

ON THE IODOMETRIC DETERMINATION OF THE BROMIDE ION

by

ZOLTÁN G. SZABÓ AND LÁSZLÓ CSÁNYI

*University of Szeged, Institute for Inorganic and Analytical Chemistry,
Szeged (Hungary)*

As bromate can readily and accurately be measured iodometrically it is most suitable to reduce the determination of the bromide ion to the measurement of bromate. In this case the equivalent weight of the bromide ion is the lowest, thus slight amounts can also be determined very accurately. On carrying out the oxidation with chlorine the estimation has further advantages:

a) The oxidation by means of chlorine can be performed readily, its excess can be easily removed, and in the course of the oxidation no products form interfering with the procedure.

b) Even large amounts of the chloride ion do not either interfere with the determination.

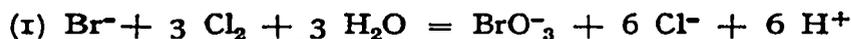
c) On using this method we meet with the least disturbances, thus their elimination is greatly simplified.

The determinations of bromide — based on oxidation with chlorine — hitherto reported in the literature can be characterized briefly as follows: The basic method by means of boric acid-alkali buffer was elaborated by VAN DER MEULEN¹. Independently of the latter author one of us (SZABÓ)² carried out the oxidation of bromide in the presence of potassium hydrocarbonate. D'ANS AND HÖFER³ used primary and secondary phosphate as buffer. Their experiments were checked by KOLTHOFF AND YUTZY⁴. WILLARD AND HEYN⁵ employed an acetate buffer, ALICINO, CRICKENBERGER AND REYNOLDS⁶ sodium hydroxide phosphate. DOERING's⁷ work ought also to be mentioned, he adjusted the medium by addition of calcium carbonate.

The analyses carried out with the methods mentioned above did not always give satisfactory results. It seemed reasonable to reinvestigate the exact conditions of the oxidation of bromide in order to be able to work out a procedure which can be satisfactorily applied.

The authors of the enumerated methods do not furnish particular data concerning the oxidation steps of bromide ion, whereas this is of fundamental significance also from the analytical point of view. At any rate the equation undoubtedly reveals the dependence of the oxidation upon the pH.

References p. 216.



On carrying out approximative calculations — utilizing the oxidation potentials — it can be shown, according to the above equation, that in a medium of $\text{pH} = 0$, the conversion ratio is

$$\frac{[\text{Br}^-]}{[\text{BrO}_3^-]} = 1.3 \cdot 10^{-1}, \text{ at } \text{pH} = 4 \quad 1.3 \cdot 10^{-25} \text{ and} \\ \text{pH} = 8 \quad 1.3 \cdot 10^{-49}, \text{ respectively.}$$

However, the brutto change illustrated in equation (1) does not interpret the fact that the decrease of the hydrogen ion concentration increases the rate of the bromate formation and its total amount, only till a certain value of pH is attained, while it exerts inhibiting effect in the case of the pH values exceeding 9.6. The purpose of this paper is to investigate this problem by virtue of experimental facts.

On oxidation of bromide two main steps can be distinguished¹². In the course of the first one bromide is converted on the action of chlorine — without liberating bromine — to hypobromite, or bromine chloride respectively, further oxidation only taking place in the second step.

The experiments of FARKAS AND LEWIN⁸ demonstrate unequivocally that in an alkaline medium exceeding $\text{pH} = 9.6$ bromate does not at all form. The authors mentioned in the introduction suggest — if also not in complete agreement — that a medium of $\text{pH} 5-8$ is the most favourable for the formation of bromate. According to our experiments a range of 6.5-7.5 pH was found to be the most suitable for the first step of the oxidation of bromide. In this case quantitative oxidation takes place in 20-50 min. In order to establish these conditions the experiments were set up in the following manner. In tests 1, 2 and 3 (Table I) 50 ml of a buffer solution of great capacity were added to the weighed potassium bromide as well as the chlorine water needed for the oxidation. It was heated for the time recorded on the table at 80°C and on cooling the pH controlled and the formed bromate titrated. There was no deviation in the pH before and after the treatment of the test.

Experiment 4. To the sample containing bromide and chlorine water 1 g borax and 1 g potassium bicarbonate was added. On instantaneous measuring of the pH it amounted to 6.1, and 5 minutes later to 6.7. After heating for 10 min the alkalinity increased, owing to the conversion of potassium bicarbonate to carbonate, to $\text{pH} = 9.64$.

