

REACTIONS IN FUSED SALTS. VIII.*¹REACTION OF IODATE IONS WITH IODIDE IONS
AND WITH CARBON DIOXIDE IN A MELT OF ALKALI NITRATES

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Kinetics of the reaction of iodide ions with iodate ions and with carbon dioxide in an eutectic melt of sodium and potassium nitrates has been studied at the temperature of 340°C. A probable reaction mechanism is proposed.

In our previous paper¹ we have studied the reaction of iodate ions with iodide ions in an eutectic mixture of LiCl-KCl at 410°C. We have found that this reaction does not proceed in a melt not containing lithium ions which because of the formation of insoluble lithium orthoperiodate play the role of oxide ions acceptors. It was therefore of interest to try out, how the reaction of iodides with iodates would proceed in an eutectic melt of KNO₃-NaNO₃, when using gaseous carbon dioxide as oxide ions acceptor. We found that in a nitrate melt this reaction has an entirely different mechanism. Besides, there is a possibility to compare it with the analogous reaction of bromate ions with bromide ions and with carbon dioxide, carried out under identical conditions².

EXPERIMENTAL

The reaction of iodide ions with iodate ions and with carbon dioxide was followed by means of a spectrophotometric device for the determination of gaseous iodide which was described in another paper³.

The chemicals used, of reagent grade purity, were dried at 110°C. Eutectic melt of NaNO₃-KNO₃ was prepared and purified similarly as described in paper⁴. The gases, *i.e.* carbon dioxide and nitrogen, were dried by passing through concentrated sulphuric acid and their flow was controlled by manostats, constructed in the Development workshops, Czechoslovak Academy of Sciences.

The reaction was followed at 340°C, in the concentration ranges 0.016 — 0.5 mol/kg potassium iodate, 0 — 1.2 mol/kg potassium iodide and 0 — 0.35 mol/kg barium nitrate, at partial pressure of carbon dioxide 0.25 — 1 atm and its flow rate 100 ml/min.

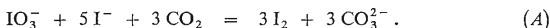
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All concentrations are given in molalities (mol kg^{-1}). The rate of iodine formation is given in mol of the evolved iodine per min. To ascertain the stoichiometry of the overall reaction we have performed several analyses of the melt after the reaction had been finished, to determine the content of iodates (iodometrically), carbonates (alkalimetrically) after previous determination of iodates and of iodides (by means of argentometry).

RESULTS AND DISCUSSION

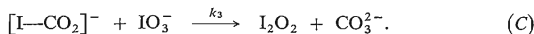
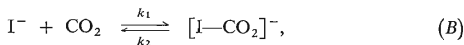
The measured rates of iodine formation are presented in Table I. Iodide ions do not react with iodate ions in the melt of $\text{KNO}_3\text{-NaNO}_3$ in the absence of carbon dioxide. If the latter is present, iodine is formed, the rate of its formation being of the 1st order with respect to iodide ions concentration and to the partial pressure of carbon dioxide. It only scarcely depends on the concentration of iodate ions. The dependence of the rate of iodine formation on the concentration of carbonate ions was determined both by adding K_2CO_3 to the melt and by adding barium ions to the melt in order to remove the formed carbonate ions. The rate of iodine formation is practically independent of the concentration of carbonate ions and only poorly depends on the concentration of barium ions which we explain rather by a change in the composition of the melt.

From the experimental results it is evident that the reaction proceeds according to equation



The rate of iodine formation depends further on the flow rate of carbon dioxide and the activation energy, calculated from the temperature dependence of the reaction rate equals 3.1 kcal/mol.

When suggesting the reaction mechanism we started from the finding that the reaction order with respect to the concentration of iodate ions is very small. Consequently, we assume that in the first phase of the reaction iodide ions react with carbon dioxide to form an unstable complex (B) and only then iodate enters the reaction (C), reacting with this complex



I_2O_2 (iodic acid iodide) reacts probably with iodide ions in a sequence of reactions (D) and (E)

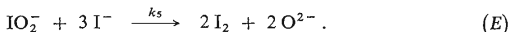
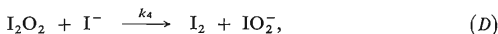


TABLE I

Values of the Rate Constant of Iodine Formation in the Reaction of Iodate Ions with Iodide Ions and with Carbon Dioxide in an Eutectic Mixture $\text{NaNO}_3\text{-KNO}_3$

p_{CO_2} 1 atm, flow rate 100 ml/min.

| t °C | [KI] mol kg ⁻¹ | [KIO ₃] mol kg ⁻¹ | r mol I ₂ min ⁻¹ · 10 ⁵ |
|-----------|------------------------------|---|---|
| 340 | 0.05 | 0.47 | 0.1 |
| | 0.28 | 0.45 | 0.56 |
| | 0.45 | 0.44 | 0.80 |
| | 0.65 | 0.42 | 1.03 |
| | 0.89 | 0.40 | 1.36 |
| | 0.92 | 0.36 | 1.53 |
| | 1.08 | 0.39 | 1.56 |
| 340 | 1.08 | 0.39 | 1.08 ^a |
| | 1.08 | 0.39 | 1.02 ^b |
| | 1.08 | 0.39 | 0.74 ^c |
| | 1.08 | 0.39 | 0.38 ^d |
| | 1.08 | 0.39 | 1.03 ^e |
| | 1.08 | 0.39 | 1.88 ^f |
| 339 | 1.12 | 0.016 | 1.02 |
| | 1.14 | 0.037 | 1.11 |
| | 1.11 | 0.040 | 1.08 |
| | 1.13 | 0.089 | 1.31 |
| | 1.09 | 0.14 | 1.25 |
| | 1.03 | 0.37 | 1.48 |
| | 1.15 | 0.45 | 1.53 |
| 340 | 1.09 | 0.43 | 1.80 ^g |
| | 1.92 | 0.38 | 1.40 ^h |
| 340 | 0.92 | 0.36 | 1.53 |
| 282 | 0.92 | 0.36 | 1.14 |
| 230 | 0.92 | 0.36 | 0.88 |

