

REACTION OF CHLORATE AND LEAD(II) IONS IN THE MEDIUM OF FUSED SODIUM CHLORATE*

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Reaction of lead(II) ions with chlorate ions was studied in fused sodium chlorate at 300–320°C; the reaction products are oxygen, chlorine, lead dioxide, and chloride ions. A kinetic equation was suggested for the interpretation of the experimental results.

Decomposition of alkali metal chlorates proceeds with the formation of oxygen and chloride ions^{1,2}. In the presence of substances, which are able to act as acceptors of oxygen ions, gaseous chlorine is formed in addition. This reaction has been followed in a nitrate melt in the presence of dichromate³ and in a chloride melt in the presence of zinc ions or carbon dioxide². The effect of barium and lead(II) ions has been examined only in the solid phase during the study of decomposition reactions of chlorates of those metals by employing methods of thermal analysis⁴.

The aim of this work was to follow the kinetic course of the reaction of lead(II) and chlorate ions in the liquid phase and to find factors affecting the reaction.

EXPERIMENTAL

All chemicals were reagent grade purity and were thoroughly dried prior to use.

The reaction vessel represented by a closed glass test tube, diam. 28 mm and height 250 mm, was placed in a metal block kept on a constant temperature with the accuracy $\pm 0.5^\circ\text{C}$. The reaction mixture in the test tube was stirred by a stream of nitrogen, which was brought to the bottom of the test tube through a glass tube. The nitrogen stream served also for the offtake of the gaseous reaction products from the reaction vessel for analysis. The nitrogen flow rate was usually 150 ml/min.

The reaction was initiated by throwing the calculated amount of lead(II) nitrate into the fused reaction mixture of sodium chlorate and sodium chloride and introducing the nitrogen stream in the reactor. The weight of the reaction mixture usually amounted to 45 g. The kinetic course of the reaction was followed by determining the content of chlorine in the outlet gas in chosen time intervals. The chlorine content was determined iodometrically after its absorption in a solution. The concentration of lead(II) ions in samples of the melt was determined chelometrically after dissolution in water, that of lead dioxide was determined iodometrically.

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RESULTS

The temperature and concentration ranges, where the reaction kinetics can be well followed, were found from orientation experiments: the temperature region of 300 to 320°C and initial concentration of lead(II) ions of 0.01–0.05 mol kg⁻¹ were chosen.

During the reaction of chlorate ions with lead(II) ions, chlorine, oxygen, and chloride ions are formed; in the melt a dark precipitate is formed, which was identified by chemical and X-ray analysis as lead dioxide. The determination of the latter in the reaction mixture after the experiment was over, evidenced that all the lead(II) ions reacted yielding PbO₂ and the total amount of chlorine evolved was in the 1 : 1 molar ratio to the amount of lead(II) nitrate at the beginning of the reaction. The mass amount of oxygen evolved is in a nonstoichiometric ratio to the amount of lead(II)-ions, as the former is formed also by parallel reactions catalyzed by the products of the reaction in question.

The reaction rate was evaluated based on the amount of chlorine evolved in a time unit. Regarding that the rate is negatively affected by chloride ions, which are formed also by side decomposition reactions, we performed all the experiments with a constant concentration of those ions. This concentration was given by the solubility of sodium chloride in fused sodium chlorate at the temperature applied, and its value is involved in the rate constant of the reaction. The area of the liquid–solid interphase boundary was found not to affect the reaction rate; in addition, it was proved that the experiments are performed in the kinetic region. When the weight of the reaction mixture was doubled, the reaction rate defined as the rate of increase of the reaction extent was found double, too. A change of the way of supplying nitrogen over the surface of the melt did not bring about any change of the reaction rate either.

The effect of the partial pressure of chlorine on the reaction rate was tested by adding chlorine to the nitrogen stream entering the reactor. The reaction rate did not exhibit changes, which indicates that the overall reaction is irreversible. Similarly no effect was caused by additions of sodium perchlorate or sodium nitrate unless they affected considerably the concentration of chlorate ions in the reaction mixture used.

