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Effect of electric fields on the thermal decomposition of solids

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Abstract

After analysing some papers on the thermal decomposition (TD) of solid substances in electric field (EF) conditions the questions of regulation of the TD rate of solid substances, the development of reaction in space and decomposition mechanisms are discussed. A field mechanism of regulation of TD reactions based on zone concepts is demonstrated.

INTRODUCTION

The application of an electric field (EF) as a method of rate regulation and study of mechanisms of thermal decomposition (TD) reactions of solid substances is receiving more and more attention. One of the first reviews on this topic is that of Zakharov and Savelev [1]. Taking into consideration the existing views on TD reaction mechanisms, analyses of the effect of an EF on the TD of ionic inorganic substances through the production of physical effects are given in their paper.

Reference is made to: (1) the effect of an EF on ion and electron transport; (2) the appearance of extra charge carriers while applying an EF, owing to Frenkel and Stark effects and to electrical ionization, axiton disintegration, ionization of admixture centres, and reduction of the width of the forbidden zone Franz–Keldish effect [2]. These effects are shown for specific examples. Subsequently [3] a more detailed analysis of EF effects on the TD rate of solids was given. Particular examples of the influence of an EF on the TD of solids were considered, in addition to the ways in which the EF affects the TD rate through its influence in crystallization and hence on crystal properties, on electronic and ionic processes in solid substances, on dislocation, luminescence and phase transition, and on adsorption and surface properties. Taking into consideration the analyses performed, an unambiguous conclusion was reached as to the possibility of regulating the TD rate of solids by EF within defined limits. However, certain researchers in this field did not identify the main features of the effect of an EF on the TD of solids.

The number of new papers that has appeared during the last 10 years has changed the situation. The notion of directed regulation of chemical reactions in the solid phase has received more thorough development. Boldyrev [4] distinguished three important stages of directed regulation of solid-state reactions: (a) change in the rate of the process without topographical considerations; (b) regulation of reaction development in space; (c) change of mechanism of chemical reactions. However, detailed methods for achieving these goals were not considered in that paper. In our opinion, one of the most promising methods for this purpose may be the EF approach. The wide range of strength, frequency and power allows the use of an EF in all stages of directed regulation. Considering this, the effect of an EF on the TD of solids has been shown.

Regulation by EF of TD rate of inorganic solid substances

Let us consider examples from the literature on the influence of an EF on the TD rate of solid inorganic substances. References 5–7 are the most typical. Zakharov et al. [5] studied the influence of a constant EF on the TD of pressed (under pressure of 9 t m^{-2}) pellets of silver oxalate. The TD of $\text{Ag}_2\text{C}_2\text{O}_4$ begins by breaking the linkage between cation and anion. The disintegration products are Ag and CO_2 . Pellets of $\text{Ag}_2\text{C}_2\text{O}_4$ were placed between graphite electrodes in a reaction vessel under a pressure of 10^{-4} Torr. An EF, applied by the contact method at an intensity of 80 V m^{-1} , was supplied for 5 s during 10 minutes heating of the pellets, or acting constantly, during heating at a rate of 0.7 K min^{-1} . The change in electroconductivity was studied. It was shown that electroconductivity depends weakly on the time that the field effect lasted. At a definite temperature the electroconductivity increases sharply and flash decomposition of the sample takes place. Without an EF this flash temperature was $143 \pm 4^\circ\text{C}$ reached in $173 \pm 8 \text{ min}$; under application of an EF for a short time the temperature was $130 \pm 2^\circ\text{C}$ reached in $155 \pm 3 \text{ min}$. In other words, there was established a decrease in the temperature of the flash and the time taken to reach it owing to the EF effect. Estimates show that sample heating by the EF can be ignored. Taking into consideration that the pressure during the flash did not change in all three cases, it was concluded that the EF changes only the TD rate of $\text{Ag}_2\text{C}_2\text{O}_4$. The authors connect the EF effect with the preagitation of the axiton $\text{C}_2\text{O}_4^{2-*}$ ion or to hindrance by the field of reverse recombination, and also to agitation during the period of increased conductivity of electrons and the radicals C_2O_4^0 or C_2O_4^- . One of the drawbacks of this paper in our opinion is the random choice of EF strength, plus the contact method used for its application, which causes many side effects, such as electrolysis ($\text{Ag}_2\text{C}_2\text{O}_4^-$ ion as conductor).

Savelev et al. [6] studied the influence of an EF on the TD rate of oxalate ($T = 127, 130$ and 138°C) and silver azide ($t = 193, 204$ and 218°C) in order to establish limiting stages of decomposition by a vacuum method under changing pressure. The decomposition system had the structure from the bottom, metal–decomposed substance–Teflon (dielectric)–metal (top). It was established that, in EF the direction from bottom to top of negative charge on the upper electrode, substances decompose more quickly, and in the reverse direction more slowly, than without the field. In the case of $\text{Ag}_2\text{C}_2\text{O}_4$, the EF chiefly influences the induction period; AgN_3 has no induction period and the EF effect is weaker.

