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KINETIC STUDY OF SOLID-SOLID REACTIONS BY DTA METHOD ($BaCl_2$ - KNO_3 SYSTEM)

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ABSTRACT

The kinetic parameters of the reaction $BaCl_2 + 2KNO_3 \longrightarrow Ba(NO_3)_2 + 2KCl$ have been evaluated by the DTA method.
The crystalline phases of the reaction mixture have been identified using the X-Ray diffraction method.

INTRODUCTION

In a previous publication /1/ two kinetic models described the occurrence of solid-solid reactions controled by the surface nucleation or crystallization. These models account for the influence of mechanical treatments, dimension of grains and degree of compactness of the sample on the reaction rate.

This paper deals with the application of these models to the nonisothermal kinetics of the reaction:

$$BaCl_{2(s)} + 2KNO_{3(s)} \longrightarrow Ba(NO_3)_{2(s)} + 2KCl_{(s)} \qquad (I)$$

EXPERIMENTAL

$BaCl_2 \cdot 2H_2O$, KNO_3, $Ba(NO_3)_2$ and KCl "Reactivul" have been used. The DTA curves have been recorded in a Paulik, Paulik, Erdey Q-1500 derivatograph at the heating rates $\beta = 5 K.min^{-1}$ and $2\ K\ min^{-1}$. The sample weight was 0,5g.

In order to identify the solid phases a Philips diffractometer P-1400 was used.

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RESULTS AND DISCUSSION

In figure 1 the thermal curves for three samples are shown namely:

- sample A, obtained through stoechiometrically mixing of the reactants $BaCl_2/2KNO_3$ (grains with mean radius r≈o,o5 cm)
- sample B, obtained through grinding of the mixture $BaCl_2/2KNO_3$ (r = o,o1 cm)
- sample C obtained by grinding of the reaction mixture $BaCl_2 \cdot 2H_2O/2KCl$ (r = o,o1 cm).

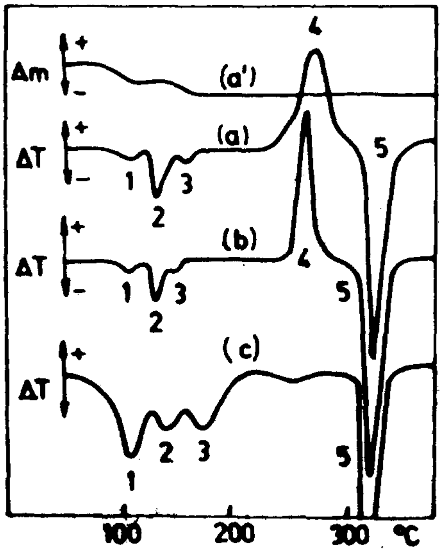

Fig.1
Heating curves of samples
A(a',a),B(b) and C(c)

The comparison between curves a'(TG) and a (DTA) corresponding to the sample A, and the same curves of the pure reactants and the mixture $Ba(NO_3)_2/2KCl$ allowed to identify the processes responsable for the peaks 1-5. The endothermic peaks 1 and 3 corresponds to the loss of water traces from $BaCl_2$. The endothermic peak 2 is exhibited by the DTA curve of pure KNO_3, too, and corresponds to the polymorphic change in this reactant. The exothermic peak 4 is exhibited only by the reaction mixtures, its areas changing with the ratio $BaCl_2/KNO_3$. The peak corresponds to the reaction (I). The X-Ray diffraatogram of the reaction mixture heated until 500°C exhibits only the peaks of $Ba(NO_3)_2$ and KCl. One can conclude that the reaction occurs practically until completion.

The last endothermic peak 5 is exhibited also by DTA curve of the mixture $Ba(NO_3)_2/2KCl$, thus it can be assigned to the melting of the eutectic of the reaction products.

The DTA curve (b) of the sample B exhibits the same processes. The only difference with respect to sample A consists in sharpness of the peak 4. It shows that the grinding determines a mechanical activation, the reaction occurring faster in a narrower temperature interval.

The DTA curve c of the sample C indicates that the presence of crystallization water leads to the integral disappearance of the peak 4. Nevertheless the X-Ray analysis shows that the reaction mixture after heating contains only the reaction tion products. The explanation consists in the fact that the reaction occurs at lower temperatures simultaneously with the loss of crystallization water. The exothermic effect is hidden by the endothermic effects corresponding to the loss of water from $BaCl_2 \cdot 2H_2O$ and the pholymorphic change 3.

The rehydration of the sample A kept in humid air determines a gradual diminuation of the peak 4 and increase of the peaks 1 and 2.

The combination molar ratio of the reactants was determined from the plot $\Delta H = f(X_{KNO_3})$, (fig.2), where ΔH(cal/g) is the specific thermal effect of the reaction, and X_{KNO_3} - the molar fraction of KNO_3.

