

REACTION OF IODATE WITH BROMIDE IONS IN AN EUTECTIC MELT OF LITHIUM AND POTASSIUM BROMIDES

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Kinetics of the reaction of iodate ions with bromide ions in an eutectic melt of lithium and potassium bromide was studied in the temperature range 420–483°C. A probable reaction mechanism was proposed and the differential equation for the rate of decrease of iodate ions was derived. This equation was numerically solved and the results were compared with experimental data. Effect of different factors on the course of the reaction of iodate with bromide ions was investigated.

Within the framework of a systematic study of the reactions of oxoanions of halogen elements we have followed in our preceding communications the reactions of iodate ions with iodide ions in a chloride¹ and nitrate² melt and further the reaction of bromate ions with bromide ions also in a nitrate melt³. Recently, Schlegel and Perrine⁴ have studied the reaction of bromate with iodides in a nitrate melt.

The present paper is a continuation of this series and is devoted to the study of the reaction of iodate with bromide ions in a bromide melt.

EXPERIMENTAL

Apparatus and experimental procedure were the same as in paper¹. Eutectic mixture of LiBr–KBr was prepared from potassium bromide, reagent grade purity, and lithium bromide (both Lachema). Both components were dried, melted and for one hour bubbled with nitrogen, containing small amount of bromine, to oxidize all organic contaminations present in the melt. The melt was then filtered through a 6 cm layer of quartz wool. All other chemicals, of the reagent grade purity, were employed without further purification.

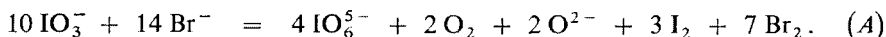
Samples of the melt, taken by a quartz pipette in appropriate time intervals, were analyzed as to their content of lithium orthoperiodate and iodate¹. Concentration of iodide ions was determined in the samples after their reduction with sodium sulphide by means of argentometry with potentiometric indication. Since iodine and bromine were formed in the course of the reaction, some experiments were performed in a closed reagent glass and the evolved gases were absorbed in a solution of sodium sulphite. Concentration of iodine and bromine was then determined argentometrically.

The measurements were carried out in the concentration range 0.774–0.136 mol/kg potassium iodide, in the temperature interval 420–483°C. The flow rate of nitrogen was 200 ml/min. Total weight of the melt was 30 g throughout.

RESULTS AND DISCUSSION

Reaction of iodate ions with bromides in an eutectic LiBr-KBr melt proceeds under the formation of iodine, bromine and lithium orthoperiodate which separates in the form of white precipitate. Its identification was carried out as described earlier¹.

Stoichiometric equation can be written in the form



The rate of decrease of the concentration of iodate ions in time $t = 0$ is of the first order with respect to the concentration of iodate (Table I), however, the reaction order changes in the course of the reaction. The ratio of the reacted amount of substance of iodate to that of the formed lithium orthoperiodate stabilized after 20 min at the value c. 2.5. From the temperature dependence of the rate of decrease of iodate ions concentration in time $t = 0$ we calculated the activation energy of the reaction (19.3 kcal/mol), which is by far higher than in the reactions of iodate with iodide ions¹ or of bromate with bromide ions³.

In order to explain the changing order of the reaction with respect to the concentration of iodate ions, we studied the effect of oxide, iodide and chloride ions, further the effect of the presence of powdered silica gel in the melt and finally also the effect of bromine in the entering gaseous mixture on the rate of the reaction of iodate with bromide ions.

To follow the effect of the presence of chloride ions on the rate of decrease of iodate ions concentration in the reaction with bromide ions, we mixed the eutectica LiBr-KBr and LiCl-KCl in defined ratios of chloride and bromide ions. The rate of de-

TABLE I

Effect of Initial Concentration of Iodate on the Rate of its Reaction with Bromide Ions and Values of Constant k_B from Eq. (I)

Temperature 483°C, flow rate of nitrogen 200 ml/min.

