TOPOCHEMISTRY OF THERMAL DECOMPOSITIONS OF SOLIDS

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ABSTRACT

This survey systematically considers the factors responsible for localization and autolocalization of thermal decomposition processes of solids. The specificity and complexity of nucleation and nuclei growth in topochemical processes are shown.

INTRODUCTION

The thermal decomposition of solids is a large field of chemistry. Its importance for the development of the theory of solid-state chemical reactions can scarcely be overestimated, since it is thermal decomposition reactions for which the first model studies in solid-state chemistry were made. At the same time, thermal decomposition — a process widely used in industry — is the most important and inherent part of technology in the production of various materials from building materials to catalysts, in the processing of a mineral raw material at the stage of its primary chemical treatment. The fundamentals of thermal decomposition are the basis for determining the stability of the components of rocket propellants and explosives. This list of applications of thermal decomposition processes is being extended more and more.

The author of the paper has devoted more than thirty years to the study of thermal decomposition processes. Now, accepting the kind offer of Professor W.W. Wendlandt to write an article for the jubilee issue, I would like to take this opportunity to glance back, to look at the traversed path, at everything what we — my colleagues in the laboratory and I — have succeeded in doing in this field.

The character of memoirs of this article may be excused since when this issue is out, I shall be sixty — the age from which people have an inclination for writing memoirs, an occupation which I treated earlier with critical contempt.

Since the well-known proverb "All the new is the old well forgotten" has

not lost its significance up to now, I hope that a consideration of the logic of our approach and the ways of solving the problems in the field of thermal decompositions of our successes and mistakes may be useful at present, in spite of the obvious fact that the means of investigation and the statement of the problem have changed. It particularly concerns those who are entering or have just entered this field of chemical science where, in spite of considerable successes, many aspects remain unclear.

As for the state of the problem by the time when we started our investigations, i.e., by the end of the forties, that time may be considered to be the time of formation of the theory of topochemical processes, a particular case of which are the majority of thermal decomposition reactions.

By that time the classical works of Langmuir [1] were already known, in which he convincingly showed that when, in the process of thermal decomposition of a solid, a solid product is formed, the reaction should be expected to proceed mostly at the interface between the two solids.

This questioned the possibility of a simple transfer of notions and concepts from common chemical kinetics on the systems under study and, in particular, the right of using first- and second-order kinetic equations in describing these processes. One of the first kinetic equations had been derived, which took into account the heterogeneity of the process of thermal decomposition [2] $(\mathrm{d}\alpha/\mathrm{d}t = K\alpha^n)$. It had been shown that, in contrast to usual homogeneous kinetics, the order of the reaction not only characterized the peculiarities of the elementary act, but also, if it may be said so, the extent of "submersion" of the reaction into heterogeneity. Thus, the zeroth order indicated primarily that the course of the process was similar to the course of evaporation from the surface, the area of which remained constant with the progress of the process; an order equal to $1/3$ or $1/2$ meant a considerable significance of the diffusion processes; an order equal to $2/3$ was considered as evidence for the reaction proceeding in the kinetic range; an order not equal to unity was believed to be a criterion that the probability for participating in the reaction is approximately equal for all regions of the bulk of the solid.

Taking into account a change of heterogeneity and complications related to the reversibility of the reaction with the progress of the process, Zavadsky and Bretsznaider [3] succeeded in finding the proper values of activation energies for the thermal decomposition of carbonates. Approximately at the same time, papers by English scientists appeared where it was shown in the instance of dehydration of crystalline hydrates that the decomposition reactions start with the formation of reaction nuclei, followed by their subsequent growth and that a correct kinetic description of thermal decomposition requires a simultaneous consideration of the progress of all these processes with time [4–6].

At the same time, many investigators took a great interest in describing their experimental results by kinetic equations derived on the basis of

various physical assumptions. Among these equations are, for example, the equations of autocatalysis, a reducing sphere, and Avrami–Erofeev which were the most popular at that time. The physical model of the last equation corresponded, strictly speaking, not to the progress of a chemical heterogeneous reaction, but to the solidification of a melt. It appeared that, in contrast to the common concepts of classical chemical kinetics, in the kinetics of solid-state processes the only coincidence of experimental data with a kinetic curve, constructed on the basis of one physical model or another, was not sufficient to prove the mechanism, and that the final conclusion on the detailed mechanism, especially at the level of its elementary stages, might be drawn only after additional data were obtained by independent and direct methods.

Due to the specific character of the course of topochemical processes (most thermal decomposition reactions belong to this group of processes), when carrying out kinetic analysis the progress of the process not only in time but also in space coordinates should be taken into account. This makes the problem of kinetic analysis much more complicated than it is in common chemical kinetics.

As is well known, in the case of chemical reactions occurring in liquids or gases, the rate of reaction is a function of the concentration of reactants taking part in the process

$$\frac{d\alpha}{dt} = K\alpha_1\alpha_2\alpha_3 \ldots \alpha_n$$

and the task of kinetic analysis is usually confined to finding a functional dependence of the rate on the concentration (the order of reaction) and the value of the reaction rate constant. Knowing the rate constant and its temperature dependence, it is possible to obtain the value of the activation energy of the process and pre-exponential factor in the Arrhenius equation. After these values are known, conclusions may be drawn on the nature of the elementary stages of the process [7].

