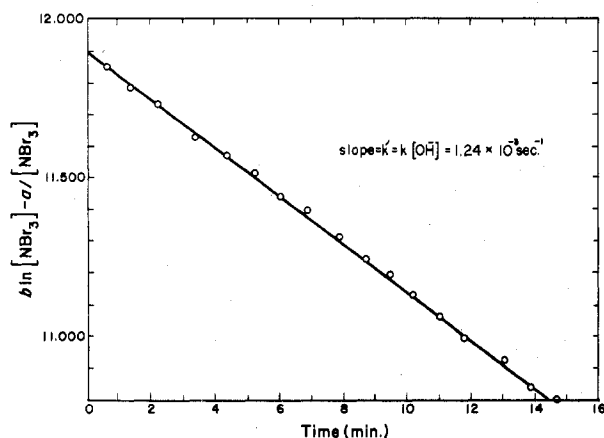


Figure 6. Test of the integrated form of the rate equation where $a = [H^+](Br_T)_0 - 3/2[NBr_3]_0 / (K_a + [H^+])$ and $b = 3/2[H^+] / (K_a + [H^+])$. The NBr_3 concentrations were taken from a kinetic run at pH 7 where $[NBr_3]_0 = 0.667 \times 10^{-4}$ M and $[HOBr]_0(\text{excess}) = 2.67 \times 10^{-4}$ M.

An integrated form of (7) may be derived by utilizing the observed stoichiometric relationship wherein 3 mol of HOBr is produced when 2 mol of NBr_3 decomposes, i.e.

$$3/2([NBr_3]_0 - [NBr_3]) = B - ([Br_T]_0 - 3[NBr_3]) \quad (8)$$

The initial total reducible bromine added is $[Br_T]_0$. If B , the concentration of HOBr + OBr^- at any time, is expressed in terms of $[HOBr]$, $[H^+]$, and the ionization of hypobromous acid,¹⁹ K_a , then eq 8 rearranges to give

$$[HOBr] = a + b[NBr_3] \quad (9)$$

where $a = [H^+](Br_T)_0 - 3/2[NBr_3]_0 / (K_a + [H^+])$, $b = 3/2[H^+] / (K_a + [H^+])$, and $K_a = (2.00 \pm 0.25) \times 10^9$. Substitution of (9) into (7) and integrating over the limits $[NBr_3]_0$ to $[NBr_3]$ and $t = 0$ to t give the integrated form of the rate equation which may be tested with concentration-time data from a particular kinetic run with the expression

$$b \ln [NBr_3] - \frac{a}{[NBr_3]} = k't + b \ln [NBr_3]_0 - \frac{a}{[NBr_3]_0} \quad (10)$$

where k' is the rate constant at any given pH and $k' = k_a \cdot [OH^-]$. Since only the K_a was used to compute $[HOBr]$ from $[HOBr] + [OBr^-]$, this equation will only be accurate in the absence of significant Br_2 . Figure 6 shows a plot of $b \ln [NBr_3] - a/[NBr_3]$ vs. t at pH 7 where the initial ratio of bromine to ammonia is 4.00 and an initial NBr_3 or ammonia concentration is 0.667×10^{-4} M. At this low ratio NBr_3 decomposes quite rapidly so there is significant production of HOBr during the time of the kinetic run. The linearity of this plot means that the integrated form of eq 7 adequately accounts for the disappearance of NBr_3 over time in a system where $[HOBr]$ is produced. The rate constant from (10), equal to 1.24×10^4 l./mol s, is in good agreement with the k computed from initial rate data. In general eq 7 is consistent with both initial rate data and data taken over a longer period of time.

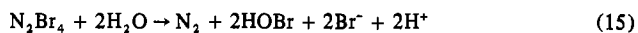
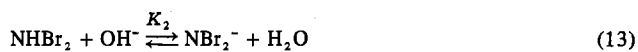
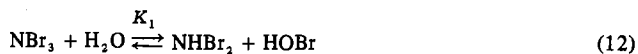
In order to account for the initial rates observed at pH 6, an additional bromine- and hydroxide-independent term must be introduced into the rate equation so that

$$\nu = k_a \frac{[NBr_3]^2 [OH^-]}{[HOBr]} + k_b [NBr_3]^2 \quad (11)$$

The latter term becomes significant only when the first term is reduced to a comparable magnitude by lowering the hydroxide concentration. A value of $k_a = 1.07 \times 10^4$ l./mol s) was obtained from the slope of a plot of $\nu_0/[NBr_3]_0^2$ vs.