The authors consider that an EF in the sample creates a volume charge having a field opposing the external one. Assuming that the TD rate of $\text{Ag}_2\text{C}_2\text{O}_4$ is determined by the stage of decomposition of radicals



the increasing electron concentration in the conductance zone of the EF makes the TD rate diminish. A decrease in the electron concentration increases the TD because of the changing possibility of electron and hole recombination, in agreement with experimental data. This finding indicates that the limiting stage of TD of these substances may be the stage of radical decomposition. It is a pity that the meaning of EF strength is not shown in the paper. Nonetheless, it is evident that EF can be used as an instrument for studying the mechanisms of TD of solid substances.

Reference 7 is a continuation of the research in refs. 5 and 6, and covered the isothermal TD of $\text{Ag}_2\text{C}_2\text{O}_4$, AgN_3 and BaN_6 in a constant EF in the temperature range $120\text{--}150^\circ\text{C}$. The strength of the external field was 6 or 10 kV m^{-1} . The EF was applied by a contactless method (dielectric–Teflon–glass). TD kinetics were observed according to pressure change in the reaction vessel at a vacuum of $\approx 10^{-4}$ Torr. It was found that an EF accelerated the TD of all these substances only slightly. With diminishing strength the influence of the EF fell. The effect of the EF was not explained. However, the authors put forward a few suggestions, among which one — the unequal influence of the zone curving up and down on the two crystal sides — seems to us the most probable. Considering that the EF was applied by a contactless method, most of it was lost in the dielectric layer. This fact accounts for the small effect of the EF. The important omission is the absence of estimations and calculations of the EF strength reaching the actual sample, which could provide the opportunity to compare a few papers simultaneously

Reference 8 is very similar to the studies already described. The TD of $\text{Ag}_2\text{C}_2\text{O}_4$ in an EF of strength $9\text{--}10 \text{ V m}^{-1}$ was analysed by the same method. One of the field electrodes was isolated from the sample, leading

to the formation of an MDP structure (positive charge on the metallic electrode). It is shown that the kinetic curves of TD of $\text{Ag}_2\text{C}_2\text{O}_4$ in an EF are displaced towards an increase in the time at which the reaction stops, and also an increase in magnitude of the induction period; i.e. the EF diminishes the rate of TD of the sample. It was found that the kinetic curve consisted of two parts, corresponding to kinetic and diffusion regimes, and that the EF is influential only during the induction period (kinetic regime). Energy activations of the TD of $\text{Ag}_2\text{C}_2\text{O}_4$ in the kinetic regime are obtained: without a field $E_a = 41 \pm 5 \text{ kcal mol}^{-1}$, and in a field $E_a = 55 \pm 5 \text{ kcal mol}^{-1}$. In the diffusion regime the activation energy in and without a field is practically the same, and equals to $40 \pm 5 \text{ kcal mol}^{-1}$. The absence of an EF effect is connected by the authors with the change in distribution of charge carriers, with the result that the sample acquires a volume charge. The external EF leads to curvature of the conduction zones and valency zones in the region of the volume charge (RVC). Taking into consideration that the curving of zones in the RVC determines the Fermi level (the Fermi level in the RVC is the intensity function of the EF), the authors explained the TD reaction rate on the sample surface as indicating that TD of $\text{Ag}_2\text{C}_2\text{O}_4$ begins from the surface. The obtained equation for the reaction rate of TD from the magnitude of zone curving satisfactorily explains the lowering of the TD rate of silver oxalate by the EF. The absence of field influence on the rate of TD of $\text{Ag}_2\text{C}_2\text{O}_4$ in later reaction periods is explained by screening of the EF by reaction products, i.e. metallic silver. The model of EF effect on the TD rate of $\text{Ag}_2\text{C}_2\text{O}_4$ shown in this paper cannot explain TD acceleration for this substance at lower EF strength, as was shown in refs. 5–7. The shortcoming arises because the authors made a wrong supposition, that the zone-curving on positively and negatively charged surfaces is the same. After taking account of this factor, the suggested model of EF influence on TD of solid substances is in our opinion very useful for contactless application of the field.

De Panafien et al. [9] studied the influence of a constant EF on the TD in the temperature range 500–540 K of single crystals and powder of potassium azide. An EF of strength 100 V m^{-1} was applied for a short time (3.5 min) perpendicularly to the sample in a contact mode. In the course of research, the dependence of the degree of decomposition on time was found to be determined according to equilibrium pressure changes in the reaction cell. It was shown that the EF effect was small. An EF influence was found for both signs of the potential on the sample surface, but the EF effect was greatest on the positively charged surface. The use of a mesh type field electrode caused the decomposed sample surface to acquire a mesh configuration. The authors assumed that the EF disturbs the charge equilibrium between surface and volume by change of the charge on the surface layer of the sample, which causes polarization of molecular groups on the surface.