By increasing the alkalinity of the medium somewhat, but in no case above $\text{pH} = 9$ the time of oxidation cannot be diminished.

Whereas, on increasing the alkalinity of the medium after the first period of the

References p. 216.

TABLE I
THE FORMATION OF BROMATE AS THE FUNCTION OF TIME AND pH

Exper.	Taken Br mg	Oxidation		Found Br mg
		time min	subsequently measured pH	
1.		5	3.0	0.927
		"	5.40	16.160
		"	6.03	16.29
		"	6.53	16.301
2.	21.783	5	6.3	17.112
		50	6.3	21.656
3.		5	7.4	18.64
		10	7.4	20.66
		15	7.4	21.19
4.		5	6.7	17.83
		10	9.64	21.71

oxidation to pH = 9.6, the time of the bromate formation diminished to half of the former, to 10-15 min.

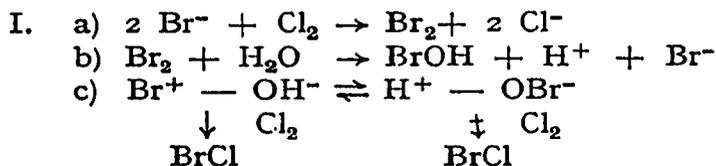
On cooling the sample after the first step of the oxidation had been completed further bromate formation could not be observed, even after several hours had elapsed.

TABLE II

Exper.	Temp.	Taken Br mg	Time min	Found Br mg
1.	+80		5	4.16
2.	"		"	4.32
3.	-6	12.26	275	3.68
4.	"		"	4.07

Procedure of the experiments 3, 4: after treating the sample as in experiments 1 and 2, it was cooled to -6°C and kept at this temperature for 3¹/₂ hours after which the excess of chlorine was removed and the formed bromate determined.

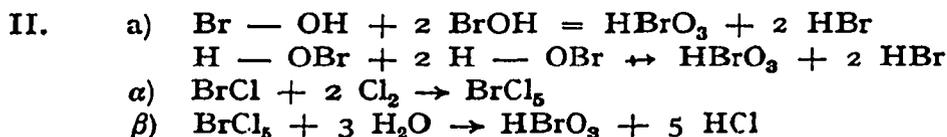
Considering these facts the first step of the oxidation of bromide may consist of the following processes:



References p. 216.

Reaction I a) is independent of the pH, whereas steps b) and c) depend to a great extent on the hydrogen ion concentration. This points to the fact of the possibility of the formation of two electromer hypobromous acids corresponding to the medium. These assumptions are supported by the observations of FÖRSTER AND JORRE⁹, as well as by the spectroscopical investigations of SCHÄFER¹⁰. Furthermore, it seems very probable that only one of the electromers enables the formation of bromate. The observation that on the addition of chlorine, liberation of bromine does not take place, is helpful for reaching a decision as to which of the electromeric forms can exist below pH = 9.6. The absence of free bromine indicates that it is immediately converted to bromine chloride on the action of the excess chlorine present. On examining the bromine chloride, a Br⁺ — Cl⁻ polarity was established, thus the transitorily formed Br⁺ — OH⁻ must also show a corresponding polarity.

Thus the second main step of the oxidation, the formation of bromate, may be built up as follows:



It is known that reaction I b), the hydrolysis of bromine, is very slow although the modification of its rate in the presence of chlorine and chloride ions has not yet been examined. Therefore reaction II a) can also be assumed.

Our experience is that an increase in the pH after the first oxidation step raises the rate of the quantitative bromate formation thus rendering probable reactions II α) and II β) as contrasted with the disproportionateness. This is strongly supported by the fact that bromate formation in a suitable medium does not require a high chloride concentration. However, if the medium is already initially more alkaline than in the most favourable case (*e.g.* pH = 8.5 - 9.0) a quantitative bromide conversion may still be attained in the presence of a high chloride concentration, whereas in its absence this does not take place. The accelerating effect of the temperature on the bromate formation supports the running down of both reactions (II α) and II β). The same holds good concerning the results listed in Table II.

