

599. Bromamines. Part I. Mono- and Di-bromamine.

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Bromine reacts with ammonium salts in aqueous solution at neutral pH to form both mono- and di-bromamine which have characteristic ultraviolet absorption spectra. The bromamines differ from their chlorine analogues in that they are strong oxidizing agents at neutral pH; in the case of mono-bromamine this is probably due to the presence of the monobromammonium ion at these pH values.

THE *N*-bromo-alkylamines have been known for a long time and in some instances have been characterised as crystalline compounds.¹ That ammonia itself reacts with bromine has also been known and has been used to determine ammonia by addition of an excess of sodium hypobromite ($3\text{BrO}^- + 2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{Br}^- + 3\text{H}_2\text{O}$) and back-titration with thiosulphate after addition of iodide,² or, more recently, by amperometric titration with hypobromite³ or with hypochlorite in the presence of bromide.⁴ The estimation has also been performed coulometrically with electrolytically generated hypobromite.⁵

Bromamine itself was first studied by Moldenhauer and Burger⁶ who showed that it was formed by the action of bromine on ammonia in ether, and that amongst other reactions it oxidized potassium iodide to iodine. Johannesson⁷ has shown that in neutral solutions monobromamine is stable in the presence of a large excess of ammonium salts and that it has a characteristic ultraviolet spectrum.

With lower ammonia : bromine ratios some dibromamine is formed, as reported by the author⁸ and by Coleman, Yager, and Soroos.⁹ It could be expected that reaction of bromine with ammonia would be similar to that of chlorine, where monochloramine, dichloramine, and nitrogen trichloride are formed. These chlorine compounds have been studied spectrophotometrically by Metcalf,¹⁰ by Corbett, Metcalf, and Soper,¹¹ and by Weil and Morris.¹² Metcalf¹⁰ showed that *N*-monochloro-amines had maxima at 260–240 m μ , monochloramine at 240, dichloramine at 297, and nitrogen trichloride at 340 m μ . The present author⁷ found monobromamine to have a maximum at 277 m μ , and dibromamine at <230 m μ , but found no evidence for the existence of nitrogen tribromide in aqueous solution. The present paper presents data on the conditions of formation, and on the existence of the monobromammonium ion and dibromamine, together with their polarographic and chemical properties. A comparison is made with the corresponding chlorine compounds.

Monobromamine.—In aqueous solution, bromine undergoes the reaction, $\text{Br}_2 + \text{H}_2\text{O} \longrightarrow \text{H}^+ + \text{Br}^- + \text{HOBr}$, with formation also of perbromides Br_3^- and Br_5^- . As the reaction of bromine with ammonia or ammonium salts may be expected to proceed by the action of hypobromous acid on the ammonium ion $\text{HOBr} + \text{NH}_4^+ \longrightarrow \text{NH}_2\text{Br} + \text{H}_2\text{O} + \text{H}^+$ this reaction would be favoured by conditions giving the greatest concentrations of hypobromous acid. Low pH and/or the presence of bromide ions will reduce the amount of hypobromous acid, and so should retard the action of bromine on ammonia. In agreement, no reaction occurred at pH 4 in the presence of an excess of bromide.

¹ Hofmann, *Ber.*, 1883, **16**, 558; Norris, *Amer. Chem. J.*, 1898, **20**, 51; Willstätter and Hottenroth, *Ber.*, 1904, **37**, 1775.

² Kolthoff and Laur, *Z. analyt. Chem.*, 1928, **73**, 177.

³ Kolthoff, Stricks, and Morren, *Analyt.*, 1953, **78**, 405.

⁴ Laitinen and Woerner, *Analyt. Chem.*, 1955, **27**, 215.

⁵ Arcand and Smith, *ibid.*, 1956, **28**, 440.

⁶ Moldenhauer and Burger, *Ber.*, 1929, **62**, 1615.

⁷ Johannesson, *New Zealand J. Sci. Technol.*, 1955, **B**, **36**, 600.

⁸ *Idem*, *Chem. and Ind.*, 1953, 97.

⁹ Coleman, Yager, and Soroos, *J. Amer. Chem. Soc.*, 1934, **56**, 965.

¹⁰ Metcalf, *J.*, 1942, 148.

¹¹ Corbett, Metcalf, and Soper, *J.*, 1953, 1927.

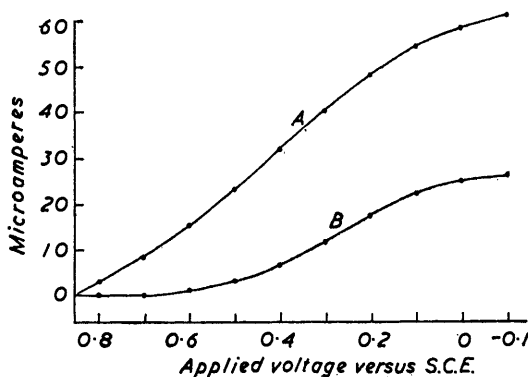
¹² Weil and Morris, *J. Amer. Chem. Soc.*, 1949, **71**, 3123.

