

Kinetic Investigation of the Decomposition of Bromite

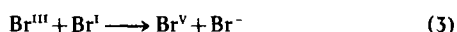
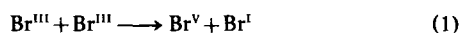
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The rate of decomposition of bromite has been studied as a function of the hydrogen and bromite ion concentrations. The order of the reaction with respect to H^+ is close to 2 at pH values between 6.26 and 8.55, and approximately 1 at pH values between 3.56 and 6.26. Calculation of the reaction orders with respect to bromide as well as to bromite and to the hydrogen ion for the reaction in the presence of an excess of bromide gave values very close to unity. The products resulting from the decomposition are bromide, bromate, bromine and hypobromite. The decomposition of bromite is strongly accelerated by bromide and hypobromite. A reaction mechanism proposed by P. Engel, A. Oplatka and B. Perlmutter-Hayman has been used to discuss the present results. Below pH 6.26, the presence of appreciable quantities of bromine can be detected at an electrode with periodic renewal of the diffusion layer. Under these conditions, the decomposition of bromite probably involves formation of $HBrO$ which reacts with bromide and hydrogen ions to form bromine. In this case the greater part of the reaction after the first few moments would proceed via a cycle involving bromide ions.

Introduction

The decomposition of bromite into bromate and bromide has been the subject of a number of studies. Chapin¹ found that the decomposition rate increases with the hydrogen ion concentration, and that this reaction is second order with respect to the bromite concentration. In the presence of hypobromite, the stability of bromite solutions is greatest around pH 13. P. Engel, A. Oplatka and B. Perlmutter-Hayman² found that bromite solutions at pH 8.5 decompose at a rate that is independent of the ionic strength in the range 0.29–0.58 M. The decomposition rate increases with decreasing pH and the reaction is second order with respect to the bromite concentration. The reaction also increases its own rate by increasing the bromide concentration. In the presence of an excess of bromide it is first order with respect to the bromite concentration. According to these authors, the decomposition involves three reactions:

(1) R. M. Chapin, *J. Amer. Chem. Soc.*, 56, 2211 (1934).

(1) is the slowest of these reactions, while (3) is the fastest. All this work has been performed using bromite solutions prepared with Chapin's method by which a crystalline salt can not be obtained. All the measurements of the quoted authors have been made by means of titrations, often using difference methods or back titrations. Finally the concentration range of the various reactants was limited because of the high reaction rate and of the available analytical methods. It is now possible to prepare pure crystalline barium bromite³ and sodium bromite as well. A direct polarographic method for bromite as well as bromate, hypobromite and bromine has been devised and controlled.⁴ Stopped-flow methods permit to follow the kinetics of very fast reactions with satisfactory accuracy.

For these reasons we deemed it useful to re-examine the decomposition of bromite in view of determining with certainty the reaction products and of widening the concentration range of the various reactants to a considerable extent. Particularly we thought it interesting to explore the field of pH lower than 6. In this way the mechanism proposed by Engel, Oplatka and Perlmutter-Hayman can be tested and corrected if necessary. Some informations can also be achieved on the pK of bromous acid.

Experimental Section

The bromite was prepared as described by Kircher and Periat^{3,4} from barium hydroxide and bromine, the product obtained being converted into the sodium salt by exchange with slightly more than the stoichiometric quantity of sodium sulphate. The resulting solution was stored at about 0°C and titrated periodically with arsenic trioxide and with potassium iodide and sodium thiosulphate to find its total oxidizing capacity. A polarogram⁴ was then made for the test solution, and the purity of the product was confirmed by the appearance of a single reduction wave. The solution remained unchanged for several months.

The hypobromite was prepared by reaction of sodium hydroxide with bromine, and stored at -20°C. The product was repeatedly crystallized from 0.1 M sodium hydroxide solution and titrated with potassium iodide and sodium thiosulphate. The absence of bromite and bromate was verified as above.

(2) P. Engel, A. Oplatka and B. Perlmutter-Hayman, *J. Amer. Chem. Soc.*, 76, 2010 (1954).(3) R. Kircher and R. Periat, *Ger. Patent*, 107, 6096 (Feb. 25-1960).(4) F. Pergola, G. Raspi and A. Massagli, *J. Electroanal. Chem.*, 22, 175 (1969).