$[\text{IO}_3^-]_{\text{init}}$ mol/kg	$r^0 \cdot 10^2$ ^a mol min ⁻¹ kg ⁻¹	$\frac{\Delta \text{IO}_3^-}{\text{Li}_5\text{IO}_6}$ ^b	$k_B \cdot 10^2$ min ⁻¹ kg ⁻¹
0.760	0.42	2.5	0.54
0.490	0.28	2.8	0.56
0.220	0.12	2.8	0.53
0.110	0.064	2.9	0.57

^a r^0 is the rate of iodate concentration decrease in time $t = 0$, ^b $\Delta \text{IO}_3^- / \text{Li}_5\text{IO}_6$ is the ratio of the amount of substance of reacted iodate to that of the formed lithium orthoperiodate.

crease of iodate concentration decreases with increasing concentration of chlorides in the melt, while the non-integer order of reaction with respect to iodate concentration remains unchanged. In the LiCl-KCl eutecticum itself the reaction of iodate with chloride ions proceeds about 13 times more slowly than in a bromide melt and the ratio of the reacted amount of substance of iodate to that of the formed lithium orthoperiodate is about 5–6 times higher. The possibility cannot be excluded that at the temperature used (483°C) iodate already partially decomposes to oxygen and iodide¹.

In order to eliminate the possibility of iodate adsorption on the walls of the quartz reagent glass and thus also the effect of the surface area of quartz on the rate of decrease of the iodate concentration, we added different amounts of powdered silica gel to the melt. However, no change in the reaction rate was observed, only the ratio of the reacted amount of substance of iodate to that of the formed lithium orthoperiodate was increased. From this we conclude that silica gel acts as a weak oxide ions acceptor, similarly as it was shown in paper¹. We also tried to carry out the reaction in a platinum reagent vessel, but even in this case the rate of decrease of iodate concentration was the same as in a quartz vessel, thus indicating that quartz itself has no essential effect on the reaction course.

The most important effect proved to be that of the oxide ions in the melt (Table II). Oxide ions were added to the LiBr-KBr eutecticum in the form of sodium peroxide which after 20 min bubbling with nitrogen decomposed to oxygen and sodium oxide. Concentration of oxide ions in the melt was determined by acido-basic analysis of the sample of the melt. Further it was established qualitatively that no bromate that could possibly be formed in a reaction of bromide with sodium peroxide, is present in the melt. Afterwards, potassium iodate was added into the melt and the

TABLE II

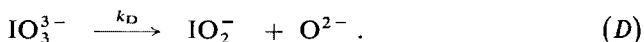
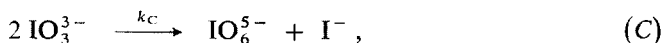
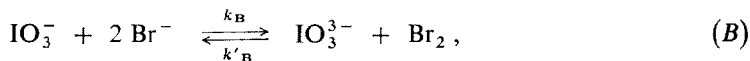
Effect of the Concentration of Oxide Ions Added at the Beginning of the Reaction on the Rate of Reaction of Iodate with Bromide Ions and Values of Constant k_E from Eq. (I)
Temperature 483°C, flow rate of nitrogen 200 ml/min.

$[\text{IO}_3^-]_{\text{init}}$ mol/kg	$[\text{O}^{2-}]_{\text{init}}$ mol/kg	$r^0 \cdot 10^2$ ^a mol. min ⁻¹ kg ⁻¹	$\frac{\Delta \text{IO}_3^-}{\text{Li}_5\text{IO}_6}$ ^b	k_E mol ⁻¹ min ⁻¹ kg ⁻¹
0.490	0	0.28	2.5	—
0.470	0.016	0.42	2.3	0.11
0.490	0.035	0.60	2.2	0.10
0.470	0.062	0.94	2.0	0.11
0.450	0.13	1.35	1.6	0.095

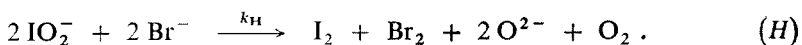
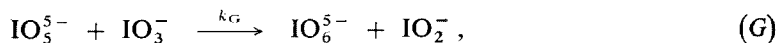
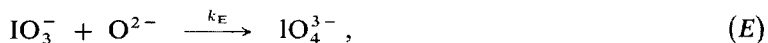
^a and ^b see Table I.

experiment was started. Oxide ions accelerated the reaction of iodate with bromides and caused a change in the reaction order with respect to the concentration of iodate. The ratio of the reacted amount of substance of iodate to the formed lithium orthoperiodate decreased with increasing concentration of oxide ions in the melt.

