were added to mixtures of blood and organic matter, and quantitative recoveries were obtained by following the procedures as outlined above.

Summary

An aeration procedure for estimating cyanides has been devised in which freed hydrogen cyanide is washed with air into dil. alkali solution, and the mixture then titrated with standard silver nitrate solution, using a little potassium iodide as indicator. The new method has the following marked advantages as compared with the older distillation methods: (1) it avoids loss from hydrolysis of hydrogen cyanide; (2) it can be used to determine cyanides in the presence of ferrocyanides, etc.; (3) it is entirely free from danger to the operator; (4) it offers an excellent method for determining mercuric cyanide provided the latter is previously reduced to mercurous chloride, metallic mercury and hydrogen cyanide with stannous chloride, in the presence of hydrochloric acid; (5) it involves easy technique, gives highly accurate results, and possesses a very wide range of application.

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THE REACTION BETWEEN BROMINE AND AMMONIUM SALTS AND ITS EFFECT ON THE PRECIPITATION OF MANGANESE DIOXIDE

BY STEPHEN G. SIMPSON

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One of the standard methods for separating titanium, iron, aluminum and phosphoric acid from bivalent elements such as manganese, magnesium and calcium, is the basic acetate procedure. In the filtrate from this separation, manganese is often precipitated from hot solution by the addition of bromine water: $Mn^{++} + Br_2 + 3H_2O = MnO_2.H_2O + 2Br^- + 4H^+$.[1] In neutral solution the oxidation and precipitation of the manganese does not take place to an appreciable extent unless the acid formed by the reaction is neutralized, for hot, dil. hydrobromic acid dissolves manganese dioxide. After the basic acetate precipitation, however, the filtrate always contains enough acetate to prevent the formation of an appreciable quantity of free hydrobromic acid, owing to the formation of slightly ionized acetic acid. Sometimes it is the practice to neutralize the solution with dil. ammonia, but owing to the fact that bromine reacts with ammonia ($8NH_4OH + 3Br_2 \longrightarrow 6NH_4^+ + 6Br^- + 8H_2O + N_2$), a great deal of bromine is used up and it is a rather troublesome operation to precipitate

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[1] Compare Wright and Menke, *J. Chem. Soc.*, **37**, 22 (1880).

the manganese completely.[2] When manganese is precipitated from weakly acetic acid solution by bromine, it carries with it elements of the alkali and alkaline-earth group[1] and a single precipitation is not sufficient to effect a complete separation of manganese and these elements, although this method of separation is given in many textbooks. Furthermore, when the solution contains ammonium salts, it is usually difficult in faintly acid solutions to obtain any precipitate of manganese dioxide at all.

The reason why ammonium salts prevent the precipitation of manganese after the basic acetate separation is not generally mentioned in textbooks, and the extent of this interference and the quantitative effects of the several factors involved have been little studied.

Bromine reacts with ammonium salts according to the equation, $2NH_4^+ + 3Br_2 \longrightarrow 6Br^- + N_2 + 8H^+$, and Ostwald and Raich[3] have shown that the velocity of reaction depends upon the strength of the acid forming the negative radical of the ammonium salt. A study of these reactions, moreover, involves a consideration of the reactions between bromine and water. Solutions of bromine contain not only free dissolved bromine, but also hypobromous and hydrobromic acids, $Br_2 + H_2O \longrightarrow Br^- + HBrO + H^+$, the reaction at 25° using up about 0.8% of the total bromine present.[4] Bromine also decomposes water according to the equation $2Br_2 + 2H_2O \longrightarrow 4Br^- + O_2 + 4H^+$, the decomposition increasing rapidly in the sunlight and with increase in temperature.[5] This latter reaction may be considered simply as a decomposition of the hypobromous acid formed above: $2HBrO \longrightarrow 2H^+ + 2Br^- + O_2$. Above 60° bromate is likewise formed:[6] $3Br_2 + 3H_2O \longrightarrow 5Br^- + BrO_3^- + 6H^+$, or, $3HBrO \longrightarrow BrO_3^- + 2Br^- + 3H^+$. The various oxidation potentials between these bromine compounds have been determined and the results have been correlated and listed by Abegg.[7] The results, however, are found to lie close to one another and likewise close to the oxidation potential between manganous ion and manganese dioxide.[8] It is of interest, therefore, to study these reactions experimentally under the conditions where manganese is often precipitated in practice.