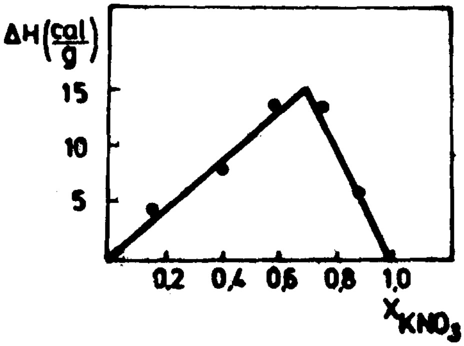

Fig.2

Plot of H versus X_{KNO_3}

The thermal effect ΔH was evaluated from the peak area divided by the sample weight. The system was calibrated with respect to the thermal effect /2/ corresponding to the phase transition of KNO_3(ΔH= 13 cal/g). The maximum value ΔH_{max}=15 cal/g corresponds to X_{KNO_3}=0,69. thus $X_{KNO_3}/X_{BaCl_2} \approx 2$ A first information concerning the kinetics of the process can be obtained by estimating the activation energy using the method of low conversions /3,4/. For the sample A E_a=7,1 Kcal/mol was obtained; a very low value in comparison with E_B=112 Kcal/mol for the sample B. This difference can be explained taking into account that the occurrence of the reaction in sample A (mechanically nonactivated) is controlled by the nucleation at the contact surface between crystalline grains. If the change of grain radius during the reaction is neglected, the following simplified rate equation was obtained /1/.

$$\frac{d\alpha}{dt} = \frac{32\gamma\ r\ hP_o n_1}{1 + R'}\ e^{-\frac{E}{RT}}\ (1-\alpha)^2 \qquad (1)$$

where α is the conversion degree t-the time, γ- the compactness factor of the sample, r-the mean radius of the grains, h-the maximum interaction distance, P_o-the change probability of a potential nucleus in a stable one, n_1- surface concentration of potential nuclei; E-activation energy R-gas constant, T-temperature (K) and R'- a constant which depends on the weight and density ratio of the reactants.

In sample, B mechanically activated, the limiting step is the crystallisation of the reaction products, which needs an activation energy close to the lattice energy. Based on this assumption one obtains the rate equation:

$$\frac{d\alpha}{dt} = P_o n_1 V_1 e^{-\frac{E}{RT}}\ (1 - \alpha) \qquad (2)$$

where V_1 is the volume of crystalline product resulted from the growth of a single nucleus. The symbols P_1 and n_1 have the same meaning as before but for the nucleation in the bulk.

The reaction rate as well as the conversion degree have been evaluated from the DTA by help of approximative relationships /5/:

$$\frac{d\alpha}{dT} = \frac{\Delta T}{A_t} ; \qquad \alpha = \frac{a}{A_t} \qquad (3)$$

where ΔT- is the ordinate of the DTA curve, A_t-the total area of the DTA peak and a- the partial area corresponding to the time interval 0-t.

Equations (1) and (2) through linearization are in better concordance with experimental data than the method of low conversion. One obtains E_a=8,3 Kcal/mol E_b= 19o kcal/mol. The high value of the activation energy is due also to the self heating of sample C as a consequence of the fast evolvement of the heat of reaction.

For sample C which contains $BaCl_2.2H_2O$ the two steps dehydration leads to a surface layer of water migrating at the KNO_3 grains. The ions of the reactants penetrate in the adsorbed layer. The chemical reaction in the adsorbed layer is followed by water desorbtion and formation of the crystalline lattice of the reaction products. These steps can be described by equations II-V.

$$BaCl_2.2H_2O_{(s)} \longrightarrow BaCl_2.H_2O_{(s)} + H_2O_{(ads)} \qquad (II)$$

$$BaCl_2.H_2O_{(s)} \longrightarrow BaCl_{2(s)} + H_2O_{(ads)} \qquad (III)$$

$$BaCl_{2(s)} + 2KNO_{3(s)} + H_2O_{(ads)} \longrightarrow (Ba^{2+} + 2Cl^{-} + 2K^{+} + 2NO_3^{-} + H_2O)_{ads} \qquad (IV)$$

$$(Ba^{2+} + 2Cl^{-} + 2K^{+} + 2NO_3^{-} + H_2O)_{ads} \longrightarrow Ba(NO_3)_{2(s)} + 2KCl_{(s)} + H_2O_{(g)} \qquad (V)$$

CONCLUSIONS

The occurrence of the solide-state reaction (i) can be described in a satisfactory way taking into account surface nucleation, bulk nucleation and mechanical activation.

The presence of water in the system determines the occurrence of the reaction in the adsorbed surface layer.

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