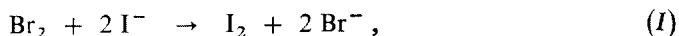
On the basis of the experimental data we attempted to propose a probable mechanism of the reaction of iodate with bromide ions in a bromide melt. Kinetic course of the reaction was expressed by a system of simultaneous reactions



Besides this also the reaction of iodate with the formed oxide ions plays an important role. These ions are regenerated in further reaction (H) and therefore have an autocatalytic effect. This is then manifested in the apparently non-integer reaction order with respect to the concentration of iodate ions.



Reactions (B) and (C) are analogous to the reaction of iodate ions with iodides¹. The formed iodide ions could react either with iodate yielding iodine and lithium orthoperiodate, or, which seems more probable, could be oxidized by bromine according to the reaction



which, according to experimental results, is very fast.

Also the decomposition of iodate to iodide and oxygen could take place to a small extent. The rate of this reaction is, however, at the reaction temperature used (483°C) very small⁴ and is not included in further considerations.

To ascertain the effect of bromine in the entering gas on the rate of decrease of iodate

ions we used a bubbling trap with bromine which was either left free on the air or was placed in a vessel with ice and was bubbled with nitrogen. In this way we could achieve that the partial pressure of bromine in the entering gas was constantly 0.024 or 0.007 atm. The rate of decrease of iodate concentration was lower at greater partial pressures of bromine. Consequently, we take reaction (B) to be a reversible process. In the presence of bromine in the entering gas the direct reaction (B) is slower and the ratio of the reacted amount of substance of iodate to that of the formed lithium orthoperiodate is higher. When the reaction is carried out at a greater flow rate of nitrogen, more bromine is released from the melt, which means that its concentration in the melt decreases, thus causing an increase of the rate of reaction (B) and at the same time a decrease in the value of the ratio of the reacted amount of substance of iodate to the formed lithium orthoperiodate (1.9) (Table III). A reverse result is obtained at a lower flow rate of nitrogen.

According to the proposed mechanism, the rate of decrease of the concentration of iodate ions was expressed as follows

$$-d[\text{IO}_3^-]/dt = k_B[\text{IO}_3^-] - k'_B[\text{Br}_2]_{\text{eq}}[\text{IO}_3^{3-}] + 2k_E[\text{IO}_3^-][\text{O}^{2-}]. \quad (1)$$

The rate of decrease of iodate concentration in time $t = 0$ was determined from the experimental kinetic curves and the value of k_B was calculated using Eq. (1) (Table I) (The second and third terms on the right-hand side were zero). An approximate

TABLE III

Effect of Bromine in the Entering Gas and Effect of the Flow Rate of Nitrogen on the Rate of Reaction of Iodate with Bromide Ions

$$[\text{IO}_3^-]_{\text{init}} = 0.480 \text{ mol/kg.}$$

p_{Br_2} atm	Flow rate of nitrogen ml/min	$r^0 \cdot 10^2$ ^a mol min ⁻¹ kg ⁻¹	$\frac{\Delta\text{IO}_3^-}{\text{Li}_5\text{IO}_6}$ ^b
0	200	0.28 ^c	2.5
0.007	200	0.26 ^c	4.0
0.024	200	0.22 ^c	5.0
0	50	0.165 ^d	2.4
0	100	0.220 ^d	2.7
0	200	0.240 ^d	2.9
0	425	0.285 ^d	3.3

^a r^0 is the rate of iodine concentration decrease in time $t = 0$, ^b $\Delta\text{IO}_3^-/\text{Li}_5\text{IO}_6$ is the ratio of the amount of substance of the reacted iodate to that of the formed lithium orthoperiodate, ^c 483°C, ^d 470°C.

value of k_E (Table II) could be calculated using Eq. (1) on the basis of experiments carried out at defined known initial concentration of oxide ions and from the values of k_B as determined earlier.

Constant k_B includes the concentration of bromide ions which are in excess in the melt and which consequently is constant. Subscript eq at the symbol of bromine concentration means that it is an equilibrium concentration in the melt.