The kinetic course of the reaction was followed also in an open reaction vessel by determining the concentration of lead(II) ions in samples of the reaction mixture. The shape of the plot of the amount of lead(II) ions *vs* time agrees with the analogous plot for the chlorine released. All the experimental results are therefore for an easier comparison transformed into the coordinate system mass amount of lead(II) ions–time.

In this coordinate system the kinetic course of the reaction is characterized by a curve with an almost linear central part; the influence of some factors on the reaction was tested in that central part.

The reaction rate was found to depend on the initial mass amount of lead(II) ions (Fig. 1) and on temperature (Fig. 2). From the temperature dependence the activation energy of the reaction was determined to be approx. 28 kcal/mol. This value supports the idea that the reaction course in the arrangement used is independent of physical processes. The kinetic course was examined also in a reaction

FIG. 1
Comparison of the Calculated and Experimental Dependence of the Mass Amount of Lead(II) Ions on Time for Various Initial Amounts of the Lead(II) Ions

Conditions of the experiments No 2, 4, and 5 are given in Table I.

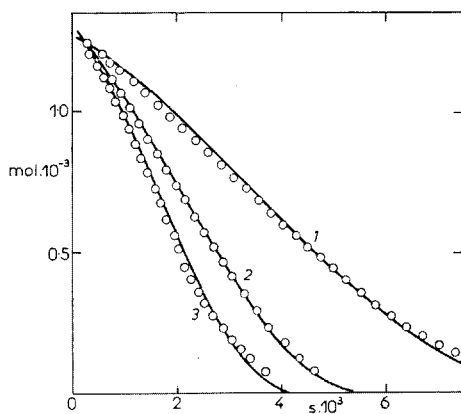
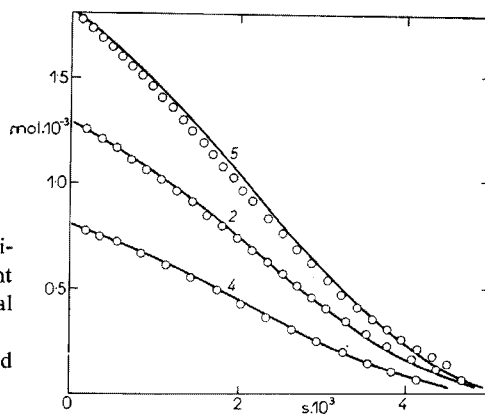


FIG. 2
Comparison of the Calculated and Experimental Values of Mass Amounts of Lead(II) Ions in Dependence on Time for Various Temperatures

Conditions of the experiments No 1, 2, and 3 are given in Table I.

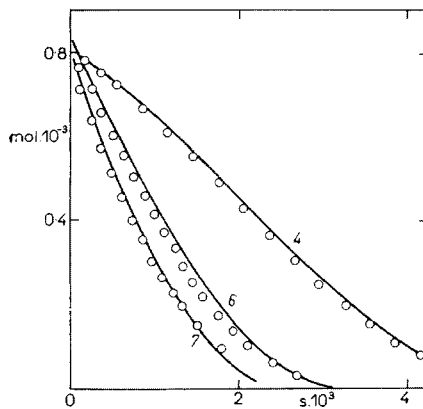
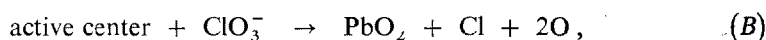
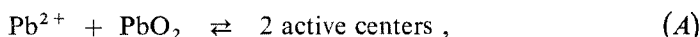


FIG. 3
Comparison of the Calculated and Experimental Time Dependences of the Mass Amount of Lead(II) Ions for Various Amounts of Reaction Products in the Reaction System

Conditions of the experiments No 4, 6, and 7 are given in Table I.

mixture containing in addition the suspended residue of lead dioxide remaining from the preceding experiment. The kinetic dependence is slightly different in this case (Fig. 3). The same effect was exerted by lead dioxide added to the reaction mixture before the beginning of the experiment.

From the experimental results it is obvious that the reaction course is affected by the presence of lead(II) ions as well as by that of lead dioxide suspended in the fused sodium chlorate. For a suggestion of the reaction mechanism we have to assume an interaction between lead(II) ions and lead dioxide, during which active centers for the decomposition of chlorate to chlorine are formed as an unstable intermediate. We suppose that this active intermediate is in an equilibrium with lead(II) ions and lead dioxide, and suggest the following scheme:



followed by a rapid recombination of chlorine and oxygen atoms.

