ANALYTICAL USES OF BROMINE MONOCHLORIDE

DETERMINATION OF HYDROXYLAMINE. CONTRIBUTIONS TO THE BROMIC ACID-HYDROCHLORIC ACID REACTION

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Summary—The oxidation of hydroxylamine by bromine monochloride, by elementary chlorine in hydrochloric acid medium, and by bromate and bromic acid has been investigated. Oxidation by bromine monochloride is utilised for the analytical determination of hydroxylamine.

Detailed examination of the reaction of bromate with hydrochloric acid proves that, in the presence of excess of hydrochloric acid, these compounds quickly react forming bromine monochloride and elementary chlorine. The proportions of the reaction products have been determined. On the basis of the results of these investigations, it is possible to present an interpretation of the analytical method suggested by Kurtenacker for the determination of hydroxylamine.

THE conventional analytical determination of hydroxylamine is based on determination of the acid component of its sulphate or hydrochloride. Rupp and Mäder¹ were the first to use oxidation by bromine for the determination of hydroxylamine, and they found that hydroxylamine is oxidised by bromine to nitric acid. Kurtenacker and co-workers,^{2,3} however, pointed out that this method is only suitable for minute amounts of hydroxylamine. With greater quantities of hydroxylamine, nitrogen oxides are also formed. In the opinion of Kurtenacker and Wagner² the best method for the determination is to oxidise hydroxylamine with bromate in strong hydrochloric acid medium. According to these authors, hydroxylamine is then oxidised to nitric acid by nascent chlorine which is formed by the reaction of bromate with hydrochloric acid.

During our investigations into the analytical uses of bromine monochloride, we studied the oxidation of hydroxylamine by bromine monochloride. It was found that hydroxylamine is quantitatively oxidised to nitric acid by an excess of bromine monochloride:

$$NH_{2}OH + 3BrCl + 2H_{2}O = HNO_{3} + 3HBr + 3HCI$$
(1)

In our attempts to utilise this reaction for the analytical determination of hydroxylamine, we used a 0.1N standard solution of bromate which contained an equivalent amount of bromide according to the equation:

$$BrO_{3}^{-} + 2Br^{-} + 3Cl^{-} + 6H^{+} = 3BrCl + 3H_{2}O$$
 (2)

This standard solution was added in excess to a weighed amount of hydroxylamine in a bromination flask. On acidification with hydrochloric acid, reaction (2) takes place and hydroxylamine is oxidised according to (1). The excess of bromine monochloride is determined iodometrically. In this reaction, the equivalent weight of hydroxylamine is M/6. On examining the reaction between bromine monochloride and hydroxylamine in detail under the conditions mentioned later it was found that:

1. When bromine monochloride is present in an excess greater than 100%, hydroxylamine is quantitatively oxidised to nitric acid in 3 min.

- 2. The results are not affected by using longer reaction periods.
- 3. It is practical to use 5-10 ml of 20% hydrochloric acid.

4. On varying the excess of bromine monochloride (greater than 100%), no change was observed in the results. The use of excesses of bromine monochloride greater than 100% is necessary because, during the oxidation, bromine monochloride is reduced to bromide which latter itself reduces bromine monochloride to elementary

NH₂OH·HCl taken, mg	0·1N BrCl added, <i>ml</i>	0.1N Na ₂ S ₂ O ₃ consumed, <i>ml</i>	0·1N BrCl consumed, <i>nil</i>	Reaction time, <i>min</i>	20% HCl used, <i>ml</i>	NH₂OH·HCl found, <i>mg</i>	Δmg	Δ %
2.971	9.96	7.40	2.56	5	5	2.965	-0.006	−0 ·2
5.010	9.96	5.63	4.33	5	5	5.015	+0.002	+0.1
9.862	20.00	11.48	8.52	5	5	9.869	+0.007	+0.1
9.862	20.00	11.20	8.50	5	10	9.846	-0.016	-0·2
9.862	20.00	11.50	8.50	10	10	9.846	-0.016	− 0·2
9.862	20.00	11.46	8∙54	10	5	9.892	+0.030	+0-3

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bromine. Because of this fact the reaction is slowed down, since the elementary bromine oxidises the hydroxylamine more slowly.