In all these considerations ions IO_3^{3-} , IO_5^{5-} , IO_4^{3-} were assumed to exist as unstable intermediates in a stationary state, whose concentration can be expressed using the Bodenstein principle. Differential equation (1) cannot be analytically integrated and therefore a numerical solution was chosen. Since there are three unknowns (iodate, bromine and oxide ions concentration) in Eq. (1), it was necessary to express also the rates of increase of concentrations of oxide ions and of bromine. In this we consider even iodide and iodite ions to be unstable intermediates in a stationary state. Then we obtain the following final equations

$$d[\text{Br}_2]/dt = 2k_D[\text{IO}_3^{3-}] + k_E[\text{IO}_3^-][\text{O}^{2-}], \quad (2)$$

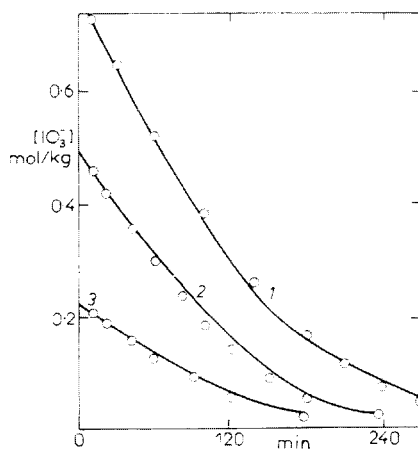
$$d[\text{O}^{2-}]/dt = 3k_D[\text{IO}_3^{3-}]. \quad (3)$$

However, Eq. (2) does not express correctly the actual state in the melt, since the formed bromine is desorbed from the melt at a definite rate which is affected by the flow rate of nitrogen. The rate of physical desorption can be expressed by the relation

$$R_{\text{des}} = (k_L^\circ \cdot F/V) ([\text{Br}_2]_{\text{eq}} - [\text{Br}_2]_{\text{p}}), \quad (4)$$

FIG. 1
Comparison of the Calculated (full line) Kinetic Curves of the Decrease of Concentration of Iodate Ions with the Measured Ones in the Reaction of Iodates with Bromide Ions

Temperature 483°C, flow rate of nitrogen 200 ml/min, $[\text{IO}_3^-]_{\text{init}}$ (mol/kg): 1 0.760, 2 0.480, 3 0.220.



where k_L^0 is the coefficient of mass transfer in physical desorption and according to Kořejš⁵ its value is c. 6 cm/min, F is the surface area of the interphase boundary, proportional to the flow rate of nitrogen (at the flow rate 200 ml/min it equals c. 30 cm²), V is the volume of the melt (c. 20 ml), $[\text{Br}_2]_{\text{eq}}$ is the equilibrium concentration of bromine in the melt and $[\text{Br}_2]_p$ is its concentration at the melt-gas interphase boundary. This latter concentration is proportional to the total rate of bromine release from the melt or also to the rate of decrease of concentration of iodate ions. The conversion factor can be determined from the stoichiometric equation

$$-\frac{7}{10}d[\text{IO}_3^-]/dt = d[\text{Br}_2]/dt. \quad (5)$$

To express the rate of the formation of equilibrium concentration of bromide in the melt we must subtract the rate of bromine desorption from the total rate of bromine formation, as expressed by Eq. (2)

$$d[\text{Br}_2]_{\text{eq}}/dt = d[\text{Br}_2]/dt - R_{\text{des}}. \quad (6)$$

After substituting from Eqs (2) and (4) into Eq. (6) and after rearrangement we obtain for the rate of formation of equilibrium concentration of bromine in the melt

$$d[\text{Br}_2]_{\text{eq}}/dt = 2k_D[\text{IO}_3^{3-}] + k_E[\text{IO}_3^-][\text{O}^{2-}] - (k_L^0 F/V)([\text{Br}_2]_{\text{eq}} + \frac{7}{10}d[\text{IO}_3^-]/dt). \quad (7)$$

The rate constants were found by solving the system of differential equations

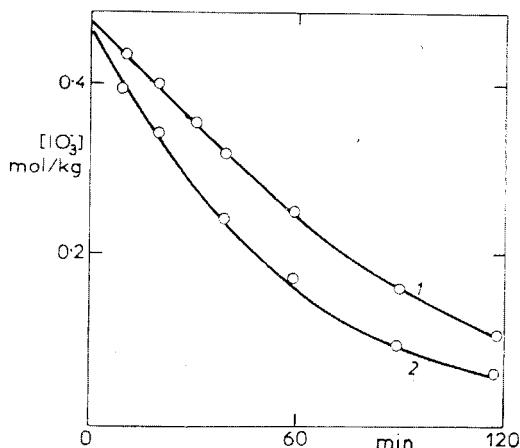


FIG. 2

Comparison of the Calculated (full line) Kinetic Curves of the Decrease of Concentration of Iodate Ions with the Measured Ones in the Reaction of Iodates with Bromide Ions

Temperature 483°C, flow rate of nitrogen 200 ml/min, $[\text{IO}_3^-]_{\text{init}}$ (mol/kg): 0.473, $[\text{O}^{2-}]_{\text{init}}$ (mol/kg): 1.0016, 2.0062.