Experimental Part

The quantitative effect of the various factors influencing the oxidation of ammonium salts and of manganous salts by bromine was determined experimentally from the amount of bromine used up in each reaction in which

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[2] Compare Hall and Williams, "The Examination of Iron, Steel and Brass," McGraw-Hill Book Co., **1921**, p. 79.

[3] Ostwald and Raich, *Z. physik. Chem.*, **2**, 124 (1888).

[4] Bray, THIS JOURNAL, **32**, 932 (1910); **33**, 1487 (1911).

[5] Richards and Stull, *Z. physik. Chem.*, **41**, 555 (1902).

[6] See Luther and Sammet, *Z. Elektrochem.*, **11**, 293 (1905).

[7] Abegg, "Handbuch der Anorganischen Chemie," S. Hirzel, **1913**, Vol. IV, p. 302.

[8] Landolt-Börnstein, "Physikalish-Chemische Tabellen," 4th ed., p. 256c.

it takes part. Since the precipitation of manganese dioxide by bromine is usually carried out in hot solution, each determination was made in this way. To do this, use was made of a special 500cc. glass-stoppered distilling flask with the side arm forming the inner tube of a Liebig condenser. The total volume of each solution was 100 cc., and in all determinations the conditions were kept as nearly constant as possible. In each case, after the addition of bromine to the solution, the mixture was allowed to remain quiet in the distilling flask for 5 minutes and then heated to boiling for 10 minutes more, all the free bromine being expelled by the end of this time. The bromine evolved was allowed to pass through the condenser and was caught in potassium iodide solution, the liberated iodine being titrated with standard thiosulfate solution. In this way, when the amount of bromine added and the amount recovered were known, the quantity used up in a reaction was found by difference. The solutions of bromine were standardized repeatedly during each series of distillations, and approximately 1.1 milliequivalents of bromine were used in each reaction, that amount being in each case in excess of the amount theoretically required.

The addition of samples of bromine water to potassium iodide solutions was found to liberate iodine from neutral solutions in amounts corresponding to an average of 98.3% of the total bromine present. After acidification of the solution with sulfuric acid, iodine equivalent to the remaining bromine was liberated. This indicates the presence of oxy-acids of bromine in the solutions used in amounts corresponding to 1.7% of the total bromine present. In any oxidation in acid solution by means of bromine water the presence or intermediate formation of hypobromite or bromate has, however, no quantitative effect, since the oxidizing power expressed in equivalents remains the same. A bromine solution in which a part of the bromine reacts with water to form hypobromite or bromate suffers no loss or gain in oxidizing power.

Ten distillations of samples of bromine water in the apparatus and under the conditions mentioned above showed a net loss in oxidizing power between the original solution and the distillate obtained corresponding to an average of 0.032 + 0.006 milliequivalent of bromine. This represents a 3% decomposition into bromide and oxygen. The residual solution did not oxidize iodide in acid solution.

The initial presence of acid in the distillation of bromine water in 10 similar experiments caused a slight decrease in the loss in oxidizing power of the distillate over the original solution taken, the average loss in terms of bromine being reduced to 0.024 + 0.004 milliequivalent. Since the reaction by which hypobromous acid is formed from bromine and water is reversible, the initial presence of acid, by its common ion effect, reverses the reaction and hence retards the loss in oxidizing power caused by decomposition of hypobromite into oxygen and bromide.