According to this mechanism, however, the reaction could not occur at all if no lead dioxide were present. Our observations in the initial stage revealed that lead dioxide forms immediately on adding small amounts of lead(II) nitrate into the sodium chlorate melt. This can be explained so, that the reaction system is not homogenized in the first stage and lead dioxide is formed in points of oversaturation, by thermal dissociation of the lead(II) salt for instance. In the first stage of examination of the kinetic course the experimental values of the reaction rate were not steady and were badly reproducible. For the evaluation of the constants of the kinetic equation those values were therefore used which correspond to a steady reaction rate with some amount of lead dioxide present in the reaction mixture. This steady and reproducible course appeared usually after 5–8% of the initial amount of lead(II) ions had reacted. During the reaction, interaction between the liquid and the solid phases occurs, and it is therefore of advantage to use the kinetic equation in the form

$$dx/dt = k_B K_A^{1/2} [(a-x)x]^{1/2} = k' [(a-x)x]^{1/2} , \quad (1)$$

where a is the mass amount of lead(II) ions at the beginning of the reaction [mol], x is the reacted amount of those ions in the time t [mol], t is the time [s], K_A and k_B are the equilibrium and rate constants of the reactions A and B , respectively, and $k' = k_B K_A^{1/2}$.

Since we suppose, however, that some amount of lead dioxide is present in the reaction system already at the start of the kinetic course, this amount must be added to the term expressing the mass amount of lead dioxide in equation (1).

For experiments with lead dioxide added in advance, this amount must be ac-

counted for in the kinetic equation too. The activity of the substance formed at the start or during the reaction appeared to differ from that of the compound added in the form of a commercial chemical. For a quantitative comparison we introduced a coefficient y , by which the mass amount of lead dioxide added at the beginning of the reaction must be multiplied. The kinetic equation takes then the form

$$dx/dt = k'[(a - x)(x + c + yd)]^{1/2}, \quad (2)$$

where c expresses the mass amount of lead dioxide formed in the reaction system before the kinetic examination of the experiment and d is the mass amount of lead dioxide added. For integration we arrange the equation to

$$\int_0^x dt = \int_0^x dx / \{k'[(a - x)(x + b)]^{1/2}\}, \quad (3)$$

where the constant $b = c + yd$ represents the sum of all active mass amounts of lead dioxide, which are constant during the experiment. This kinetic equation approaches by its form closely equations suggested by other authors⁵⁻⁷ for the description of autocatalytic reactions. Carrying out the integration we obtain

$$t = (2/k') \{ \text{arctg} [(b + x)/(a - x)]^{1/2} - \text{arctg} [b/a]^{1/2} \}. \quad (4)$$

The calculated dependences of the mass amount of lead(II) ions on time are depicted for typical experiments in Figs 1-3. The values of the constants used are given in Table I. The comparison of the calculated and experimental reaction courses

TABLE I

Values of the Constants for the Calculation of the Dependence of the Mass Amount of Lead(II) Ions on Time

No of the experiment	Temperature °C	$k' \cdot 10^4$ s ⁻¹	$a \cdot 10^3$ mol	$c \cdot 10^3$ mol	$d \cdot 10^3$ mol	a
1	300	2.64	1.280	0.1390	—	—
2	310	4.60	1.290	0.1210	—	—
3	320	6.06	1.310	0.1130	—	—
4	310	4.60	0.805	0.0876	—	—
5	310	4.60	1.818	0.1730	—	—
6	310	4.60	0.825	0.9550	—	—
7	310	4.60	0.793	1.8010	—	—
8	310	4.60	0.799	0.0598	0.419	0.5
9	310	4.60	0.749	0.0440	0.839	0.5

indicates a good agreement in limits of experimental errors. Still open to discussion remains the value of the coefficient γ for the activity of lead dioxide. It is, however, consistent with experience that a freshly formed or prepared substance has a higher activity than one exposed to "ageing".

It should be finally mentioned that for the interpretation of this rather unusual reaction course a series of different mechanisms were tested (*e.g.* trace catalysis, system of consecutive reactions *etc.*), but none of them complied with the experimental results.

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