$[OH^-]/[HOBr]_0$. The intercept of the pH 6 plot in Figure 3 gave $k_b = 0.34$ l./mol s).

Mechanisms. The first term in eq 11 is consistent with a mechanism involving equilibria among NBr_3 , $NHBr_2$, NBr_2^- , HOBr, and OH^- . The negative first-order dependence with respect to HOBr and the second-order dependence of NBr_3 in the same term mean that the final redox reactions must be initiated by NBr_3 reacting with some intermediate which also reacts with HOBr to give NBr_3 . The reaction scheme shown by eq 12-15 is in agreement with eq 7 and the first term in



eq 11. The intermediate, NBr_2^- , can form from the reaction of OH^- with either NBr_3 or $NHBr_2$ as shown by eq 13. Reaction 14 is the rate-determining step in which an unstable bromohydrazine is proposed from the $N_2Br_5^-$ transition state suggested by (7). Equation 15 is the final formation of products. The rate of NBr_3 disappearance for the above scheme is

$$\nu = k_1 [NBr_3][NBr_2^-] \quad (16)$$

where the remaining terms sum to zero if the equilibrium is assumed. Solving for $[NBr_2^-]$ in terms of NBr_3 and OH^- and using the equilibrium expression derived from reaction 13 give the rate equation

$$\nu = k_1 K_2 [OH^-][NBr_3][NHBr_2] \quad (17)$$

which shows the instability of mixtures of dibromamine and tribromamine observed previously.¹ Equation 17 reduces to (7) using reaction 12 where $k_a = k_1 K_1 K_2$.

The following bromine- and pH-independent pathway is necessary to account for the second term in eq 11



The rate-determining step is (18), and (19) is the first in a series of rapid reactions leading to nitrogen and hypobromous acid.

Conclusions

The decomposition of nitrogen tribromide occurs by a rate-determining step in which NBr_3 reacts with NBr_2^- . This step is preceded by equilibria involving NBr_3 , $NHBr_2$, NBr_2^- , HOBr, and OH^- . The pH dependence of the reaction rates may be accounted for by hydroxide attack of either NBr_3 or $NHBr_2$ to form NBr_2^- . Decomposition rates are also dependent on the bromide concentration and there is a second pathway in which NBr_3 reacts with itself. The latter reaction is only significant in acid solutions.

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Registry No. NBr_3 , 15162-90-0.

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Reactions of (Dimethylamido)halophosphorus(III) with Aluminum(III) Chloride and with Some Etherates of Aluminum(III) Chloride

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The chloro(dimethylamido)phosphorus(III) ligands interact with AlCl_3 under appropriate conditions to give $(\text{CH}_3)_2\text{N-PCl}_2\cdot\text{AlCl}_3$, $((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$, and $[2((\text{CH}_3)_2\text{N})_2\text{PCl}]\cdot\text{AlCl}_3$. Tris(dimethylamido)phosphorus(III) and AlCl_3 react under comparable conditions to give $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$. The tris ligand will also react with $((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ to give $((\text{CH}_3)_2\text{N})_3\text{P}\cdot((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$ but it will *not* react with $((\text{CH}_3)_2\text{N})_3\text{P}\cdot\text{AlCl}_3$ to give $[2((\text{CH}_3)_2\text{N})_3\text{P}]\cdot\text{AlCl}_3$. Trimethylamine will gradually replace some of the phosphorus ligand from the complex to give some $(\text{CH}_3)_3\text{N}\cdot\text{AlCl}_3$. A solution of dichloro(dimethylamido)phosphorus(III) ligand in isopropyl ether was stable as was a solution of aluminum chloride in isopropyl ether. On the other hand, an isopropyl ether solution containing AlCl_3 and the dichloro(dimethylamido)phosphorus(III) ligand gave 1 mol of isopropyl chloride for each mole of PCl_3 and each mole of the dichloro(dimethylamido)phosphorus ligand. The ether solution turned red as a result of the formation of an aluminum chloride-olefin complex. The splitting process to generate alkyl halide was not observed with diethyl ether. The chloride transferred came from the phosphorus ligand, not the AlCl_3 . The ligand $((\text{CH}_3)_2\text{N})_2\text{PCl}$ will displace about 70% of the diisopropyl ether from the diisopropyl etherate of AlCl_3 and $((\text{CH}_3)_2\text{N})_3\text{P}$ will displace 100% of the ether. Models to interpret these facts are presented.