By utilising the afore-mentioned observations, 3-12 mg of hydroxylamine hydrochloride could be determined with an error of $\pm 0.5\%$ (cf. Table I).

The bromatometric method suggested by Kurtenacker² for the determination of hydroxylamine was also examined.

First, in the reaction between bromate and hydrochloric acid it was found that, on pouring only 5 ml of 20% hydrochloric acid* into 10 ml of 0.1N bromate solution in a volume of 20 ml, no bromate is present in the solution after 5 min. To disclose this fact we used the method suggested by us⁴ for the eventual bromate content of a bromine monochloride standard solution. By raising the concentration of hydrochloric acid, the rate of reaction was increased. The proportions of reaction products were established as well. Thus, bromine monochloride and elementary chlorine formed in the reaction were converted into halogen cyanides, and the amount of cyanogen bromide measured by iodometry in the presence of the iodometrically inactive cyanogen chloride. According to our investigations, the following reaction takes place quantitatively between bromate and an excess of hydrochloric acid:

$$HBrO_3 + 5HCl = BrCl + 2Cl_2 + 3H_2O$$
(3)

By raising the concentration of hydrochloric acid the rate of reaction increases. The kinetics of the reaction will be discussed in another communication.

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^{*} In his determination Kurtenacker used 40 ml of 20% hydrochloric acid.

The oxidation of hydroxylamine by chlorine and bromic acid, respectively, were studied too. It was found that hydroxylamine is oxidised to nitric acid by elementary chlorine at approximately the same rate as by bromine monochloride. In our studies of the oxidation by bromic acid, it was necessary to maintain conditions which exclude the possibility of formation of bromine monochloride, elementary bromine or elementary chlorine. Therefore, oxidation was carried out in a medium containing sulphuric acid, in the presence of mercury^{II} ions, which are capable of preventing interference from halide ions binding them as poorly dissociating mercury halides. Under these conditions the reaction is extremely slow and ambiguous. No equation can be given for this process.⁵

Accordingly, as proved by our investigations, in the oxidations by bromate carried out in a medium of hydrochloric acid, bromine monochloride and elementary chlorine are always the oxidising reagents. The situation is the same in the method suggested by Kurtenacker.²

EXPERIMENTAL

Determination of hydroxylamine by oxidation with bromine monochloride

Reagents

0.1N bromate solution: 2.7835 g of potassium bromate and 3.9670 g of potassium bromide dissolved in water and diluted to 1000 ml in a standard flask.

Hydrochloric acid: 20%.

Potassium iodide.

0.1N solution of sodium thiosulphate.

Potato starch solution: 1%, decomposed and preserved by 0.1% of salicylic acid.

All the reagents were of analytical grade. The hydroxylamine hydrochloride was Merck analytical grade.

Procedure

An aliquot of solution, containing 3-12 mg of hydroxylamine hydrochloride was, transferred to a Schulek bromination flask and treated with sufficient 0.1N standard solution to maintain, on acidification with hydrochloric acid, an excess of bromine monochloride greater than 100%. Subsequently, the volume of the reaction mixture was diluted with distilled water to 30-40 ml. Then 5-10 ml of 20% hydrochloric acid were poured into the cup-shaped, broadened neck of the bromination flask. On loosening the stopper, the liquid flowed into the flask. After 5 min, 10 ml of a freshly prepared 5% solution of potassium iodide were added to the reaction mixture in a similar way. The amount of iodine liberated was determined, without allowing the mixture to stand, with 0.1N standard sodium thiosulphate solution using potato starch solution as indicator.

1 ml of 0.1N solution corresponds to 1.1583 mg of hydroxylamine hydrochloride (equivalent weight is M/6 in this reaction).

The error of the results is $\pm 0.5\%$.

Investigation of the reaction between bromate and hydrochloric acid

Reagents

0.1N bromate solution. Hydrochloric acid: 20%, distilled, free from bromide. Potassium cyanide. Potassium iodide. Sodium hydroxide: 20%. Potato starch solution: 1%, decomposed and preserved by 0.1% of salicylic acid. All the reagents were of analytical grade.