The other chemicals were Carlo Erba RP products. To follow the kinetics of the decomposition of bromite, a series of buffer solutions having pH values between 3.56 and 8.55 were prepared. Acetic acid and sodium acetate were used for the range 3.56-4.89, monosodium phosphate and disodium phosphate for the range 5.33-7.26, and monosodium phosphate and borax for the range 7.41-8.55. The pH measurements were carried out with a Metrohm E 388 potentiometer. The solutions used were prepared from 0.5 M sodium perchlorate and the buffer salts to give a final ionic strength of 0.6 M.

The kinetic measurements were carried out at $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$. The decomposition reaction was followed to a maximum conversion of 75-80%. Various methods were used to measure the reaction rate, depending on the half life. For half lives, $t_{1/2}$, greater than 15 minutes, the rate was determined by the polarographic method described by D. Cozzi *et al.*,⁵ using an electrode with periodic renewal of the diffusion layer; this method has been shown to be suitable for analytical determinations.⁴ The apparatus used was a Metrohm Polarecord E 261. For $t_{1/2}$ greater than 0.5 minute, the absorption at 298 m μ , corresponding to the bromite absorption band, was measured with a Uvispek Spectrophotometer, and for $t_{1/2}$ less than 0.5 minute, a Durrum stopped flow apparatus was used. Where possible, measurements were carried out by two different methods, and the results were found to agree. Only the polarographic method was used for measurements carried out in the presence of hypobromite and bromide, since the hypobromite absorption band was superimposed on the bromite band, while bromide led to the formation of bromine, which also absorbs in the same region as bromite. With the polarographic method, on the other hand, separate reduction waves were obtained for the various species.

Results

The decomposition of bromite is apparently a first order reaction in many cases. A plot of the logarithm of the concentration against time gives a straight line for 50% decomposition (see Figure 1). The initial velocity V_0 was calculated by multiplication of the slope of the line by the initial bromite concentration. The order of the reaction with respect to bromite was calculated for pH 7.09, the bromite concentration being varied between $7.5 \times 10^{-4} M$ and $1.25 \times 10^{-2} M$. Line (a) in Figure 2 shows a plot of $\log V_0$ against $\log C_0$, which gives $n=1.75$. The fact that during a single run the order appears to be 1 is clearly due to some other change taking place during the reaction. A plot of $\log V_0$ against the pH gives line (b) in Figure 2. The order with respect to H^+ is 1.87 between pH 8.55 and pH 6.26, whereas it is a value of 0.9 between pH 3.56 and pH 6.26. A series of measurements was then carried out in the presence of bromide at concentrations between $3.75 \times 10^{-3} M$ and $3.75 \times 10^{-1} M$ and at pH 7.41. The reaction rate was found to increase considerably. The

orders with respect to bromite and to H^+ in the presence of an excess of bromide were calculated for bromite concentration between $7.5 \times 10^{-4} M$ and $1 \times 10^{-2} M$ and for pH values of 7.09 to 8.06. Subtraction of the rate found in the absence of bromide from that found in its presence gives the rate of the simultaneous reaction of bromite with bromide.

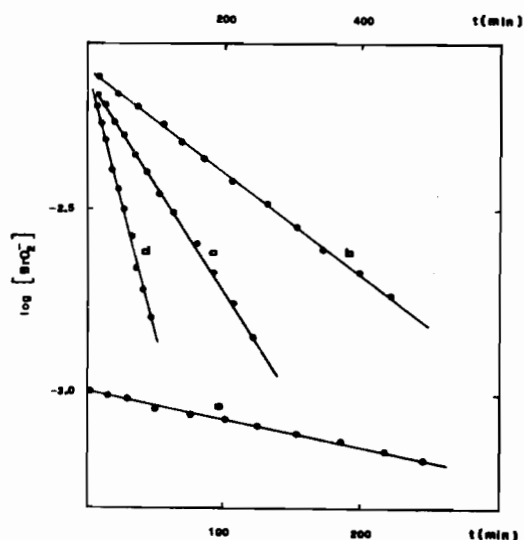


Figure 1. Decomposition of bromite ion alone or in the presence of bromide ion at several pH values:

- (a) $[\text{BrO}_2^-] = 1 \times 10^{-3} M$; pH=7.09
 (b) $[\text{BrO}_2^-] = 7.5 \times 10^{-3} M$; $[\text{Br}^-] = 3.25 \times 10^{-2} M$; pH=7.41
 (c) $[\text{BrO}_2^-] = 7.5 \times 10^{-3} M$; $[\text{Br}^-] = 7.5 \times 10^{-2} M$; pH=7.41
 (d) $[\text{BrO}_2^-] = 7.5 \times 10^{-3} M$; $[\text{Br}^-] = 7.5 \times 10^{-2} M$; pH=7.09

The method employed in the measurements in the polarographic one. Curves (a) and (d): left and upper scale. Curves (b) and (c): left and lower scale.