Rajeshwar et al. [10] used the method of differential scanning calorimetry (DSC) for studying the TD of KMnO_4 and NH_4ClO_4 in a constant EF in a flow of dry nitrogen (flow rate 500 ml min^{-1}) with a heating rate of 10 K min^{-1} . The EF was applied in a contact mode perpendicular to the sample, using platinum and gold electrodes. It was shown experimentally that the exothermal temperature peak for KMnO_4 in an EF (strength 200 kV m^{-1}) increased approximately 10 times and shifted 65°C towards a lower temperature in comparison with a control sample without an EF. Change in direction of the EF did not influence the effect. The authors observed the dependence of the onset of the temperature peak T_e in DSC on the strength for KMnO_4 . With increase in EF strength to 400 kV m^{-1} T_e decreased exponentially. The average value of T_e at 100 V m^{-1} was 0.03 . Additionally, for NH_4ClO_4 in an EF of intensity 100 kV m^{-1} , T_e was decreased by 25°C , and the exothermal peak increased 1.5–2.0 fold.

Similar studies performed on KClO_4 , $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and NaN_3 showed that the EF effect depends on the nature of the studied material. The effect of decreasing T_e is determined by the charge shift in the early stages of TD. For KMnO_4 this involves an electron jump from one anion to another, and for NH_4ClO_4 it means electron and proton transfer. It is noted that local heating of the substance may occur, owing to the contact method of EF application, and is difficult to estimate. It can cause a shift which makes the analysis of results more difficult and its value lower.

Verneker et al. [11] studied the influence of a constant cross EF on the TD of pressed and single crystal samples of ammonium perchlorate (PCLA) in isothermal conditions. The observed changes of sample mass in the process of TD of PCLA at $T = 230^\circ\text{C}$ in an EF of strength 100 V m^{-1} during 1 h corresponded to 140 h of sample processing in the same EF at $T = 150^\circ\text{C}$; at an EF strength of 50 V m^{-1} the time of heating was much greater. It was found that the degree of decomposition of PCLA at 230°C on the side of the negative electrode was higher than on the side of the positive electrode. The conclusion was thus reached that an EF at a different temperature influenced the transfer of different charges: at 230°C , negative charges of ClO_4^- ; at 150°C , positive charges, which may be H^+ or NH_4^+ . The same authors later [12], using the same method, observed TD of a fuel mixture of PCLA–polystyrene (PCLA–PS) under the same temperature and EF conditions. It was shown that an EF decreases the temperature of TD of the PCLA–PS mixture. A change in EF for this mixture was also observed, as it was for pure PCLA. The kinetic research shows two mechanisms of TD of orthorhombic PCLA with activation energies 15 kcal mol^{-1} (150 – 180°C) and 30 kcal mol^{-1} (180 – 230°C). Despite the fact that the mechanisms of the EF effect on the TD of PCLA were not studied by the authors, the results obtained are very important for application of EF methods for determination of the charge transferred during TD. Macken-

zie and co-workers [13–20] performed a number of studies on the EF effect on TD of solid substances. In ref. 13 the TD of powders and single crystals of CaCO_3 in a constant cross EF was observed with use of X-ray diffraction and X-ray photoelectron spectroscopy (ESCA). Thermolysis of the samples was carried out isothermally at a temperature of 850°C during heating from $600\text{--}1000^\circ\text{C}$ in an EF (field strength $4.2 \times 10^4 \text{ V m}^{-1}$). Reaction time and the duration of EF application in contact mode using platinum mesh electrodes was 0.5 h. It was found that the degree of reaction increased more markedly on the side of the positive electrode. The results are explained on the basis of estimation of the electroadsorption effect of CO_2 on the sample surface using the electron theory of catalysis by semiconductors [21]. In ref. 14 Mackenzie studied the kinetics of dehydroxylation of pseudoboehmite ($\alpha\text{-AlOOH}$) in an EF using an electrolysis cell with platinum mesh electrodes. The kinetics of TD of pseudoboehmite were studied by observing the change in sample mass on the thermal analyser at heating rates of $6\text{--}10 \text{ K min}^{-1}$ from room temperature to 1160°C in the ambient atmosphere. It was found that, when the field strength increased to $2.35 \times 10^6 \text{ V m}^{-1}$, the initial reaction temperature decreased, and the TD rate increased considerably at the negative electrode. The energy of activation of TD in the EF changed only slightly; thus, at a negatively charged surface $E_a = 94 \text{ kJ mol}^{-1}$, and at a positively charged one $E_a = 89 \text{ kJ mol}^{-1}$, and at an uncharged surface $E_a = 81 \text{ kJ mol}^{-1}$. The dependence of the rate constant of dehydroxylation of pseudoboehmite on the field strength at positively and negatively charged surfaces has been obtained. At first, with the field strength increasing to $1 \times 10^6 \text{ V m}^{-1}$, the rate constant decreases 1.2–1.3-fold then it increases, reaching on the positively charged surfaces its initial value, and on the negatively charged surface 1.5 times its initial value. In the author's opinion, the mechanism of the EF effect is connected with the removal of hydrogen from the molecule and proton migration to the cathode, where they discharge and can enter the structure of the decomposition products and stabilize them.