According to the facts mentioned above it can be seen that the first rapid and complete oxidation step — consisting of the formation of hypobromous acid or bromine chloride — necessitates a medium of pH = 6.5 - 7.5, whilst a subsequent slight alkalizing of the initial, almost neutral medium, leads readily to the end product, to bromate, showing clearly that a stable buffer system in the solution is not desirable. Thus namely only either the initial lower pH or the final higher one can be adjusted. This apparently difficult task can be solved by means of potassium bicarbonate. The initial application of 1 g of potassium bicarbonate in a

References p. 216.

volume of 60-100 ml produces $\text{pH} = 7 - 7.5$ since the chlorine water employed always containing hydrochloric acid diminishes the alkalinity. In the course of the oxidation carried out under heating the potassium bicarbonate is converted to carbonate, thus the alkalinity increases. After one hour the pH of the medium increases to about 10-10.5. As the time of oxidation does not last longer than half an hour, the final alkalinity never exceeds a $\text{pH} = 8.5-9.5$. This is the advantage of employing potassium bicarbonate.

Potassium bicarbonate can, however, also neutralize the acid contained in the chlorine water added to the sample. This takes place under vigorous effervescence, and the evolution of carbon dioxide — causing bumping — may lead to a negative error. This can, however, easily be overcome by adding borax, in addition to potassium bicarbonate, to the solution. The former neutralizes the acid, consequently carbon dioxide hardly forms. The use of borax has yet another significant advantage at the initial adjustment of the pH due to the fact that, on neutralizing the acid contained in the chlorine water, boric acid forms, diminishing the pH and increasing the concentration of the hypochlorous acid which is the chief oxidizing agent. However, the borax-boric acid system has not got the capacity to inhibit the desired alkalizing of the medium by formation of carbonate.

In the light of these considerations let us now discuss VAN DER MEULEN'S procedure, in which the pH of the medium is initially 10.5, diminishing after the addition of boric acid to 8.5. Thus just the reverse of the favourable conditions outlined above is induced, inhibiting a smooth oxidation. However, by the prolongation of the reaction and by increasing the excess of the oxidizing agent, good results may after all be achieved. This is to a great extent promoted by the presence of a high sodium chloride concentration shifting the equilibrium I.c. in the direction of the bromine chloride formation, although, from the point of view of the pH the conditions are not favourable.

But a high salt concentration interferes with the indication of iodine-starch at the titration of the bromate. The delay of the end point is rather a result of the high salt concentration than of the slackness of the bromate-iodide reaction assumed by VAN DER MEULEN, as this delay also occurs in the case of the bromate and iodide reaction having sufficient time to run down. To overcome this difficulty he suggested the use of molybdate as catalyst, which certainly accelerates the reaction giving, however, rise to another source of error, owing to the chlorate formed as by-product of the oxidation. Molybdate accelerates the reaction of chlorate-iodide in the same manner as that of bromate-iodide causing a positive error. This was termed chlorate error, and depending on the rate of the titration it may amount to 0.5-1.0 per cent. About the same holds for the other methods which will hence not be discussed in detail in this paper.

Let us now deal briefly with the quantity and quality of the oxidizing agent. Considering that the oxidation is a complex and branching process it undergoes several reactions leading to the loss of a part of the oxidizing agent (*e.g.* the

References p. 216.

formation of chlorate, the thermal decomposition of hypochlorous acid, etc.), necessitating the employing of appreciably larger amounts of chlorine than the theoretical. Thus it seems advisable to introduce the chlorine dissolved in water into the reaction mixture. Chlorine water can be prepared most quickly from pure substances by introducing chlorine gas into distilled water cooled to 0°C , having previously bubbled it through concentrated sulphuric acid and distilled water. As a suitable flow rate the preparation of 1 litre of chlorine water — sufficient for about 30 analyses — lasts approximately 12-15 min. On introducing the chlorine, yellowish-white flocks of chlorine hydrate are precipitated which deposit on the bottom of the vessel. Before use, to ensure an equal distribution, it is shaken, and the chlorine water containing the chlorine hydrate pulp is added to the sample. The chlorine water prepared in this way has the great advantage that its chlorine content is considerably higher, and that, owing to the presence of chlorine hydrate, it can be stored at 0° for a fairly long time.

Using a 80-100 fold excess of chlorine, and a suitable medium the reaction takes place in 10-15 min quantitatively. An increase in temperature accelerates the reaction, but it is limited by the thermosensitivity of the bromate and the escaping of chlorine. The sample, the initial volume of which is 50-60 ml, is placed on an asbestos wire gauze into a beaker and condensed in 20 min to 10-20 ml. During this time the reaction is completed and the greater part of the excess chlorine expelled. The residual chlorine can be removed by means of phenol. Though phenol does not instantaneously bind the chlorine, however, under the prescribed experimental conditions, chlorine can no more be observed 5 min after its addition even in traces. A practical device should still be mentioned. Subsequently to the binding by phenol, interfering oxidizing components *e.g.* chlorite, may still be in the solution. Their indirect removal by phenol is carried out as follows: potassium iodide is added to the still alkaline solution, before beginning the iodometric measurement of bromate. In this case the chlorine present possibly not yet bound, hypochlorous acid and chlorite liberate equivalent iodine which is instantaneously bound by phenol, thus ensuring their certain removal. It should be remarked that the phenol-iodine reaction does not later cause any errors owing to phenol only binding iodine in alkaline and not in acid medium. Whereas the bromate-iodide reaction only takes place in acid medium.