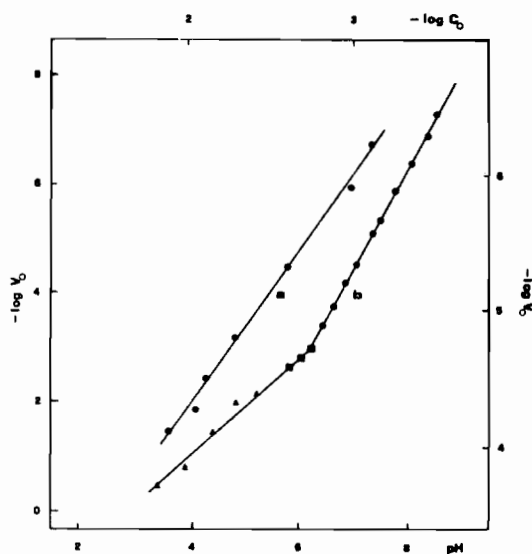


Figure 2. Dilogarithmic plots of initial rates of decomposition of bromite ion: (curve a) as function of bromite concentration, pH=7.09; (curve b) as function of pH, $[\text{BrO}_2^-] = 7.5 \times 10^{-3} M$. The measurements are carried out with the methods: polarographic+spectrophotometric (\bullet); spectrophotometric (\blacksquare); stopped flow (\blacktriangle). Curve (a): right and upper scale; curve (b): left and lower scale.

(5) D. Cozzi, G. Raspi and L. Nucci, *J. Electroanal. Chem.*, 12, 36 (1966).

Lines (a), (c), and (b) in Figure 3 show the logarithm of the initial rate as a function of the logarithm of the bromide, bromite and hydrogen ion concentrations. The points give straight lines having slopes of 1.09, 0.92, and 1.16 respectively. In most cases, the rate in the absence of bromide was negligible in comparison with the rate with bromide in excess.

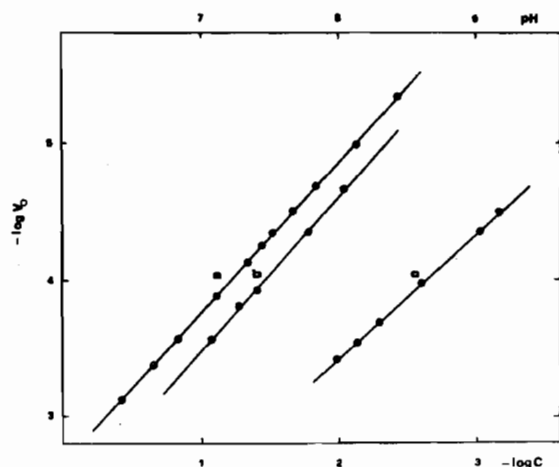


Figure 3. Dilogarithmic plots of decomposition rates of bromite ion in the presence of excess of bromide: (curve a) against bromide ion concentration, $[\text{BrO}_2^-] = 7.5 \times 10^{-3} M$, $\text{pH} = 7.41$; (curve b) against pH , $[\text{BrO}_2^-] = 7.5 \times 10^{-3} M$, $[\text{Br}^-] = 7.5 \times 10^{-2} M$; (curve c) against bromite concentration, $[\text{Br}^-] = 7.5 \times 10^{-2} M$, $\text{pH} = 7.09$. Curves (a) and (c): left and lower scale; curve (b): left and upper scale. The measurements are carried out with the polarographic method.

Table I.

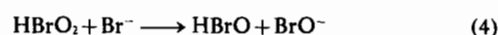
pH	Initial rate of bromite decomposition in a hypobromite free solution	Initial rate of bromite decomposition in a $1.2 \cdot 10^{-2} M$ solution of hypobromite
	$[\text{BrO}_2^-] = 7.5 \times 10^{-3} M$	$[\text{BrO}_2^-] = 7.5 \times 10^{-3} M$
	$V_0/M \text{ min}^{-1}$	$V_0/M \text{ min}^{-1}$
7.8	1.5×10^{-6}	2.46×10^{-4}
8.06	4.95×10^{-7}	1.13×10^{-4}
8.36	1.36×10^{-7}	6.25×10^{-5}
8.55	5.69×10^{-8}	2.58×10^{-5}