Procedure

10.00 ml of 0.1N standard bromate solution were diluted with distilled water to 20 ml, and acidified with 5 (10 and 20) ml of 20% hydrochloric acid. On allowing the mixture to stand for 5 min, 0.5 g

of potassium cyanide was dissolved in the mixture and then 20% sodium hydroxide was added to attain an alkali excess of about 2 ml. Bromine monochloride and elementary chlorine reacted with cyanide forming cyanogen bromide and cyanogen chloride and, in the alkaline medium, both hydrolysed to cyanate and bromide or chloride ions, indifferent to iodometry. Accordingly, the bromate content of the solution could be measured iodometrically after 5 min.

Results

Our results showed that, after a reaction period of 5 min, no bromate could be detected.

In order to determine the proportion of the reaction products, about 0.20 g of potassium cyanide was dissolved in the acidic solution when the reaction between bromate and hydrochloric acid was already completed. In a period of about 10 min, bromine monochloride was quantitatively converted into cyanogen bromide and chloride ions even in an acidic solution, while cyanogen chloride and chloride ions developed from elementary chlorine. In the solution containing an excess of cyanide, cyanogen chloride is present as a complex, $[Cl(CN)_a]^-$, which is iodometrically inactive due to its high stability. Thus, it is possible to measure cyanogen bromide iodometrically in the presence of cyanogen chloride.

According to our results, one third $(33\cdot35\%)$ of the products formed in the reaction of bromate and hydrochloric acid consists of bromine monochloride, while two thirds $(66\cdot65\%)$ consist of elementary chlorine (cf. equation (3)).

Oxidation of hydroxylamine by elementary chlorine

In these experiments, aliquots of chlorine water containing exactly known amounts of chlorine were added to the solution of hydroxylamine hydrochloride with the aid of the bromine monochloride apparatus suggested by Schulek.⁶ Excess chlorine was determined iodometrically.

With oxidation by elementary chlorine for 5 min, 98.7% of the weighed amount is recovered. On considering that, under the applied experimental conditions, a deviation of 1-2% in the results is hardly avoidable, oxidation by chlorine can be accepted as quantitative.

Oxidation of hydroxylamine by bromic acid

The aqueous solution of hydroxylamine hydrochloride was allowed to flow into a mercury^{II} sulphate solution (0.2 g of mercury^{II} oxide dissolved in a few ml of 50% sulphuric acid) and the necessary amount of 0.1N standard bromate solution was added. Excess bromate was determined by iodometric titration after 5 (in another experiment after 30) min.

The results obtained showed a marked deviation, and it was impossible to evaluate them from an analytical point of view. On calculating with the equivalent weight of the oxidation by bromine monochloride, only about 25% of the weighed substance could be recovered after 30 min oxidation.

Zusammenfassung—Die Oxydation von Hydroxylamin durch Bromchlorid, elementarem Chlor sowie in salzsaurem Medium durch Bromat und Bromsäure wurde untersucht. Die Oxydation durch Bromchlorid wurde zur Bestimmung von Hydroxylamin gebraucht.

In Gegenwart von Säureeüberschuss reagiert Bromate rasch mit Salzsäure unter Bildung von Bromchlorid und elementarem Chlor. Das Verhältnis der entstehenden Produkte wurde bestimmt. Auf Grund der erhaltenen Resultate war es möglich die von Kurtenacker ausgearbeitete Metlische zur Bestimmung von Hydroxylamin zu interpretieren.

Résumé—L'oxydation de l'hydroxylamine par le chlorure de brome, le chlore élémentaire et, en milieu acide chlorhydrique par le bromate et l'acide bromique, a été étudiée. L'oxydation par le chlorure de brome a été utilisée pour le dosage de l'hydroxylamine.

En présence d'un excès d'acide, le bromate réagit rapidement avec l'acide chlorhydrique formant du chlorure de brome et du chlore élémentaire. Les proportions des produits ont été déterminées. En se basant sur ces résultats, il a été possible de donner une interprétation de la méthode analytique suggérée par Kurtenacker pour le dosage de l'hydroxylamine.

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