While researching the effect of an EF ($3.2 \times 10^5 \text{ V m}^{-1}$) applied to allophane ($\text{Al}_2\text{O}_5\text{Si}$) pellets [15] with heating from $600\text{--}750^\circ\text{C}$ in a dynamic atmosphere of oxygen-free nitrogen (flow rate 1 l min^{-1}) a change in the TD rate was detected. Pellets of allophane, 10 mm in diameter and 4.5 mm thick, were pressed at 500 bar. It was shown that the change of TD rate is connected with the formation and transfer of protons of the remaining water towards the negative electrode, where they too discharge, as in ref. 14. The result is that the content of crystalline product increases, as can be measured from both sides of the pellet and in the volume of the material, by the method of X-ray diffraction. The degree of TD reaction depends more on the direction of inert gas flow than on the electrode polarity. In the initial stage the product formed is mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Products at other stages include kyanite (Al_2SiO_5), which further reacts with the Ca

impurity, forming anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and transferring into a disordered mullite-like phase, which appears at the positive electrode only. It is shown that the EF does not affect the outcome of the reactions, or the crystallization and microstructure of the products. Work similar to that in ref. 15 comprises other research by the same author [16,17]. The formation of Portland cement clinker at $t = 1200^\circ\text{C}$ and constant EF was studied by the X-ray diffraction method in ref. 16. The EF, applied as in ref. 15, was changed from 0 to $2.5 \times 10^5 \text{ V m}^{-1}$. The time of reaction and EF application was 2 h. It was found that samples burnt in the presence of an EF contained increased amounts of $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}_2\text{AlFeO}_5$, mostly at the positive electrode, where the expenditure of CaO was also higher. It was shown that the EF noticeably influences the TD of CaCO_3 (the initial material), especially at the positive electrode. The temporal dependences of formation temperature of different phases presented very complicated curves, which could not be kinetically analysed. However, the curves allowed the determination of reaction rate constants of TD in an EF and without it. It was shown that the expenditure of CaO in clinker formation was raised by the EF, but in the presence of $\beta\text{-Ca}_2\text{SiO}_4$ such expenditure decreased.

In this connection, the increased formation of other phases due to $\beta\text{-Ca}_2\text{SiO}_4$ is seen. With increasing temperature the phase content of $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}_2\text{AlFeO}_5$ in an EF is less evident. The theoretical studies of the EF effect on the reactions on which the formation of Portland cement clinker are based show [17] that an EF may cause the generation of active oxides from the raw components of the mix and their combination to form the various clinker phases. The EF effect observed in reactions of clinker formation is explained, in Mackenzie's opinion, by a simple model which takes into consideration the difference in diffusion and electrical mobility of various ions which diffuse through the oxygen packing of the matrices, and the relative orientations of the reactant particles with respect to the field direction.

Mackenzie [18] developed a method for the thermogravimetric study of solids in the presence of an applied EF, which has been used in a study of the dehydroxylation of kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] in an argon flow (300 ml min^{-1}) in the electrolysis cell during heating from $400\text{--}600^\circ\text{C}$ at a rate of 2 K min^{-1} . An EF ($1 \times 10^5 \text{ V m}^{-1}$) applied in contactless mode via platinum electrodes decreases the initial reaction by over 60 and decreases the activation energy by $3\text{--}12 \text{ kcal mol}^{-1}$. The reaction rate constant increases in an EF, but at high temperatures this effect is weak, as normal thermal processes prevail. The author assumes that these effects are caused by the growing possibility of tunnelling and mobility of ions. The effect of a directed inert gas flow is observed, which changes the concentration gradient of water vapour across the sample. The same method was used to study the EF effect on the thermal dehydroxylation of $\text{Mg}(\text{OH})_2$ (brucite)

