

REACTIONS IN FUSED SALTS. V.*

REACTION OF BROMATE IONS WITH BROMIDE IONS
IN MELTS OF ALKALI NITRATES

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The kinetics of oxidation of bromide ions by bromate ions in fused alkali nitrates has been studied in the presence of barium ions and carbon dioxide. The dependence of the reaction rate on the flow rate of CO_2 through the melt was determined in the temperature interval 260–290°C and a probable reaction mechanism has been suggested.

Reaction of bromate ions with bromide ions proceeds in the medium of fused alkali metal nitrates under the formation of oxygen as reaction product¹. Bromide ions can be oxidized by bromate ions in the presence of nitrates only after acidification of the melt, *i.e.* on adding acceptors of oxide ions. Zinc, nickel, copper and cobalt^{2,3} cations and bichromate anions^{4,5} were used as oxide ions acceptors. Bichromate ions were also applied when studying the oxidation of chloride ions by chlorate ions^{6,7}.

It was of interest to verify the application of carbon dioxide as oxide ions acceptor in the oxidation of bromide ions by bromates in the medium of fused nitrates.

EXPERIMENTAL

All chemicals used in the study of the above mentioned reaction were of reagent grade purity and were perfectly dried at higher temperature. The eutectic melt $\text{NaNO}_3\text{--KNO}_3$ was prepared as described earlier⁸. The gases used, nitrogen and in some cases oxygen, were taken from cylinders.

The reaction vessel, represented by a closed glass test tube of 40 mm diameter and 250 mm height was placed in a high-temperature thermostat filled with a mixture of fused alkali metal nitrates. Bath temperature was measured with a mercury thermometer and maintained within $\pm 1^\circ\text{C}$.

The weighings of the components of the reaction mixture were chosen so that its total weight was 60 g, unless otherwise stated. Molar ratio of sodium to potassium ions was always 1 : 1. The reaction mixture formed by ions BrO_3^- , Br^- and Ba^{2+} in an eutectic of sodium and potassium nitrate was prepared by melting the components weighed in appropriate ratio. After bubbling

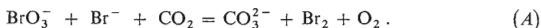
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nitrogen through the melt for 10 min the reaction itself was started by admission of a stream of carbon dioxide (200 ml/min) or carbon dioxide diluted by nitrogen through a thin tube to the bottom of the reaction vessel. The content of bromine in the final leaving gaseous mixture was determined after absorption in potassium iodide solution by titration of the released iodine with thiosulphate or argentometrically, after absorption in sulphite solution. Concentration of bromate ions in the reaction vessel was determined iodometrically in samples taken from the melt.

RESULTS AND DISCUSSION

Preliminary experiments carried out in the absence of barium ions allowed us to find appropriate temperature and concentration intervals for studying the oxidation of bromide ions by bromate ions. It was established that the rate of increase of the concentration of bromine increases with increasing concentration of bromide ions, with increasing partial pressure of carbon dioxide and gas flow, while the formed carbonate ions cause a slow-down of the reaction.

Further experiments were performed so that both bromate and bromide were in excess in comparison to their concentration changes during measurement and the carbonate ions formed in the reaction were removed by addition of barium salt to the melt. The measurements were carried out in the temperature interval 260–290°C where the parallel decomposition of bromate to oxygen does not markedly affect the concentration of bromate ions¹. It was verified in preliminary experiments that oxidation of bromide ions by nitrates does not proceed in the presence of such a weak oxide ion acceptor as carbon dioxide in the presence of barium ions. This was proved by the accordance of the results of both iodometric and argentometric titrations of gaseous reaction products. Consequently, in compliance with previous works, the overall process of bromide ions oxidation can be described by the equation



Substitution of nitrogen by oxygen does not cause any change in the reaction rate and we can therefore assume that oxygen is not formed in a reversible reaction.

With the experimental arrangement used the rate of increase of the concentration of bromine attains, after an initial period, a steady value which does not change further (c. 40 min). The dependence of the rate of bromine formation on the concentration of individual components was followed at constant concentration of the remaining components (Table I). From the experimental values an empirical equation was obtained expressing the dependence of the rate of increase of the concentration of bromine on the concentration of the starting components in the following form

$$r = k' p_{\text{CO}_2}^{0.6} [\text{Ba}^{2+}]^{0.6} [\text{Br}^-]. \quad (I)$$

TABLE I

Dependence of the Rate of Bromine Formation on the Concentration of Reaction Components
Temperature 270°C, flow rate of gas 200 ml/min.