In the experimental study of the reaction between bromine and ammonium salt, the sulfate of ammonium was used because of the fact that it reacts with bromine moderately rapidly, being intermediate between the chloride or nitrate and the acetate. The amount of bromine used up in each reaction was determined by means of the apparatus and under the conditions described above. In the absence of sodium acetate and with a large excess of bromine, the reaction between ammonium ion and bromine was found to take place quantitatively according to the reaction, $3Br_2 + 2NH_4^+ \longrightarrow 6Br^- + N_2 + 8H^+$, but the reaction is moderately slow, so that with comparatively great amounts of ammonium sulfate the time of contact with the bromine water was not sufficient to cause the oxidation of all the ammonium salt, for the bromine was expelled before the oxidation was complete. The presence of increasing amounts of acid in the original solutions, on the other hand, caused a corresponding retardation of the reaction and the presence of a moderately high concentration of hydrogen ion was capable of stopping the reaction practically completely.

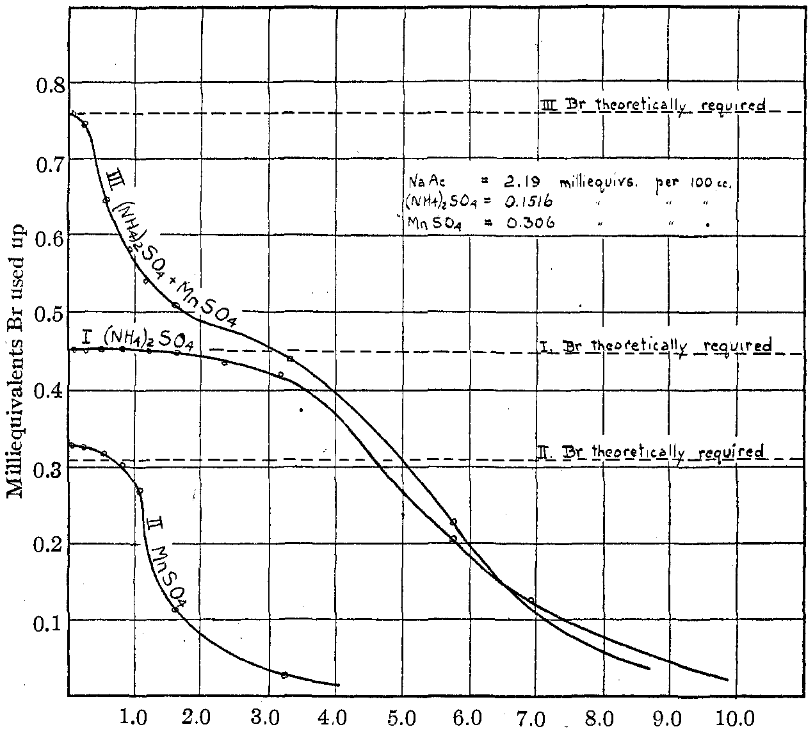

Fig. 1.—Consumption of bromine by boiling for 10 minutes with (I) $(NH_4)_2SO_4$; (II) $MnSO_4$; (III) $(NH_4)_2SO_4$ + $MnSO_4$ in various concentrations of acid

The extent of the oxidation of ammonium ion by bromine in the presence of sodium acetate under varying concentration of acid and under the experimental conditions is shown in Fig. 1 (I). With a moderate excess of acetate it is seen that the theoretical amount of bromine required for the ammonium salt is consumed. Only when the concentration of acid exceeds that of the acetate is the reaction retarded, and to a degree which increases with the excess of acid present.