and $\text{Al}(\text{OH})_3$ (gibbsite) at temperatures of 200–500°C [19]. It is noted that a field strength of $1 \times 10^5 \text{ V m}^{-1}$ has practically no effect on the TD reaction of gibbsite. However, a slight effect is observed for the TD of brucite in the same EF, whereby the initial temperature and the activation energy are decreased. Differences found in the behaviour of these two hydroxides correspond to the various mobilities of anionic defects and oxygen-containing proton-transfer complexes. For the explanation of the results obtained in refs. 18 and 19 on the EF effect on the reaction rate of dehydroxylation of $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$ and kaolin, the model [20] is used for splitting energetic levels in symmetric and asymmetric potentials with a double minimum in an EF. The tunnelling probability of protons is as for excited and not excited potentials. Tunnelling probability is increased weakly by an EF (10^5 V m^{-1}). A considerable increase takes place if a symmetrical potential becomes asymmetrical. It is shown that the tunnelling process is too fast to explain the observed differences during reactions of dehydroxylation of $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$ and kaolinite in an EF.

We studied the effect of a.c. and d.c. EF on the TD rate of potassium permanganate [22,23]. The EF effect at the initial stage of TD is especially well observed, when the process develops on the surface. It is shown that the reaction rate of TD reaches its minimum on raising the field strength to 310 kV m^{-1} for KMnO_4 and to 240 kV m^{-1} for CsMnO_4 . In the EF strength intervals from $310\text{--}775 \text{ kV m}^{-1}$ ($240\text{--}750 \text{ kV m}^{-1}$) the TD rate of KMnO_4 (CsMnO_4) is practically constant. Further increase in the field strength by 160 kV m^{-1} increases the TD rate to attain the initial value. Thus the TD rate of KMnO_4 decreases 3.0–3.5-fold and that of CsMnO_4 2.5–3.0-fold. The application of variable EF with frequency from 50 Hz–200 kHz and field strength up to $1 \times 10^6 \text{ V m}^{-1}$ has practically no influence on the TD rate of permanganate. The change of TD rate of KMnO_4 and CsMnO_4 at constant EF is explained by the model of changing zone curve of EF in the layer next to the surface.

EF regulation by the development of TD reactions in space

The work of Laptanov et al. [24–27] can serve as a good example of space regulation of an EF by TD reaction owing to the change of formation and growth of nuclear rate of the new phase. As is shown in [25], space regulation may take place through (a) change of properties of the given solid reagent; or (b) change of the conditions of process development. The latter route is more probable for EF. In ref. 24, using the method of optical microscopy in combination with thermogravimetry, the EF effect on kinetics of TD of orthorhombic single crystal PCLA at 200–235°C in air was studied. The application of an external EF led to a change in the linear centre growth rate of decomposition and the initial reaction rate, as determined by the mass loss. The EF effect was studied in two field

orientations: $E \parallel \langle 010 \rangle$ and $E \parallel \langle 100 \rangle$. For $E > 400 \text{ kV m}^{-1}$ an increase in the linear rate of centre growth was accompanied by an increased initial rate of decomposition in both field orientations. After formation of an unbroken reaction front, the EF effect on the kinetics of TD is absent. For $E > 4 \text{ kV/sm}$ the TD kinetics of PCLA depended on the strength and the volume and space orientation of the EF towards crystallographic directions of PCLA. In orientation $E \parallel \langle 100 \rangle$ the observed regularities are analogous to the case with $E < 4 \text{ kV/sm}$. However, for $E \parallel \langle 100 \rangle$, the EF causes an increase in the decomposition rate of PCLA, both at the stage of development of reaction centres and at the stage of movement of the reaction front inside the crystal. Formation of the reaction front occurs owing to the appearance of new centres. The form of these centres in an EF becomes less orderly, which shows the possibility of changing the form of the EF embryo. This is in accordance with the theoretical work of Boldyrev and co-workers [4,28]. The authors assumed that an EF effect depending on the crystallographic direction of PCLA can be produced in two ways: (1) EF action on the charged boundary dislocations through direct action or on the centres where they are retained; (2) EF change of the condition of proton transfer in the crystal lattice.

Laptenkov et al. [25] also studied the TD of single crystals of PCLA in the cubic modification in a space EF of field strength up to 800 kV m^{-1} in ambient air in the temperature interval $250\text{--}290^\circ\text{C}$, using the same method. Taking into consideration that decomposition centres of PCLA exist in two types: (1) centres of partial decomposition, the formation and growth of which accompany dislocations; (2) centres of full decomposition, the growth of which takes place in the liquid phase, it was demonstrated that a greater EF effect takes place at the stage involving dislocations. A more noticeable increase of centre growth rate of type 1 was observed in the direction $\langle 010 \rangle$ with an EF orientation of $E \parallel \langle 010 \rangle$. The EF did not greatly affect the centre growth rate of type 2. It is shown that in the TD of PCLA there appears a considerable EF effect, chiefly at the initial stages of decomposition under field orientation $E \parallel \langle 010 \rangle$, in the form of a decreasing induction period and an increased initial decomposition rate.