The (dimethylamido)halophosphorus(III) ligands contain at least two quite different Lewis base centers. For example, the compound $((\text{CH}_3)_2\text{N})_2\text{PF}$ contains two potentially basic nitrogen atoms and one potentially basic phosphorus atom. The site utilized in a given acid–base process is dependent upon the nature of the acid used. When borane fragments such as BH_3 , B_3H_7 , and B_4H_8 are used as the acid, bonding is known to be through the phosphorus atom.^{1–5} When other boron acids such as BF_3 , BCl_3 , or $\text{B}(\text{CH}_3)_3$ are used, evidence indicates probable bonding through a nitrogen atom.^{1–3,6,7} When aluminum alkyls are used as the acid, the behavior is more complicated. Clemens, Sisler, and Brey⁸ studied the reaction of $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2$ with $\text{Al}(\text{C}_2\text{H}_5)_3$. They reported that a P–Al bond formed when the reagents were directly combined but that the structure changed to give an N–Al bond when the adduct was heated.

In this work the reactions of (dimethylamido)halophosphorus(III) ligands with AlCl_3 have been studied. Although it was originally assumed that a conventional acid–base adduct would be formed, structures and stoichiometry turned out to be quite different from those originally visualized.⁹ In this paper the appropriate chemistry is summarized. Subsequent reports will probe questions of structure and molecular dynamics.

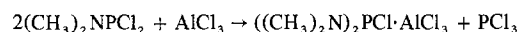
The System $(\text{CH}_3)_2\text{NPF}_2\cdot\text{AlCl}_3$

Initial work with $(\text{CH}_3)_2\text{NPF}_2$ and AlCl_3 revealed a halogen-exchange process similar to that reported¹⁰ for the system $\text{F}_3\text{P}\cdot\text{AlCl}_3$. To eliminate complications resulting from halogen

interchange to give AlF_3 , the chloro ligand, $(\text{CH}_3)_2\text{NPCI}_2$, was used in place of its fluoro counterpart.

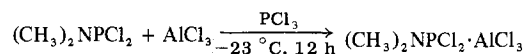
The System $(\text{CH}_3)_2\text{NPCI}_2\cdot\text{AlCl}_3$

When excess $(\text{CH}_3)_2\text{NPCI}_2$ and AlCl_3 were directly combined at 20 °C in the vacuum system, the following reaction occurred almost quantitatively in 0.5 h or less



Even at a temperature of –23 °C some PCl_3 formed as soon as the reactants were brought into contact. The foregoing observations were quite unexpected, since the equilibrium constant for the disproportionation of the *free ligand* to give $((\text{CH}_3)_2\text{N})_2\text{PCl}$ and PCl_3 has been estimated as 5×10^{-4} , and according to Van Wazer and Maier,¹¹ an equimolar mixture of PCl_3 and $((\text{CH}_3)_2\text{N})_2\text{PCl}$ undergoes essentially complete conversion to $(\text{CH}_3)_2\text{NPCI}_2$ in less than 30 s at 25 °C; PCl_3 is definitely not an expected product.

An application of simple mass law arguments to the equation for the reaction of $(\text{CH}_3)_2\text{NPCI}_2$ and AlCl_3 suggested the use of PCl_3 as a solvent to minimize PCl_3 formation and thus promote the formation of $(\text{CH}_3)_2\text{NPCI}_2\cdot\text{AlCl}_3$. Indeed, the monoadduct $(\text{CH}_3)_2\text{NPCI}_2\cdot\text{AlCl}_3$ can be prepared from *equimolar* quantities of acid and base in PCl_3 at –23 °C, over a 12-h period. The pertinent equation is



The solid 1:1 adduct remaining after removal of the PCl_3 solvent undergoes disproportionation upon standing at 25 °C. The products are $((\text{CH}_3)_2\text{N})_2\text{PCl}\cdot\text{AlCl}_3$, PCl_3 , and AlCl_3 .

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