

## REACTIONS IN FUSED SALTS. IV.\*

REACTIONS OF PERCHLORATE IONS  
WITH CHLORIDE IONS IN ACIDIC MELTS

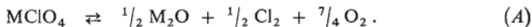
I. HORSÁK, I. SLÁMA and Z. KODEJŠ

*Institute of Inorganic Chemistry,**Czechoslovak Academy of Sciences, 160 00, Prague 6*

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The reaction of perchlorate ions with chloride ions has been studied in a heterogeneous system of fused alkali nitrates with admixture of barium ions. The system was bubbled through by carbon dioxide. Reaction orders with respect to concentrations of each of the components were determined as well as the dependence of the rate of perchlorate decomposition on the flow rate of carbon dioxide, in the temperature interval 420–450°C. Correlation of the values of rate of perchlorate decomposition as calculated by substitution into the derived kinetic equations with the values measured allowed to determine the most probable reaction mechanism.

In acidic medium, represented in melts by acceptors of oxide ions, as *e.g.*  $Zn^{2+}$ ,  $S_2O_7^{2-}$ ,  $Cr_2O_7^-$  or  $(PO_3^-)_n$  ions, decomposition of perchlorate leads to the formation of a mixture of chlorine and oxygen. Similar reactions of bromates<sup>1,2</sup> and chlorates<sup>3–6</sup> were studied in the presence of these acceptors. Up to now, reaction of perchlorate ions in acidic melts has not been studied, with the exception of the equation derived for the decomposition of potassium perchlorate in the presence of metaphosphate ions<sup>7</sup>



A drawback of the use of the mentioned oxide ions acceptors directly in the melt is that their concentration changes during the reaction. In the case of  $Zn^{2+}$  still another disadvantage arises, namely that their concentration in the melt is not known exactly, since a number of complex ions are formed with halide ions, able to accept oxide ions. In the present paper we have employed carbon dioxide as acceptor of oxide ions. Although its ability to accept oxide ions is weak, it can be achieved, by bubbling it through the melt, that its concentration is constant. The ability to bind oxide ions depends, however, also on the ratio of concentrations  $[CO_2]/[CO_3^{2-}]$  and it decreases<sup>8</sup> with increasing concentration of the formed carbonate ions. Therefore

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we added  $\text{Ba}^{2+}$  ions to the melt to keep constant the concentration of  $\text{CO}_3^{2-}$  ions in the melt which is given by the solubility product of  $\text{BaCO}_3$ .

## EXPERIMENTAL

The same procedures were used as described in the preceding publication<sup>9</sup>. Weighings of the individual components were chosen so as to keep the total weight always the same (28 g). The flow of  $\text{CO}_2$  or of the  $\text{N}_2\text{-CO}_2$  mixture (80–200 ml/min) was controlled by a liquid manostat. Only chlorine was determined analytically, by the conventional iodometric method, in the leaving gaseous mixture. The measurements were carried out at temperatures in the interval 420–450°C.

## RESULTS AND DISCUSSION

$\text{Ba}^{2+}$  ions were verified to be only weak acceptors of oxide ions in the absence of  $\text{CO}_2$  and consequently their contribution to the rate of chlorine formation in the system ( $\text{ClO}_4^- - \text{Cl}^- - \text{Ba}^{2+}$ ) was negligible. The system without perchlorate ( $\text{NO}_3^- - \text{Cl}^- - \text{Ba}^{2+} - \text{CO}_2$ ) did not yield any measurable amounts of chlorine, either, so that nitrates did not act as oxidizing agent under these conditions.

Concentrations of  $\text{ClO}_4^-$  and  $\text{Cl}^-$  in fused nitrates were chosen in the range 5 to 25 mol%. Higher concentrations could not be attained owing to the solubility of both components in the nitrate melt at 440°C. Concentration of  $\text{Ba}^{2+}$  ions was chosen so that they were in excess compared to the amount of  $\text{CO}_3^{2-}$  ions formed in the course of the experiment.

Weighed components were fused in a test tube and the mixture was bubbled through with nitrogen for 10 min to secure a complete homogenization and temperature equilibration. A stream of carbon dioxide or of its mixture with nitrogen was then admitted and the time of experiment was measured from this moment. The leaving gaseous mixture was led into the solution of iodide and the evolved iodide was determined titrimetrically in 5 min intervals. The reaction was followed for 50–75 min in average. Time dependence of the total amount of chlorine formed was linear except for the starting period. The rate of chlorine formation was read off from a graph as the slope of the most probably positioned straight line.