The explanation of these phenomena follows from a consideration of the fact that although the reaction $3Br_2 + 2NH_4^+ \longrightarrow 6Br^- + N_2 + 8H^+$ is in itself practically irreversible, the reaction $Br_2 + H_2O \rightleftarrows Br^- + HBrO + H^+$ is distinctly reversible, and it is the hypobromous acid formed that causes rapid oxidation of ammonium ion:[9] $2NH_4^+ + 3HBrO \longrightarrow N_2 + 3Br^- + 3H_2O + 5H^+$. The initial presence of acid, by reversing the equilibrium reaction between bromine and water and hence lowering the concentration of hypobromite, retards the oxidation of ammonium ion. Conversely, the presence of acetate, by removing hydrogen ion in the form of relatively non-ionized acetic acid, causes the equilibrium reaction as written above to proceed to the right and thereby accelerates the oxidation of ammonium ion by the hypobromous acid formed.

Experiments in which a great excess of sodium acetate over the acid initially present was used, showed a consumption of bromine slightly greater than the amount theoretically required for the ammonium alone. The hypobromous acid, in this case being formed in comparatively large amounts, after oxidizing the ammonium ions present, decomposes appreciably into oxygen and hydrobromic acid, and hence causes a corresponding loss in oxidizing power.

In the study of the oxidation of manganese by bromine, the sulfate of manganese was used and the reactions were carried out in the apparatus and under the same conditions as in the oxidation of the ammonium salt. The values obtained are expressed graphically in Fig. 1 (II). Without the presence of alkali acetate, the oxidation of manganese by bromine takes place to a very slight degree; with sodium acetate present in excess, manganous ion is completely oxidized and precipitated by bromine water, provided no acid is originally present in the solution. An increase in the initial concentration of acid causes a marked decrease in the extent of the reaction, and the effect, be it noted, is much greater than in the case of the ammonium salt oxidation.

These reactions can be explained in exactly the same way as was the oxidation of ammonium ion, for although the reaction, $Mn^{++} + Br_2 + 3H_2O = MnO_2.H_2O + 2Br^- + 4H^+$, is in itself reversible, yet the same oxidation may be expressed through the hypobromous acid formed as a product of the equilibrium reaction between bromine and water: $Mn^{++} +$

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[9] Compare Bray and Livingston, THIS JOURNAL, **45,** 1251 (1923).

$HBrO + 2H_2O = MnO_2.H_2O + Br^- + 3H^+$. As with the ammonium-ion oxidation, the initial presence of acid or acetate affects the hypobromite equilibrium sufficiently to retard or accelerate the manganese precipitation. With small amounts of acid, the quantity of bromine used up is seen from the graph to be in excess of the amount theoretically required for the manganese alone, due, as in the case of the ammonium salt reaction, to decomposition of the hypobromous acid into oxygen. Increasing the acetate concentration, even when a moderate concentration of acid had been added, caused increased precipitation of manganese dioxide, but also caused increased loss in oxidizing bromine.

The conditions resulting when bromine reacts with solutions containing both manganous ions and ammonium ions are shown in Fig. 1 (III), where the same experimental conditions were maintained as in the individual reactions. These experiments show that with sodium acetate present, but with little or no acid initially present, the amount of bromine used up is approximately equal to the sum of the theoretical amounts calculated for the manganese salt and for the ammonium salt. Increasing acid concentration, however, rapidly reduces the bromine consumption to a point where both reactions practically cease. Comparison with the individual effects of manganese sulfate and ammonium sulfate shows that under the experimental conditions, when manganous ion and ammonium ion are present together, the addition of bromine causes more rapid oxidation of the ammonium ion than of the manganous ion.

The extent of precipitation of manganese dioxide in the presence of various amounts of ammonium sulfate was next determined using an excess of sodium acetate and a great excess of bromine water. No acid was added, and 0.302 milliequivalent of manganese was employed in each case. After the solution had been boiled, the precipitated manganese dioxide was determined by titration. The results obtained are given below, and from them it is seen that a moderate concentration of ammonium ion inhibits to a marked degree the precipitation of manganese dioxide.