(1), (3) and (7) using the Runge-Kuta-Merson method. The values determined from experimental data were substituted for constants k_B and k_E and the remaining constants were modified so as to make the sum of squares of the deviations between the calculated and the measured values minimum. The calculated kinetic curves agree with the experimental results approximately up to 85% of the reaction at higher degrees the calculated iodate concentrations differ slightly. This may be caused by the effect of thermal decomposition of iodate or by the effect of the reaction of iodate with bromides yielding bromate, on the rate of decrease of iodate ion concentration. These effects were neglected in our mathematical treatment. However, it should be noted that at low concentrations of iodate ions in the melt the analyses are rather inaccurate so that the source of the deviations may also lie here. The comparison of the calculated kinetic curves with the measured ones is presented in Figs 1 and 2. The rate constants have the following values (at 483°C): $k_B = 0.54 \cdot 10^{-2} \text{ min}^{-1} \text{ kg}^{-1}$, $k'_B = 0.5 \text{ mol}^{-1} \text{ min}^{-1} \text{ kg}^{-1}$, $k_c = (0.2 \pm 0.1) \text{ mol}^{-1} \text{ min}^{-1} \text{ kg}^{-1}$, $k_D = 0.5 \text{ min}^{-1} \text{ kg}^{-1}$, $k_E = 0.1 \text{ mol}^{-1} \text{ min}^{-1} \text{ kg}^{-1}$. Constant k_B includes the concentration of bromide ions which are present in a considerable excess in the melt. Constant k_C does not appear in Eqs (1)–(7) but it occurs in the expression for the concentration of orthoperiodate ions.

We further followed the effect of addition of iodide ions at the beginning of the reaction on the rate of decrease of iodate ions in their reaction with bromides. During the first 5 minutes all the iodide added is consumed and a considerable amount of gaseous iodine is formed. At the same time a decrease in the concentration of iodate ions starts very quickly. After 1–10 min (according to the amount of iodide added) the kinetic curves of the decrease of iodate ions concentration approximately agree with those measured in the absence of iodide ions (Fig. 3). The amount of substance

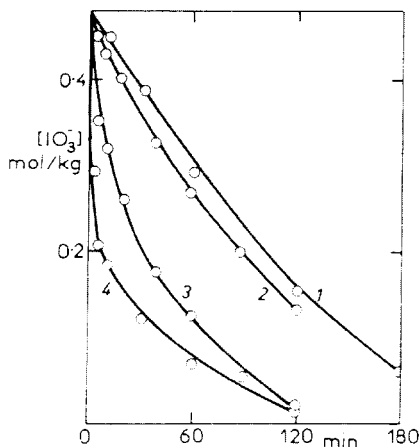


FIG. 3

Kinetic Curves of the Decrease of Concentration of Iodate Ions in their Reaction with Bromide Ions in the Presence of Iodide Ions

Temperature 483°C, flow rate of nitrogen 200 ml/min, $[\text{IO}_3^-]_{\text{init}} 0.480 \text{ mol/kg}$, $[\text{I}^-]_{\text{init}}$ (mol/kg): 1.0, 2.0, 3.0, 4.0.

of the reacted iodate in a defined time interval and with the addition of iodide corresponds to the amount of substance of the formed iodine and of lithium orthoperiodate.

The rates of decrease of the concentration of iodate ions in their reaction with iodides in an eutectic melt LiCl–KCl as described earlier¹ could be compared with those in LiBr–KBr melt as studied in this work. These corresponding rates at iodate ions concentration c. 0.5 mol kg^{-1} and that of iodide 0.5 mol kg^{-1} at 483°C extrapolated for zero time are for LiCl–KCl eutecticum $5.62 \cdot 10^{-1} \text{ mol kg}^{-1} \text{ min}^{-1}$ and for LiBr–KBr $150 \cdot 10^{-2} \text{ mol kg}^{-1} \text{ min}^{-1}$. Reaction (I) is probably accelerated by addition of iodide ions, whereby the concentration of bromine is lowered which results in an increase of the rate of reaction (B). At the beginning of the reaction also the direct reaction of iodate with iodides¹ is probably effective.

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