The measured rates of chlorine formation at various concentrations of  $\text{ClO}_4^-$ ,  $\text{Cl}^-$  and  $\text{Ba}^{2+}$  and at various partial pressures of  $\text{CO}_2$  are presented in Table I. The numerical value of constant  $k$  equals  $0.91 \cdot 10^{-5}$  mol  $\text{Cl}_2/\text{min}$  and is valid for 440°C, flow rate of  $\text{CO}_2$  200 ml/min and the above given experimental arrangement. The rates of perchlorate decomposition,  $r$ , for various flow rates of  $\text{CO}_2$  at  $p_{\text{CO}_2} = 1$  atm and for different temperatures at constant concentration of the participating components are summarized in Table II. The dependence of the rate of perchlorate decomposition on the flow rate of carbon dioxide is linear; the equation of the straight line which does not intersect the coordinates origin is:  $r \cdot 10^5 = 0.52 + 0.0033 \cdot P'$ , where  $P'$  is the flow rate in ml/min. This finding agrees with the known fact that the reaction rate in heterogeneous systems is directly proportional to the flow rate of the

gas bubbled through the liquid. The temperature dependence of the reaction studied is rather pronounced. The activation energy, obtained by correlating  $\log r$  against  $1/T$  is approximately 40 kcal. On the basis of this value we can postulate that the rate

TABLE I  
Effect of the Concentration of Reaction Components on the Rate of Chlorine Formation  
 $t = 440^\circ\text{C}$ , flow rate of  $\text{CO}_2 = 200 \text{ ml/min}$ ,  $p_{\text{CO}_2} = 1 \text{ atm}$ .

$[\text{ClO}_4^-]$ $\text{mol kg}^{-1}$	$[\text{Cl}^-]$ $\text{mol kg}^{-1}$	$[\text{Ba}^{2+}]$ $\text{mol kg}^{-1}$	$r \cdot 10^5$ $\text{mol min}^{-1}$	$r' \cdot 10^5$ $\text{mol min}^{-1}$	$r'' \cdot 10^5$ $\text{mol min}^{-1}$
0.5574	2.2307	0.1373	0.527	0.493	0.468
1.0944	2.1886	0.1370	0.787	0.772	0.770
2.1017	2.1053	0.1371	1.150	1.142	1.191
2.5762	2.0607	0.1372	1.434	1.277	1.350
2.0161	0.5038	0.1368	0.730	0.426	0.671
2.0444	1.0209	0.1372	0.955	0.705	0.900
2.0779	1.5528	0.1369	1.161	0.936	1.062
2.1300	2.6663	0.1375	1.360	1.332	1.301
2.1014	2.1025	0.0686	0.782	0.866	0.925
2.1011	2.1030	0.2739	1.440	1.462	1.479
2.1010	2.1044	0.5469	1.730	1.811	1.762
2.1015	2.1027	0.1369	1.060	0.992	1.025 <sup>a</sup>
2.1013	2.1030	0.1372	0.980	0.825	0.842 <sup>b</sup>
2.1010	2.1036	0.1368	0.826	0.629	0.629 <sup>c</sup>
2.1011	2.1035	0.1372	0.640	0.385	0.370 <sup>d</sup>

$p_{\text{CO}_2} = \text{}^a 0.8 \text{ atm}$ ;  $\text{}^b 0.6 \text{ atm}$ ;  $\text{}^c 0.4 \text{ atm}$ ;  $\text{}^d 0.2 \text{ atm}$ .

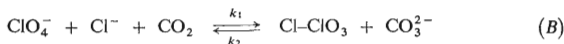
TABLE II  
Effect of the Flow Rate of Carbon Dioxide and of Temperature on the Rate of Perchlorate Decomposition

$[\text{ClO}_4^-] = 20 \text{ mol } \%$ ,  $[\text{Cl}^-] = 20 \text{ mol } \%$ ,  $[\text{Ba}^{2+}] = 0.1371 \text{ mol kg}^{-1}$ ,  $p_{\text{CO}_2} = 1 \text{ atm}$ .

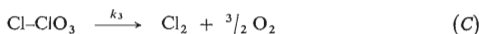
Flow rate of $\text{CO}_2$ $\text{ml min}^{-1}$	$t$ $^\circ\text{C}$	$r \cdot 10^5$ $\text{mol min}^{-1}$	Flow rate of $\text{CO}_2$ $\text{ml min}^{-1}$	$t$ $^\circ\text{C}$	$r \cdot 10^5$ $\text{mol min}^{-1}$
200	440	1.150	200	420	0.813
160	440	1.055	200	430	0.961
120	440	0.905	200	440	1.150
80	440	0.766	200	450	1.411

controlling step in the studied reaction is a chemical reaction and that diffusion processes, absorption of  $\text{CO}_2$  and desorption of  $\text{Cl}_2$ , are faster.