The explanation of the EF effect in the kinetics of TD of PCLA through cubic modification is given in terms of the dislocation growth model of reaction centres. The authors think that the cause of increasing centre growth of type 1 (dislocation centres) on applying an EF is an increase in the sliding rate and the length of run of the leading dislocation in ionic crystals owing to coulombic interaction between the external EF and charged dislocations of boundary type. In favour of such a nature is the fact that considerable increase in the rate of centre growth of type 1 was observed only in one direction, along $\langle 010 \rangle$. Lowering of the observed effect during the development of the reaction zone may be caused by electrical scanning of the part of the crystal with a centre of type 1 in the

liquid phase, covering the inner surface of the centre cavity of type 2. The decrease in the induction period of TD of PCLA in an EF is connected, in the authors' opinion, with the increasing dislocation concentration because of mechanical strength during the evolution of gaseous products when a strong EF affects the crystal.

Further developments of the ideas about the mechanism of EF effects on TD of PCLA were given in refs. 26 and 27 by Laptentkov and co-workers. It was established, that the formation and growth rate of reaction centres without EF is 10 times as prevalent in the direction $\langle 010 \rangle$ as in directions $\langle 100 \rangle$ and $\langle 001 \rangle$. Application of an EF causes an additional increase by 1.5 times in the growth rate of centres in direction $\langle 010 \rangle$, which is shown with the help of a microphotograph of the surface. There was observed a considerable EF effect in the direction $E \parallel \langle 100 \rangle$ with $E > E_{cr}$ ($E_{cr} = 480 \text{ kV m}^{-1}$), much less than under EF orientation $E \parallel \langle 010 \rangle$, with a decrease in the induction period and an increasing surface density of reaction centres. A reaction front was formed in that case, mostly as a result of the appearance of new centres of reaction. In this way the anisotropic character of the EF effect on TD of PCLA was established. The increase in growth rate of centres of decomposition for $E \langle 100 \rangle$ was analysed by the authors on the basis of ideas about the reorientation by an EF of local centres of breaking of dislocations, which can be associated with anionic or cationic vacancies or separate double-field vacancies of the type " H_3O^+ -cationic vacancy".

The papers discussed [24—27] point to the principle of the possibility of regulation by a strong EF of the space form of reaction centres, in addition to the consequences and kinetics of chemical changes in solids which take place with participation of dislocations.

EF regulation of the mechanism of TD reactions of solids

The work of Berdov et al. [29,30] provides a good example of the directed regulation of reaction development of TD due to changes of reaction mechanism. The authors studied the effect of a high-frequency (h.f.) field (40.68 MHz) with maximum power 4 kW on the TD of sodium hydrogencarbonate and Al-K alums [29]. The h.f. field was applied only during the last 1–5 minutes of TD. It was shown that a h.f. EF accelerated the TD of these substances, and this accelerating influence was directly dependent on the time of EF action and its power. It is noted that the EF effect is stronger for the compounds containing larger fragments of particles. It was assumed that the accelerating h.f. EF effect is connected with the energy absorption of the field by the solids. A dielectric study in the frequency range 10^5 – 10^7 Hz of the process of TD of solids proves it; in this study the maximum of tangent of dielectric losses was determined which in the authors' opinion leads to the breakage of chemical linkages and thus changes the mechanism of TD. It is pity that there is no discussion of the

method of measurement of the heating effect of the h.f. EF, which lessens the importance of this work to a great extent.

Berdov et al., using the analogous method, also studied the TD of technical gypsum [30], containing about 80% of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in a h.f. EF for 15 min. An accelerating effect of the h.f. EF on the dehydration of gypsum was revealed. This accelerating effect increased particularly with increase in the field power. The time for full conversion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ into $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ without an EF was 47 minutes; that with a h.f. EF with anode current of 0.4 A (the anode current characterizes the EF power) was 32 minutes, and that when the anode current was 0.6 A was 22 minutes. In other words, the TD rate was increased more than 2-fold. It was noted that an EF of maximum power 4 kW acting for 3 min, had the same effect as 105 min of additional heating in a thermostat at the same temperature without the EF. In refs. 29 and 30 it was noted similarly that, with increasing h.f. power of the EF, the accelerating effect on the TD of NaHCO_3 became greater. It was estimated experimentally that the sample temperature changes by 6–7°C owing to the h.f. EF. The authors assumed that, together with the heating effect, the h.f. EF caused a specific effect. It was postulated that the EF activates separate local areas of the solid, the nature of which was not studied further.