[BrO ₃ ⁻] mol kg ⁻¹	[Ba ²⁺] mol kg ⁻¹	[Br ⁻] mol kg ⁻¹	<i>p</i> _{CO₂} atm	<i>r</i> · 10 ⁵ , mol min ⁻¹	
				exp.	calc.
0.64	0.095	0.517	1.0	0.527	0.533
0.62	0.087	0.679	1.0	0.701	0.690
0.60	0.081	0.855	1.0	0.866	0.822
0.59	0.076	1.101	1.0	0.993	1.013
0.58	0.069	1.179	1.0	1.105	1.018
0.60	0.043	0.655	1.0	0.388	0.433
0.58	0.084	0.639	1.0	0.606	0.618
0.56	0.128	0.628	1.0	0.743	0.760
0.55	0.174	0.614	1.0	0.888	0.874
0.54	0.219	0.601	1.0	0.957	0.963
0.62	0.134	0.646	1.0	0.882	0.839
0.61	0.130	0.639	0.8	0.696	0.714
0.60	0.126	0.631	0.6	0.596	0.583
0.59	0.122	0.623	0.4	0.460	0.442
0.58	0.120	0.618	0.3	0.373	0.362
0.57	0.117	0.613	1.0	0.748	0.711
0.33	0.090	1.094	1.0	0.916	0.856
0.47	0.083	1.062	1.0	0.907	0.934
0.62	0.076	1.030	1.0	0.877	0.967
0.75	0.070	1.000	1.0	0.842	0.968

This equation is valid only in the studied concentration range and yields approximate values of the rate constant $2-4.5 \cdot 10^{-5}$ mol Br₂/min at 270°C and at a flow rate 200 ml/min. The values of the constant *k'* depend on both the flow rate of gas through the melt and on the concentration of bromate ions in the melt in the concentration range 0.02–0.15 mol kg⁻¹. At higher concentrations of bromate ions it is concentration independent.

At *p*_{CO₂} = 0.5 atm, 270°C, [BrO₃⁻] = 0.6 mol kg⁻¹, [Ba²⁺] = 0.13 mol kg⁻¹ and [Br⁻] = 0.6 mol kg⁻¹ the following dependence of *k'* on the CO₂ flow rate (*P*, ml min⁻¹) was found:

<i>P</i>	100	140	180	220	260	300	340
<i>k'</i> · 10 ⁵	2.90	3.38	3.89	4.40	5.00	5.62	6.03

The dependence is linear and for 270°C it can be expressed by the equation

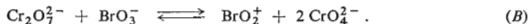
$$k' \cdot 10^5 = 0.0134P + 1.52, \quad (2)$$

where P is the flow rate of gas through the melt in ml/min. The dependence of the reaction rate on the weight of the melt and on the geometrical arrangement of the reactor, i.e. on the height of the melt column and on the test tube diameter was followed too, keeping all concentrations constant. The obtained results can be mathematically described in the form

$$k' = A \cdot h + b \cdot q, \quad (3)$$

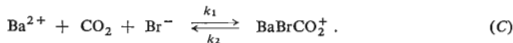
where h is the height of the melt column in the reactor in cm, q is the ring cross section of the reactor in cm² and A and B are constants. Total rate of increase of the concentration of bromine is independent of the weight of the reaction mixture.

We attempted to suggest a mechanism of oxidation of bromide ions by bromate ions in fused nitrates which would explain the experimentally found data. Schlegel⁵ who used in his studies bichromate ions as oxide ion acceptors, assumes that in the reaction of the acceptor with bromate ions

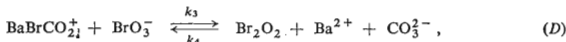


BrO_2^+ ion is formed as intermediate which further reacts with bromide ion to form bromine and oxygen. A similar reaction sequence was also suggested in the studies of oxidation of bromine ions by bromate ions in the presence of some cations as oxide ion acceptors^{2,3}. In preliminary experiments we could verify that barium ions do not act as oxide ion acceptors. We tried to explain the role of carbon dioxide as oxide ion acceptor, similarly as in the case of bichromate ions. However, none of the proposed mechanisms showed a plausible accordance with the experimental data.