$(NH_4)_2SO_4$ added Millieq.	Mn pptd. Millieq.	Mn pptd. %
0.000	0.301	100
.030	.303	100
.091	.302	100
.152	.289	95
.243	.280	91
0.303	0.267	87
.394	.170	56
.606	.008	1.4
.909	.004	0.7

Conclusions

In the precipitation of manganese by oxidation with bromine water to manganese dioxide in hot solution, the presence of ammonium salts has a decidedly inhibiting effect. The extent of the effect depends principally upon three similar reactions, as follows:

$$2Br_2 + 2H_2O = 4Br^- + O_2 + 4H^+$$
$$3Br_2 + 2NH_4^+ = 6Br^- + N_2 + 8H^+$$
$$Br_2 + Mn^{++} + 3H_2O = 2Br^- + MnO_2.H_2O + 4H^+$$

Each of these reactions may be expressed through the intermediate formation of hypobromous acid according to the equilibrium: $Br_2 + H_2O \rightleftarrows Br^- + HBrO + H^+$, and the subsequent oxidation of the reducing agent in question by the hypobromous acid thus formed, the hypobromous acid reacting more rapidly with the reducing agents than does bromine itself. The initial presence of acid by its common ion effect, and the presence of alkali acetate by its ability to cut down the hydrogen-ion concentration, disturb the above equilibrium reaction, causing marked variation in the hypobromite concentration and hence retard or accelerate the oxidation reactions, as the case may be.

In hot solution and in the presence of alkali acetate, bromine water oxidizes ammonium ion more readily than it does manganous ion. With no acid initially present and with a moderate excess of acetate, ammonium ion is quantitatively oxidized by an excess of bromine. After this oxidation is complete, the presence of large amounts of acetate causes consumption of any excess bromine present, due to the decomposition of hypobromous acid into bromide and oxygen with corresponding loss in oxidizing power. Without the presence of acetate, ammonium salts are likewise oxidized quantitatively by bromine water in neutral solution, but the reaction proceeds much more slowly, and the rate of reaction varies inversely with the ionization of the acid forming the negative radical of the ammonium salt.

The precipitation of manganese by bromine water in hot, neutral solution is almost inappreciable in the absence of acetate. With alkali acetate present, in neutral solution manganese is quantitatively oxidized and precipitated from solution on boiling with excess bromine. The extent of precipitation is greatly influenced by the initial acidity of the solution, more so than in the ammonium salt reaction. A large excess of sodium acetate makes the precipitation of manganese dioxide more complete, but causes excessive consumption of bromine by its decomposition of water which occurs almost simultaneously. Manganese dioxide can be precipitated quantitatively from neutral solution in the presence of a slight amount of ammonium salts when sodium acetate is present in excess, and in such a case both the ammonium salt and the manganese salt are completely oxidized. With an increase in the concentration of the ammonium salt, the precipitation of the dioxide is retarded, and with a moderate excess of ammonium salt can be almost entirely prevented. The ammonium salt, being oxidized more rapidly, forms by its reaction a sufficient concentration of hydrogen ion to prevent the manganese precipitation.

When manganese is to be precipitated as dioxide after a basic acetate separation, it is important, therefore, that no appreciable amounts of ammonium salts are present. If present, they should be removed previous to the precipitation by evaporation with aqua regia. It sometimes happens that in the evaporation of the filtrate from a basic acetate separation, a small precipitate results which may be (1) manganese dioxide due to oxidation of the manganese by the air; or (2) more basic acetate of a tervalent element due to incomplete basic acetate separation; or (3) a mixture of the two. In such a case, the precipitate should either be put through another basic acetate procedure, or it may be dissolved in acid and the tervalent element precipitated by ammonium hydroxide in the presence of ammonium salt[10] and removed by filtration. In the latter case, the filtrate containing any possible manganese should not be added to the main filtrate, since it now contains ammonium salts and would prevent the subsequent precipitation of manganese dioxide. This auxiliary filtrate should, therefore, be saved and added to the main solution after the manganese dioxide has been precipitated, redissolved, and is ready for precipitation as manganese ammonium phosphate.