One of the most interesting papers by these same authors relates to research on the h.f. EF effect at the same frequency on the TD of Al–K alums and lead oxalate [32]. A h.f. EF was applied to $\text{KAl}(\text{SO}_4)_2$ at $t = 60^\circ\text{C}$, and to PbC_2O_4 at $t = 260^\circ\text{C}$. A considerable effect of the h.f. EF was seen only at high power. To minimize the heating effect, there was used a h.f. EF of such power and duration that the temperature was constant to the end of field action. The time of action of the h.f. EF was 1.5–5 min. It was shown that a h.f. EF greatly accelerates the dehydration of alums. Thus, 5 min at a h.f. EF power of 2 kW had the same effect as additional thermal heating for 60 min. The kinetic analysis of the process of TD of alums in a h.f. EF showed that the process moves from the kinetic to the diffusional regime. The TD of lead oxalate was conducted in a h.f. EF at a maximum output power of 70 W. The increase in rate of the TD of PbC_2O_4 was determined. The accelerating effect of a h.f. EF was evident at the temperature corresponding to the beginning of chemical reaction. In agreement with our work [3], the authors showed that, in the TD of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and PbC_2O_4 , a h.f. EF seems to influence the point and linear defects of the crystal lattice in addition to the growth of the diffusion coefficient.

It was assumed that the h.f. EF energy is absorbed by the structural defects, which leads to their additional excitation and consequently to acceleration of the rate of TD.

The shortcoming of all the papers on the h.f. EF effect on the rate of TD of solids is the absence of any study of the mechanism of the field effect,

and this is the most important problem. The kinetic analysis of TD reactions of solids in a h.f. EF shows that there are two mechanisms of TD: (a) thermal, and (b) field.

Of some interest for analysis of the EF effect on the TD of solids is the specific effect of a strong EF, the general regularities of which were studied by Sukhushin and Zakharov [33]. They carried out a review of experimental results on the decomposition of solid thermodynamically labile substances under the influence of a strong EF. Apart from TD in an EF, under EF decomposition electrons and holes are injected into the solids where they interact with the substance. It is shown that EF decomposition is not observed under equilibrium conductivity according to Ohm's law. However, if Ohm's law is broken, e.g. N-peculiarity of volt-ampere characteristics appears, decomposition is observed which increases strongly even when a general current level is maintained. In the realization of electric field decomposition, non-equilibrium conductivity (non-conformity to Ohm's law) plays an important role. The transfer of the system into the non-equilibrium condition can occur by two routes: (1) exciting the subsystem of charge carriers; (2) excitation in the EF of the constituent elements of the crystal lattice—the ionic and molecular subsystems. The activation of the charge carriers can be conducted as concentrated non-equilibrium, when the carrier concentration injected into the crystal exceeds greatly the concentration of equilibrium carriers in the lattice. The activation of carriers can take place through the carriers being retained by positively and negatively charged traps. Thus their effective charge is compensated and the reaction may take place practically inactively. If the energy of the charge carriers is increased (hot carriers), they can react with the crystal lattice and its components to cause ionization processes. Space-time organization of the electron and hole movement with high energy causes the formation of domain and flex electrical instability. The development of these types of instability can result from the instantaneous increase of reactivity by heating or from the multiplication of chemically active carriers under forced ionization. Examples of these mechanisms of transfer into the non-equilibrium state were studied [33] for the system AgN_3 and NH_4ClO_4 , for which electrofield decomposition was observed; this is a new class of solid-phase reaction.

It is evident that in a strong EF the TD of solids will involve electric field decomposition in its mechanism, so complicating the situation greatly. Nevertheless, in our opinion, the use of a strong EF or of a h.f. EF will allow regulation of the mechanism of TD of solids. It is regrettable that electric field decomposition is not yet used for the regulation of TD reactions of solids.

Taking into consideration the work analysed here it is possible to draw an unambiguous conclusion concerning the directed regulation of TD

reactions by an EF through change in the process rate, change in the reaction development in space, and change of the reaction mechanism.

Field mechanism of rate regulation of TD of solids

In the papers discussed above that deal with the EF effect on the TD of solids, the mechanism of the field effect has been subject to almost no study. The reasons for this are: (a) mechanisms of reactions of TD of solids have not been studied; (b) the choice of field strength and frequency is not systematic.

In this respect we have used an approach which does not depend on either the mechanism of TD or the choice of field parameters. It is the field mechanism from the viewpoint of zone concepts. The possibility of using such a model was referred to in refs. 3, 6 and 8. The fact that an EF influences mainly the initial stages (induction period), when the process develops only on the sample surface, is in favour of the model.