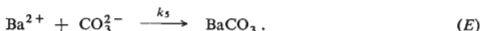
Taking into account the fact that the reaction order with respect to bromate ions is variable, approaching zero with their increasing concentration, we assumed a reaction of bromate with the intermediate, formed in the reaction of other participants



This intermediate is the complex of bromocarbonate ions with barium ions. It reacts in the second step with bromate ions

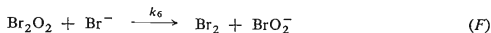


which is followed by a relatively slower precipitation of barium carbonate



This reaction is considered irreversible because of the probable low solubility product of BaCO_3 .

The final step is the irreversible reaction of Br_2O_2 (bromic acid bromide) with bromide ions



leading to the formation of bromine taken off by the carrier gas and of hypobromite ions which undergo a very fast decomposition



The mechanism of oxidation of bromide ions was solved on the basis of Bodenstein's principle under the assumption that BaBrCO_2^+ and CO_3^{2-} ions and Br_2O_2 are unstable intermediates. The solution leads to a final expression for the rate of bromine formation

$$r = [\text{Br}^-] \left\{ \sqrt{a[\text{BrO}_3^-][\text{Ba}^{2+}] \cdot p_{\text{CO}_2} + (1/4)(b[\text{BrO}_3^-] + c)^2} - (1/2)(b[\text{BrO}_3^-] + c) \right\}, \quad (4)$$

where constants a , b , c are products of the rate constants $a = k_1k_3k_5k_6/k_2k_4$; $b = k_3k_5k_6/k_2k_4$; $c = k_5k_6/k_4$. This equation complies with the experimental data, affording an exact explanation of the first order of the reaction with respect to bromide ions, of the nonintegrity of the reaction order with respect to both barium ions and to carbon dioxide and of the variable reaction order with respect to bromate ions.

When correlating the experimental data according to this equation we obtained a small and negative value of constant c and therefore we assumed that its real value was negligibly small and the change of its sign was the result of the scatter of experimental data. For this reason we used a simplified form of Eq. (4) and introduced the following substitutions: $R = r/[\text{Br}^-]$; $x = [\text{BrO}_3^-]$; $y = [\text{Ba}^{2+}] \cdot p_{\text{CO}_2}$. Then

$$R = \sqrt{axy + (1/4)b^2x^2} - (1/2)bx. \quad (5)$$

Using the method of least squares the following optimum values of the constants a and b were found: $a = 2.601 \cdot 10^{-9}$; $b = 5.893 \cdot 10^{-6}$. The theoretical values of the reaction rates were calculated by resubstitution and were compared with the experimental ones (Table I). The mean relative error is less than 5%.

|| We have further followed the dependence of the rate of increase of the concentration of bromine on temperature, however, the obtained data are charged with a considerable error, since the reaction of bromate ions with bromide ions to oxygen, proceeding parallel to the oxidation of bromide ions, has a high activation energy. Nevertheless, the results obtained indicate only a poor dependence of the rate of increase of the concentration of bromine on temperature. This result is in accordance with the found dependence of the rate of increase of the concentration of reaction product on the geometrical arrangement of the reactor and on the flow rate of the gas through the melt.

Similarly as most of the heterogeneous reactions also in this case the retardation effect of the processes of mass transfer on the overall reaction rate can be observed. Consequently, the reaction does not proceed in a kinetic region, but in a region where the rate of increase of the concentration of the product is proportional to the size of the interphase boundary and does not depend on the melt volume. The size of the interphase boundary is defined as the sum of the vertical stable surface area of the melt, given by the diameter of the test tube and the surface area of the gas bubbles. The surface area of the bubbles is given, provided that they are of the same size, by the height of the melt column in the reactor and by the flow rate of the gas, *i.e.* by the number of bubbles per unit time. These conclusions are in agreement with the experimentally found dependences as well as with the low value of the activation energy.

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