At this pH, in the absence of added bromide, the reaction commenced but was rapidly halted through the conversion of the available bromine into the unreactive tribromide ion, the bromide ion for this reaction arising from rapid decomposition of the products at this pH. Attempts to use bromide-free hypobromous acid were also unsuccessful, for the same reasons. The formation of the tribromide ion was followed spectrophotometrically, as this ion has a very intense absorption near 260 m μ . The unreactivity of the tribromide ion towards aromatic compounds has been noted by other workers.¹³

At neutral pH, bromine reacted readily with ammonium salts even in the presence of an excess of bromide ion, giving monobromamine in the presence of an excess of ammonium ion. At pH 8.2, monobromamine had an absorption maximum at 277 m μ , and a molar absorbance of 260. At slightly lower pH values, and in the presence of an excess of ammonium ion to suppress the reaction, $H^+ + 2NH_2Br \rightarrow NHBr_2 + NH_4^+$, the reaction $H^+ + NH_2Br \rightarrow NH_3Br^+$, occurred. Presence of the monobromammonium ion NH_3Br^+ was shown by the absorption spectra, which with decreasing pH values showed a decrease in absorbance at 277 m μ , and an increase in the region below 230 m μ . Over the pH range concerned, a family of absorption curves was obtained with well-defined isosbestic points at 260 and 310 m μ .

The positive ionic nature of the substance formed in the above reaction was demonstrated by electro dialysis, active bromine passing to the cathodic chamber where it was combined with fluorescein to form eosin, after the manner of the positive bromine-ion experiments of Gonda-Hunwald, Graf, and Korosy.¹⁴

Current-voltage curves for hypobromite (A) and monobromamine (B) with the platinum electrode versus the S.C.E.



Attempts to determine the molar absorbance of the monobromammonium ion by lowering the pH to the point where only the ion would be present were unsuccessful owing to the rapidity of decomposition and the presence of hydrolysis at these lower pH values.

By Weil and Morris's method,¹² measurement of the change of absorbance with change of pH gave for the equilibrium constant $K_a = [H^+][NH_2Br]/[NH_3Br^+]$ the average value of 1.07×10^{-6} (see Table). Correcting for activity effects gives the true thermodynamic constant $K_a = 0.408 \times 10^{-6}$. Since $K_b = K_w/K_a$, $K_b = 2 \times 10^{-8}$, to be compared with 1.8×10^{-5} for ammonia and 1×10^{-15} estimated by Weil and Morris¹² for monochloramine. The weaker basicity of the monochloramine and monobromamine may be ascribed to the greater inductive effects of the halogens.

Dibromamine.—At pH 8.3, a low ratio ammonium : bromine gave a different spectrum with high absorbance in the region below 230 m μ , and a reduced absorbance near 277 m μ due to the formation of dibromamine. This work has been described elsewhere by the author.⁸ Successive additions of ammonium sulphate solution to a solution prepared as above caused the spectrum to change progressively to that of pure monobromamine as

¹³ Bradfield, Davies, and Long, *J.*, 1949, 1393; Bartlett and Tarbell, *J. Amer. Chem. Soc.*, 1936, **58**, 467.

¹⁴ Gonda-Hunwald, Graf, and Korosy, *Nature*, 1950, **166**, 68.

Acid dissociation constant of monobromammonium ion. Molar absorbance for monobromamine base is 260.

$10^6[\text{H}^+]$	$\epsilon_{\text{obs.}}$	$\epsilon_{\text{B}} - \epsilon_{\text{obs.}}$	$10^{-6}(\epsilon_{\text{B}} - \epsilon_{\text{obs.}})/[\text{H}^+]$	$10^6 K_a$	$10^6[\text{H}^+]$	$\epsilon_{\text{obs.}}$	$\epsilon_{\text{B}} - \epsilon_{\text{obs.}}$	$10^{-6}(\epsilon_{\text{B}} - \epsilon_{\text{obs.}})/[\text{H}^+]$	$10^6 K_a$
2.56	165	95	37.1	1.08	0.850	200	60	70.8	1.08
1.91	174	86	45.0	1.08	0.605	210	50	82.7	1.04
1.44	182	78	54.1	1.06	0.480	218	42	88.0	1.09
1.12	190	70	62.5	1.04					
								Average	1.07

represented by $\text{NHBr}_2 + \text{NH}_4^+ \longrightarrow 2\text{NH}_2\text{Br} + \text{H}^+$. It was not possible to determine the equilibrium constant for this reaction. These solutions were very unstable and it appears that there was a minimum ratio for any stability for a mixture of the mono- and di-bromamines, below which there is almost instantaneous decomposition. Attempts at electro dialysis were not successful owing to the speedy decomposition, and the minimum ratio described in the preceding sentence.