Summary

(1) The effect of the presence of ammonium salt on the precipitation of manganese dioxide by bromine water following a basic acetate separation was studied by determining the amounts of bromine used up in reactions with solutions of (a) ammonium sulfate, (b) manganous sulfate, (c) mixtures of the two, under varying degrees of initial acidity and in the presence of varying amounts of alkali acetate. The numerical values obtained are graphically tabulated for comparison.

(2) The tabulated results show that each of the reactions is progressively retarded by an increase in the initial concentration of acid, and progressively accelerated by an increase in the concentration of acetate present, and the effect is greater in the case of the manganese salt than in the corresponding case of the ammonium salt.

(3) In the absence of acid, ammonium ion and manganous ion are quantitatively oxidized by bromine water, but the amount of free bromine used up is slightly in excess of the amount theoretically required.

(4) The results obtained can be explained by considering the mass-action effect of hydrogen ion and of acetate ion on the equilibrium reaction between bromine and water, and assuming that the hypobromous acid formed oxidizes ammonium ion and manganous ion more readily than does bromine, and under the existing conditions also decomposes slightly into oxygen and bromide.

(5) When ammonium salts and manganese salts are present together in neutral solution in the presence of acetate, the ammonium ion is more

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[10] See Lundell and Knowles, This Journal, **45,** 676 (1923).

readily oxidized by bromine water, and by its formation of hydrogen ion retards the precipitation of manganese dioxide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

PARTIAL AND CONSECUTIVE REACTIONS IN THE PHOTOSENSITIVE SYSTEM: QUININE SULFATE, CHROMIC AND SULFURIC ACIDS

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The general photochemical equation of Plotnikow[1] provides for reactions involving more than one photosensitive substance, and also "dark" reactants indispensable but not activated under the given conditions

$$-\mathrm{d}M/\mathrm{d}t = KA_1A_2 \ldots A_n(a-x)^{n_1}(b-x)^{n_2} \ldots (p-x)^{n_n}$$

where A_1 and A_2 are the rates of light absorption by Reactants 1 and 2, to which the concentrations of their activated molecules C_1' and C_2' are approximately proportional, while $(a - x)$, $(b - x)$ .... are concentrations of "dark" reactants. The reaction between these molecular species, determined by these concentrations, has a velocity constant k_1.

The photochemical oxidation of quinine by chromic acid in the presence of sulfuric acid was investigated in 1906–7 by Luther and Forbes.[2]

The first two reactants are known to be photosensitive in various reactions; the third is undoubtedly a dark reactant. The data of this research should, therefore, serve to test Plotnikow's equation. When the test is made, however, it is found that chromic acid seems to behave only as an inert light filter, and that the reaction velocity is independent, within the limit of error, of the light absorbed by it, and not proportional to the latter, as Plotnikow's equation requires. Plotnikow[3] is of the opinion that some experimental error or inadequate analysis of the data on absorption is responsible for the discrepancy. We desire first to show deductively that in a system containing 2 photosensitive reactants capable of reacting even in the dark, there are doubtless partial reactions not provided for in Plotnikow's equation. The discrepancy may be explained in terms of these. Also, with the help of new experimental data, we shall thereafter demonstrate the limitations inherent in that factor of Plotnikow's equation which deals with the dark reactant.

Let the concentrations of unactivated molecules of 2 photosensitive reactants be C_1 and C_2. In the dark, $-\mathrm{d}M/\mathrm{d}t = k_2C_1^pC_2^q(a - x)^{n_1}$ .... and k_2 may be evaluated. During illumination, according to the usual

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[1] Plotnikow, "Allgemeine Photochemie," Vereinigung Wissenschaftlicher Verleger, **1920**, p. 185.

[2] Luther and Forbes, THIS JOURNAL, **31**, 770 (1909).

[3] Ref. 1, pp. 215, 416, 583.