To explain the non-integrity of reaction orders with respect to individual components in the final kinetic equation several mechanisms have been suggested. The simplest one of them postulates the formation of an unstable intermediate  $\text{Cl}-\text{ClO}_3$  in a reversible reaction



followed by its decomposition in a one-way reaction



and precipitation of  $\text{BaCO}_3$  by an irreversible reaction



Chlorine is formed in reaction (C), the rate of its formation being proportional to the concentration of the intermediate  $\text{Cl}-\text{ClO}_3$

$$r = k_3[\text{Cl}-\text{ClO}_3]. \quad (2)$$

If  $\text{CO}_3^{2-}$  is also taken as unstable intermediate and if Bodenstein's principle is applied, one obtains the following relations for the concentration of intermediates

$$[\text{Cl}-\text{ClO}_3] = \frac{k_1[\text{ClO}_4^-][\text{Cl}^-]p_{\text{CO}_2}}{k_2[\text{CO}_3^{2-}] + k_3}, \quad (3)$$

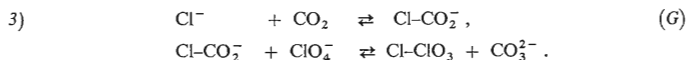
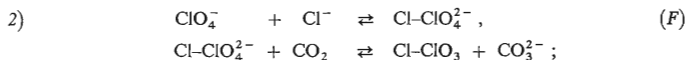
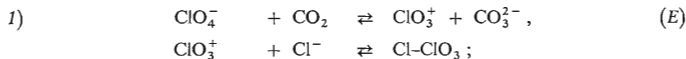
$$[\text{CO}_3^{2-}] = \frac{k_1[\text{ClO}_4^-][\text{Cl}^-]p_{\text{CO}_2}}{k_2[\text{Cl}-\text{ClO}_3] + k_4[\text{Ba}^{2+}]}. \quad (4)$$

By combining these equations we obtain a quadratic equation for  $[\text{Cl}-\text{ClO}_3]$  and substituting one of the solutions into expression (3) we obtain the final form of the kinetic equation

$$r = k_3 \left\{ \left( \frac{k_1 \cdot k_4}{k_2 \cdot k_3} [\text{ClO}_4^-][\text{Cl}^-][\text{Ba}^{2+}]p_{\text{CO}_2} + \frac{k_4^2 [\text{Ba}^{2+}]^2}{4k_2^2} \right)^{\frac{1}{2}} - \frac{k_4}{2k_2} [\text{Ba}^{2+}] \right\}. \quad (5)$$

This equation allows already to explain the non-integrity of the reaction orders (approximately 0.5). To verify this expression by correlation with experimental data, it was transformed into the form  $r^2 + r \cdot B \cdot x - A \cdot x \cdot y = 0$ , where  $A = k_1 k_3 k_4 / k_2$ ;  $B = k_3 k_4 / k_2$ ;  $y = [\text{ClO}_4^-] [\text{Cl}^-] p_{\text{CO}_2}$ , and optimum values of constants  $A$  and  $B$  were computed using the methods of least squares. The new values of reaction rates were then calculated by re-substitution (column  $r'$  in Table I). The mean standard deviation of the calculated and measured reaction rate values is 19.6%.

Since trimolecular reaction (B) is improbable from the kinetic point of view, partial mechanisms were sought of the formation of  $\text{Cl}-\text{ClO}_3$ . The following three possibilities were considered:



Further reactions, *i.e.*, precipitation of  $\text{BaCO}_3$  and decomposition of  $\text{Cl}-\text{ClO}_3$  are already common. All three mechanisms were solved similarly as described above, considering  $\text{ClO}_3^+$ ,  $\text{Cl}-\text{ClO}_4^{2-}$ ,  $\text{Cl}-\text{CO}_2^-$ ,  $\text{Cl}-\text{ClO}_3$  and  $\text{CO}_3^{2-}$  to be unstable products. A criterion for the decision between the suggested mechanisms were the sum of squares of deviations of the measured and the calculated reaction rates. The least sum of squares was that for mechanism (E) which, moreover, was smaller than the sum of squares of deviations for the original mechanism of reactions (B), (C) and (D). The calculated rate values for mechanism (E) are given in Table I, column  $r''$ . The mean relative standard deviation of the calculated and measured values is 13.2%.

With respect to the scatter of experimental results and also because the sums of squares of deviations of the measured and the calculated rates are of the same order of magnitude, one can hardly distinguish unambiguously between the suggested mechanisms. However, each of them can explain the observed non-integer reaction orders.

Concluding it should be pointed out that in spite of the fact that the studied reaction takes place in a complex heterogeneous system, we succeeded to prove that the governing process is a chemical reaction and we could suggest a plausible mechanism, explaining the observed phenomena.

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