It is essential to avoid the employment of molybdate to eliminate the chlorate error.

Summarizing the enumerated facts the procedure is as follows: A mixture consisting of borax 1.0 g and potassium bicarbonate 1.0 g is introduced into the bromide solution (0.1-25.0 mg Br) to be examined and, depending on the bromide quantity, the required amount of chlorine water containing chlorine hydrate is added. Even for the maximum quantity of bromine 35-40 ml of chlorine water are sufficient. The sample is heated on an asbestos wire gauze over a gentle flame till vigorous evaporation sets in. The heating is continued till the volume of the

References p. 216.

sample is condensed to 10-20 ml. After removing from the flame it is diluted with 50 ml distilled water, the chlorine remaining in the sample is bound by the addition of a phenol solution (5 per cent). After the elapse of 6 min, during which the beaker is covered with a watch-glass, about 1 g of potassium iodide is added to the solution which is dissolved by shaking. When the potassium iodide is dissolved the sample is acidified by addition of 20 ml of 20 per cent sulphuric acid and after the elapse of further 5 min the liberated iodine is titrated with 0.05 or 0.01 *N* thiosulphate, respectively, using starch as indicator.

The results of the analyses carried out according to the above prescription are summarized in Table III.

TABLE III

No	Taken Br mg	0.05 <i>N</i> Thio- sulphate ml	Found Br mg	Average Br mg	Difference	
					mg	%
1.	1.380	2.072	1.380	1.368	-0.012	-0.87
2.	"	2.036	1.356			
3.	2.759	4.054	2.70			
4.	"	4.108	2.736	2.748	-0.011	-0.40
5.	"	4.184	2.786			
6.	"	4.148	2.763			
7.	5.519	8.23	5.482	5.517	-0.002	-0.04
8.	"	8.40	5.594			
9.	"	8.23	5.482			
10.	"	8.27	5.510			
11.	13.80	20.53	13.68	13.72	-0.08	-0.58
12.	"	20.58	13.72			
13.	"	20.62	13.74			
14.	"	20.62	13.74			
15.	27.598	41.16	27.413	27.404	-0.194	-0.67
16.	"	41.20	27.44.			
17.	"	41.16	27.413			
18.	"	41.08	27.35			

Numerous experiments have been carried out to establish the accuracy of our procedure in the presence of different foreign ions. The results are summarized as follows:

1. The Ag, Cd, Sn, Al, Ca, Sr, Ba, Mg, Na, K, Li, Rb, Be, La, Y, Te, Cs, W, Ce, Bi, SO_4^{-2} , SiO_3^{-2} , PO_4^{-3} , BO_3^{-3} , F^- , Cl^- , CH_3COO^- , $\text{S}_2\text{O}_3^{-2}$ ions do not interfere with the process. It should be noted that neither the Ce(IV) nor Bi ions interfere with the reaction owing to the following reasons. The oxidizing potential of the Ce(IV) ion approaches that of permanganate yet it does not interfere, since in the weak alkaline medium only slightly soluble cerium dioxide or basic cerium salts form which do not dissolve; thus not liberating iodine on acidification.

The only difficulty arising from the presence of bismuth is the formation of potassium bismuth iodide. The reddish-yellow colour of this compound can be the

References p. 216.

source of errors as the solution keeps its yellowish-brown colour also after the titration of iodine. If, however, the starch solution is introduced in time the estimation may be carried out accurately as the change of colour from blue to orange-red exhibits a sufficient contrast.

2. Pb, Fe, As, Sb, Co, Ni, Mn, Cr, V, iron(II) — and iron(III) — cyanide cause positive errors. These ions reach through the reaction with chlorine a higher state of oxidation, thus liberating iodine when the titration is carried out.

3. Negative errors are caused:

a. by the presence of a great amount of $S_2O_3^{2-}$, S^{2-} , SO_3^{2-} , CNS^- , oxalate, tartrate ions and other organic substances due to their consumption of chlorine.

b. by increasing the alkalinity: OH^- , CO_3^{2-} ,

c. by: Cu, Fe, Hg, Mo.