p_{CO_2} : ^a 0.75 atm; ^b 0.56 atm; ^c 0.50 atm; ^d 0.25 atm. Flow rate: ^e 50 ml/min; ^f 200 ml/min; Added: ^g 0.21 mol $\text{Ba}(\text{NO}_3)_2/\text{kg}$; ^h 0.1 mol $\text{K}_2\text{CO}_3/\text{kg}$ of melt.

Oxide ions are then removed by reaction with CO_2 (F)



The change of concentration of the evolved iodine per min was expressed with respect to this mechanism by applying the Bodenstein's principle. We assumed that ions $[\text{I}-\text{CO}_2]^-$, I_2O_2 and IO_2^- can be taken as unstable intermediates. The solution

yields the final form of the kinetic equation

$$r = \frac{d[I_2]}{dt} = \frac{3k_1k_3 \cdot K \cdot p_{CO_2} [I^-] [IO_3^-]}{k_2 + k_3 [IO_3^-]}, \quad (1)$$

where K is the proportionality coefficient of the Henry's law for carbon dioxide in an eutectic melt of $NaNO_3$ - KNO_3 .

The dependence of the reciprocal value of the rate of increase of the concentration of iodine on the reciprocal value of the concentration of iodate ions allows to estimate the ratio of constants k_2/k_3 which equals $1.8 \cdot 10^{-2}$. From this value it follows that $k_2 < k_3$, which means that the reaction order with respect to the concentration of iodate will be small and will, at great iodate concentrations, approach the limiting value zero. All consequences of Eq. (1) comply therefore with the experimentally found data.

The comparison with the analogous reaction of bromate ions with bromide ions and carbon dioxide under identical conditions² indicates that the course of the reaction depends only poorly on the concentration of bromate, as well.

The difference in the reaction mechanism of iodate with iodide as compared with the reaction of bromate with bromide is probably caused by the differing reaction of iodite and bromite ions. Whereas bromite is assumed to decompose to bromide and oxygen with iodite the more probable reaction is that with iodide to yield iodine and oxide ions^{3,5}. It should be noted, however, that the reaction of iodate was not complicated by its possible decomposition to oxygen, as it was in the case of bromate.

Recently some papers appeared⁶⁻⁸ in which the difference in the reactions of iodates and bromates in the melt was clearly demonstrated. The authors found⁶ that bromate dissolved in the melt of nitrate eutecticum can stabilize permanganate to a considerable degree (*e.g.* at 210°C for more than two months). Iodate does not show this stabilization effect. The effect is interpreted by the preference of the reaction of bromate with nitrite formed in thermal decomposition of the nitrate melt. By removing nitrite ions the reduction of permanganate is hindered. The authors correlated the reactivity of halogenates and perhalogenates which have the stabilization effect and found a good agreement.

A further support for the differing reactivity of iodate and bromate is their reaction with halide ions which was studied in a nitrate melt⁷. It was found that already at 250°C the transformation of bromate to iodate proceeds at a sufficiently great rate. In this connection it is worth mentioning that in the study of this reaction the effect of added carbonates was also found. The authors explain this effect so that the reaction proceeds also as a heterogeneously catalyzed on the surface of the vessel, while carbonates, iodates and bromates are adsorbed on the active surface. Carbonate is

adsorbed preferentially so that its amount is sufficient to block the active centers and thus to lower the reaction rate.

Reactivity of iodate in nitrate melts has also been studied in paper⁸. Interestingly enough, iodate is the most stable of all oxoanions of halogens in the nitrate melt and only above 500°C it decomposes to oxygen. It is far less stable in the presence of nitrites and also in an acidic medium it is much more reactive, since in an acidic nitrate melt it decomposes already at about 200°C.

Thus, the results of the present paper are in good agreement with the most recent experimental data.

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REFERENCES

1. Pacák P., Sláma I., Horsák I.: This Journal 38, 2347 (1973).
2. Kodejš Z., Horsák I., Sláma I.: This Journal, in press.
3. Pacák P., Sláma I.: This Journal 38, 2355 (1973).
4. Pacák P., Sláma I.: This Journal 36, 2988 (1971).
5. Abel E., Hilferding K.: J. Phys. Chem. 136, 194 (1928).
6. Brough B. J., Habboush D. A., Kerridge D. H.: Inorg. Chim. Acta 6, 259 (1972).
7. Schlegel J. H., Perrine J.: J. Inorg. Nucl. Chem. 34, 2087 (1972).
8. Habboush D. A., Kerridge D. H.: Inorg. Chim. Acta 4, 81 (1970).

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