Polarographic Behaviour.—With an electrode system consisting of a rotating platinum electrode together with a saturated calomel half-cell (S.C.E.) free halogens give diffusion currents which commence near +0.8 v *versus* the S.C.E.³ The wave commences near +0.1 v *versus* the S.C.E. for monochloramine and at even more negative values for dichloramine. The exact values are a function of the pH and the pre-treatment of the electrodes. For monobromamine the diffusion current was found to commence near +0.5 v *versus* the S.C.E. and for solutions containing dibromamine the wave commenced near that for free bromine. In each case, however, the current was much lower than that for free bromine at the same applied E.M.F. Addition of ammonium salts to a solution containing dibromamine gave diffusion currents intermediate in value until, with an excess of ammonium ion present, the wave was that of monobromamine.

Chemical Reactions.—Both monobromamine and dibromamine act as strong oxidizing agents and, in neutral solution, oxidize phenyl arsenoxide, sodium arsenite, Methyl Orange, Methyl Red, benzidine, *o*-tolidine, and potassium iodide amongst other compounds. By contrast, monochloramine liberates iodine from iodide in neutral solutions but does not oxidize the other compounds unless the pH is 3 or less. Dichloramine is less reactive and does not oxidize even iodide unless the solutions are acidified to pH 4 or less. In solution at pH 8 monobromamine reacts with dimethylamine to form *N*-bromodimethylamine, probably by the reaction, $\text{NH}_3\text{Br}^+ + \text{Me}_2\text{NH} \longrightarrow \text{Me}_2\text{NHBr}^+ + \text{NH}_3$, an equilibrium mixture being formed. This reaction was observed spectrophotometrically and will be discussed in a further communication.

Discussion.—It has been shown that both monobromamine and dibromamine may be formed by the action of bromine on ammonia solutions at neutral pH and exhibit characteristic ultraviolet absorption spectra. In more acid solutions the monobromammonium ion is formed with K_b of 2×10^{-8} .

The stronger oxidizing properties of monobromamine than of monochloramine are probably due to the presence of significant amounts of the monobromammonium ion. Thus at pH 7.0 approximately 10% is present as the ion, and at pH 8.0 approximately 1%, the actual amount depending upon the ionic strength of the solution and the temperature. Monochloramine with K_b 10^{-15} will have only about one part in 10^8 , at pH 7, of the positive ion, an insignificant amount. The oxidizing reactions of these compounds probably proceed: $\text{NH}_3\text{Br}^+ \longrightarrow \text{NH}_3 + \text{Br}^+$. Brown and Soper¹⁵ demonstrated that chlorination of phenol by *N*-chlorodialkylamine involved the action of the *N*-chlorodialkylammonium ion on phenol. Monobromamine and dimethylamine probably react by a similar mechanism, whilst monochloramine does not react with dimethylamine under these conditions. Dichloramine is a much weaker oxidizing agent than monochloramine, but

¹⁵ Brown and Soper, *J.*, 1953, 3576.

by contrast dibromamine appears to be a stronger agent than monobromamine, as shown by its polarographic behaviour.

In the ultraviolet spectrum, the bromamines differ from the chloramines in that the dibromamine has an absorption maximum at a much lower wavelength than monobromamine whereas dichloramine has an absorption maximum (297 $m\mu$) at a greater wavelength than monochloramine has (240 $m\mu$), as demonstrated by Metcalf.¹⁰

EXPERIMENTAL

Ultraviolet absorption spectra were measured with an Unicam S.P. 500 spectrophotometer, and the pH measurements with a Beckman Model G pH meter.

For electro dialysis a multicompart ment apparatus was used. In the absence of the extra electrode compart ment, bromide ion would migrate to the anode and there be oxidized to bromine, which would react with the fluorescein and form eosin, giving erroneous results. With monobromamine in the presence of a large excess of ammonium salt at pH 8.2 in the central compart ment and with 100 v applied the quantities of eosin formed in the reaction compart ments were small and equal, being due in each case to diffusion. With the conditions as above, but at pH 6.0, the fluorescein in the cathodic compart ment was rapidly converted into eosin, showing the presence of a stable positive ion containing active bromine.

Conventional forms of rotating platinum electrode systems were used for polarography; for measurements at negative applied potentials, the solutions were deoxygenated by passage of a stream of nitrogen through the solution.

Hypobromous acid was prepared by vacuum-distillation of bromine water treated with an excess of silver nitrate, with exclusion of light.

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