An external EF changes the distribution of charge carriers, and as a result the sample acquires a volume charge. The internal EF induced by this charge is described by the Poisson equation [34]. Application of an EF leads to curvature of the valence zone and conduction zone for the sample surface. Under a positive charge the zones curve up, and under a negative one they curve down. These changes take place virtually only in the surface region, disappearing at distances greater than the length of Debye screening. In consequence the distance of the Fermi level from the conduction zone is a function of EF strength

$$F_s = F_s(E) \quad (2)$$

Under positive charging of the surface the distance of the Fermi level depending on the conductivity zones increases

$$F_s^+ = F_v + y_s^+ \quad (3)$$

where F_v is the Fermi level in the crystal volume, and y_s^+ is the value of curvature of the zones on the positively charged surface, which is a function of EF strength. With negative charging of the surface this distance decreases

$$F_s^- = F_v - y_s^- \quad (4)$$

Reaction rates on the positively and negatively charged surfaces, corresponding to the electron theory of catalysis by semiconductors and taking into consideration the basic electron transfer, are described by the equations [21]

$$V_+ = K' \exp \left[- \frac{W - (F_v + y_s^+)}{kT} \right] \quad (5)$$

$$V_- = K' \exp \left[- \frac{W - (F_v - y_s^-)}{kT} \right] \quad (6)$$

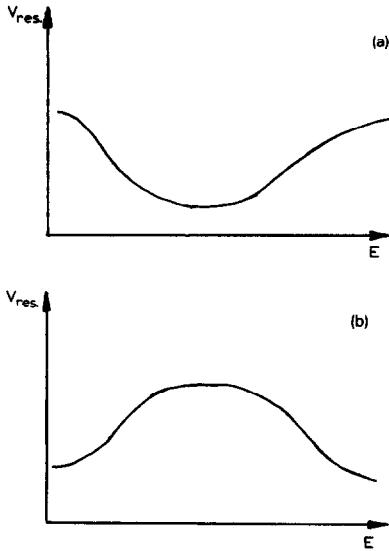


Fig. 1. Dependence of the resulting TD reaction rate of solids on EF strength for (a) n-type and (b) p-type conductivity of samples.

where K' = rate constant (its structure is determined by the particular TD mechanism); k = Boltzmann's constant; W = level energy, and V_+ , V_- = reaction rates on the positive and negative surfaces. The resulting rate is determined by the formula

$$V_{res} = K'' \exp\left[-\frac{W + F_v}{kT}\right] \left\{ \exp\left[-\frac{y_s^+}{kT}\right] + \exp\left[\frac{y_s^-}{kT}\right] \right\} \quad (7)$$

The analysis of this expression for the samples with n-type and p-type conductivity gives the following picture (Fig. 1a and 1b). With low EF strength there will be only the first branch of these curves. At high values of EF, taking into consideration the inversion zone curve, the second branch of these curves appears.

There are virtually no papers in which the dependences of the reaction rates of TD of solids on EF strength have been obtained. Thus, in ref. 8 it is shown only qualitatively that an EF slows the process of TD of silver oxalate. In ref. 15 the dependence of the rate constant of TD of pseudoboehmite on EF strength on the negatively and positively charged surfaces at 325°C was obtained (Fig. 2). We obtained [22,23] the dependence of the rate constant of TD of potassium and caesium permanganates on EF strength (these permanganates have n-type conductivity) (Fig. 3).

The results from these papers are qualitatively well described by the suggested model. To test the given model, new experimental studies of TD reactions in an EF are necessary. The model, taking into consideration the conductivity types of the decomposing substances and the EF strength,

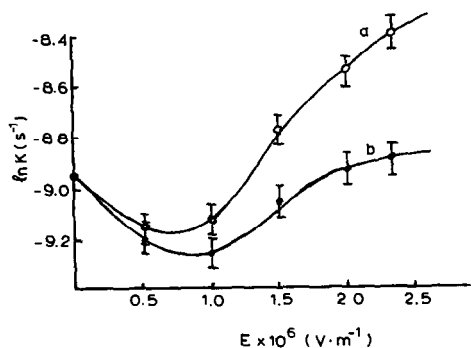


Fig. 2. Dependence of TD rate constant of pseudoboehmite on EF strength on negatively (a) and positively (b) charged surfaces.

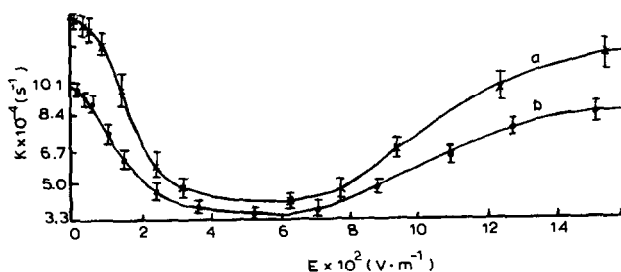


Fig. 3. Dependence of TD rate constant of potassium permanganate (a) and caesium permanganate (b) on EF strength at $t = 220$ and 240°C , respectively.

allows one to forecast the acceleration or slowing of TD of solids by an electric field.

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