The effect of the latter 4 ions must be dealt with in detail.

The effects of the Cu and Fe ions correspond. Their presence even in very insignificant amounts decomposes HOCl and HOBr¹¹. They also increase the rate of the chlorine hydrolysis to a great extent. The chlorate forming in the course of the hydrolysis causes a positive error, the chlorate error. However, the bromate formed during the oxidation is no more decomposed by either iron or copper. Under certain conditions iron may also be the source of positive errors. On the one hand, by catalyzing the chlorate-iodide reaction resulting in an excess of iodine. On the other hand, in the presence of iron, phenol does not only bind the chlorine by substitution (trichlor-phenol), but is also itself oxidized by chlorine. The oxidized phenol derivative is probably a compound belonging to the quinone type liberating iodine from potassium iodide.

In the presence of the Hg and Mo ions a negative error, amounting to 10-15 per cent, could be observed. On the basis of our experiments it can be assumed that these ions do not exert any effect on the actual oxidation process. The source of the negative error is due to the catalytic decomposition of the already formed bromate. This could also be demonstrated by a similar treatment of weighed out amounts of bromate. This was, however, not investigated in detail.

1. By treatment with soda, all ions with the exception of lead and the cations of class II are precipitated. After having neutralized the filtrate the cations of class II — with the exception of arsenic and molybdenum — are removed. The precipitate is filtered, well washed, and from the filtrate, acidified with hydrochloric acid, the lead, arsenic and molybdenum are separated by introducing hydrogen sulphide gas. If in the starting material chromium and manganese are present as chromate and manganate respectively, they must first be reduced by means of sulphur dioxide.

2. An easier method, causing less trouble, requiring, however, about the same time, is the liberation of bromine from bromide by means of potassium permanganate and distilling it into an alkaline solution. This alkaline distillate is neutralized with hydrochloric acid and treated according to the procedure.

References p. 216.

SUMMARY

The oxidation of bromide effected by chlorine was investigated and it was established that it runs down in two steps. In the course of the first step in a medium of pH between 6.5-7.5, $\text{Br}^+ - \text{OH}^-$ electromer hypobromous acid forms. This BrOH electromer leads, on further oxidation, to the product BrCl_3 furnishing on hydrolysis bromate. In a medium in which the pH is adjusted to about 8.5-9 the hydrolysis takes place at such a rate that it can be used for analytical purposes.

On the basis of these investigations the determination of the bromide ion amounting to 0.1-25 mg can be carried out rapidly with an error of a few tenths of one per cent. Besides the oxidizing substances only iron, copper, mercury and molybdenum ions interfere with the procedure. The interfering ions can either be eliminated by treatment with soda and hydrogen sulphide, or by the distillation of bromine.

RÉSUMÉ

Les auteurs étudient l'oxydation des bromures par le chlore. Cette réaction semble avoir lieu en deux stades: au pH 6.5-7.5, il se forme d'abord $\text{Br}^+ - \text{OH}^-$ (électromère de l'acide hypobromeux). Ce BrOH conduit ensuite à BrCl_3 donnant un bromate par hydrolyse. Au pH 8.5-9, l'hydrolyse est très rapide, ce qui permet une application analytique.

On peut ainsi doser rapidement 0.1 à 25 mg de Br^- avec une erreur de quelques 0.1 %. A part les oxydants, seuls Fe, Cu, Hg et Mo gênent. On peut séparer les ions gênants par la soude et l'hydrogène sulfuré. On peut également séparer le brome par distillation.

ZUSAMMENFASSUNG

Die Oxydation der Bromide mit Chlor wurde untersucht. Festgestellt wurde, dass sie in zwei Stufen verläuft. In der ersten Phase wird bei pH 6.5-7.5 $\text{Br}^+ - \text{OH}^-$ (elektromere Form der unterbromigen Säure) gebildet. Dieses wird weiter oxydiert und gibt BrCl_3 und, nach Hydrolyse, Bromat. Bei pH 8.5 bis 9 geht die Hydrolyse so rasch vor sich, dass sie in der Analyse angewendet werden kann.

Auf diese Weise können 0.1 bis 25 mg Br^- mit einem Fehler von einigen % bestimmt werden. Mit Ausnahme der Oxydationsmittel stören nur Eisen, Kupfer, Quecksilber und Molybdän. Die störenden Ionen können mit Hilfe von Soda oder von Schwefelwasserstoff abgetrennt werden. Man kann aber auch die Bromide oxydieren und das Brom abdestillieren.

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