Another series of measurements was carried out in the presence of hypobromite, which greatly accelerates the disappearance of the bromite. This can be seen from Table I, which shows the initial rates for $7.5 \times 10^{-3} M$ bromite solutions containing hypobromite $1.2 \times 10^{-2} M$ and for solutions that are initially free from hypobromite. The reaction products obtained from the various solutions examined differ considerably. Bromate and bromide only are obtained from solutions that were initially free from bromide and hypobromite and at $\text{pH} > 7.2$; at low pH values (< 7.2), hypobromite and bromine are also found and their concentration increases with decreasing pH. In the presence of an excess of bromide, the decomposition products included hypobromite, as well as a large quantity of bromine, at $\text{pH} \leq 7.4$, in addition to the bromate that is always present. In the presence of

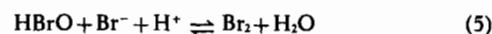
hypobromite, bromine is obtained at $\text{pH} \leq 7.6$, though in concentration lower than those found in solutions containing bromide.

Results and Discussion

Since appreciable quantities of bromide are formed as a final product in the decomposition of bromite, it is clear that completely significant results can be obtained only if the reaction is carried out in the presence of such an excess of bromide that the quantity formed is negligible for all practical purposes. This is so in the reactions to which lines (a), (b), and (c) in Figure 3 refer; the order found in this case, with respect to bromide as well as to bromite and to H^+ , is substantially equal to 1. In the reaction scheme proposed by P. Engel, A. Oplatka and B. Perlmutter-Hayman,² therefore, the rate observed corresponds to the rate of equation (2), which can be expressed explicitly in the form:



There are reasons to think that HBrO_2 is practically completely dissociated in the pH range in question (see below), and this explains the order of 1 with respect to the hydrogen ions. The subsequent reaction of the hypobromite with bromite is much faster, as is shown by the specific experiments carried out. The reaction leading to the formation of bromine:



should not be of great importance, in view of the low H^+ concentration.

The rate of disappearance of bromite as measured for solutions that were initially free from bromide is that due to the sum of the various reactions with all the species present in the solution. However, since the measurements always related to the first part of the reaction and the quantities of bromide and of hypobromite present are always rather small, it may be assumed that for solutions that initially contain neither bromide nor hypobromite, the rates approximately correspond to the initial V of the reaction. From the fact that an order of 1.75 is found with respect to bromite and 1.87 with respect to H^+ at $\text{pH} > 6.26$ in the absence of bromide, it is concluded that the reaction rate under these conditions can be expressed by the equation:

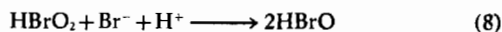
$$V = kC_{\text{H}^+}^2 + C_{\text{BrO}_2^-}^2 \quad (6)$$

and that the deviations of the orders from 2 are due to the unavoidable influence of the reaction products. Reaction (1) of the scheme given by P. Engel, A. Oplatka and B. Perlmutter-Hayman can therefore be expressed as follows:



The subsequent reaction of hypobromous acid (or BrO^-) with BrO_2^- (or HBrO_2) to give bromate and bromide is again rather faster, and so does not affect the measured orders. The second order dependence on the H^+ concentration extends down to a pH of 6.26,

after which there is a fairly sudden change to an order of about 1. This indicates that the pK of bromous acid must be around 6, a more precise value can not be obtained from the present measurements since the change in slope is probably less sharp than it appears from Figure 2. On the other hand, it may seem surprising at first that the order with respect to H^+ does not fall to zero, as would be expected from equation (7). However, when the pH falls below 6.26, appreciable quantities of bromine can be detected with an electrode with periodic renewal of the diffusion layer. This indicates that bromide ions must be present for a considerable part of the reaction. In measurements by the stopped flow method, on the other hand, it is not possible to ignore the presence of appreciable quantities of bromide ions. In view of the fairly short time used, therefore, it is probable that in addition to equation (4), the decomposition of bromite under these conditions also involves a reaction of the type:



where hypobromous acid can react with bromide and

H^+ to form bromine. In this case the major part of the reaction, after the first few moments, would proceed by a cycle involving the bromide ion. The reaction of bromide and bromite should, according to reaction (4) and (8), obey a law of the type:

$$v = k_1[HBrO_2][Br^-] + k_2[HBrO_2][Br^-][H^+]$$

This corresponds to an order of 1 with respect to hydrogen ions both when $HBrO_2$ is dissociated and $[H^+]$ is low, and when $HBrO_2$ is not dissociated and $[H^+]$ is high. A complete treatment should take into account the initial reaction (7) and the successive steps as well. However, the results obtained with the stopped flow apparatus are not sufficiently accurate to be applied to the rather complex differential equation that takes into account the catalytic action of the reaction products.

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