For heterogeneous reactions occurring not in the bulk of the system but in some part of it, it is essential to distinguish this part and to normalize the rate of the process by this value. For example, in the case of a catalytic process, it is necessary to divide the rate by the size of the surface of the catalyst on which the catalytic reaction proceeds.

$$\frac{d\alpha}{dt}\frac{1}{S} = K\alpha_1\alpha_2\alpha_3 \ldots \alpha_n$$

In the case of topochemical processes, the size of the surface (or, since the surface in question may not be smooth, but some layer, speaking more strictly, the size of the reaction zone) changes with the progress of the process. Therefore, before the specific rate of the reaction and, hence, the rate constant may be determined, it is necessary to find a function describ-

ing the change of the reaction zone with time.

In the general case, the size of a reaction zone at a given instant of time may be calculated if we know the number of reaction nuclei present by the time $t = y$ and the rate of their growth in the range $y-t$.

An expression for the size of a reaction zone can be represented in general form as a certain function:

$$\int_0^t \sigma \left[\int_y^t g(x) dx \right]^x \left[\frac{dN}{dt} \right]_{t=y} dy$$

where σ is the factor of the form which allows for passing from the bulk of the substance which has reacted to the size of the reaction zone, $g(x)$ is a function describing the nuclei growth, and dN/dt is the rate of their appearance at potential centres of the reaction (the nucleation rate).

Only after the problem of the evolution of the reaction zone with time is solved (these problems in the kinetics of chemical heterogeneous reactions were given a special name: "topokinetic") can the value of the specific reaction rate be found and, hence, the reaction constant be determined [8,9]. Microscopic observations applied to investigations of the kinetics of the process made it possible to construct real kinetic models of the thermal decomposition of solids. Besides, important observations were made concerning the structure of the reaction zone separating the initial substance and the reaction product, these observations allowing a representation of this zone not as a planar interface as it had previously been considered, but as a certain layer with distinctive structural, chemical and thermodynamic properties. The specific character of this layer is particularly pronounced in the dehydration of crystalline hydrates on which, as far back as the end of the thirties and the beginning of the forties, although experimental possibilities were obviously limited at that time, the main ideas were formulated, which led to many scientific trends being developed after the war. I could cite as an example the works of Slonim [10] who anticipated our contemporary ideas of topotaxy and formation of the so-called vacancy structures in the process of thermal decomposition [11–16] as long ago as the beginning of the thirties. Another example might be a study of the effect of the heat evolved or absorbed within the reaction zone on the kinetics of a process. These studies showed that self-heating or self-cooling at the interface between the starting substance and the reaction product may reach an appreciable value (up to several tens of degrees Celsius) and this factor should be taken into account if we wish to find the real value of the rate constant of the process [15–18].

Experimental data had been obtained which showed a connection between the pre-history of the crystals of a solid and their reactivity in the decomposition reactions. It appeared that the kinetics of the process of thermal decomposition for one and the same substance may be quite different depending on the way of its preparation, storage conditions and

preliminary treatment. In contrast to liquids and gases, a solid turned out to have a good memory [19], which makes chemical solid-state processes essentially different from classical kinetics of the processes occurring in liquids and gases.

It was necessary to take this into account when studying the kinetics of the processes.

In the chemistry of solid state by that time, the classical works of Hedvall [20] were already known, in which he showed that the state of the lattice of a solid, which may be changed, for example, at the moment of phase transition, essentially affects the reactivity of the crystal.

All this led to the idea that in a crystal along with atoms, ions and molecules, occupying normal sites in the lattice, distinct sites also exist where for some reason the conditions for a change in crystal composition or structure are facilitated. The reason for this facilitation might be one of many: it may be, for example, due to a decrease in the well-known "cage" effect, favouring the progress of the reverse process; a local decrease in activation energy for the cleavage of chemical bonds; or better steric conditions for structural rearrangement. The sites in the crystal where the reaction is facilitated are called "potential centres", and the effect that the reaction may start not in the whole bulk (nor on the whole surface) but at distinct sites in the crystal is called "localization of the process".

LOCALIZATION OF THE PROCESS

It is quite obvious that without revealing physico-chemical causes leading to localization of the process in topochemical reactions and without a detailed study of autolocalization of the process (i.e. the capacity of the reaction to continue its progress near the site where the reaction has already started) it is impossible to approach a study of its mechanism at the level of elementary stages. Therefore, one of the main aims of our research at that time was to understand the causes of localization and autolocalization of processes of thermal decomposition. In the literature of that time the potential centres leading to localization of the process of thermal decomposition, as well as in the case of other topochemical reactions, were associated with the real structure of the crystal, with the presence of defects in it. However, in accordance with energetic concepts of real structure which predominated at that time (the theory of active states [21], the theory of supersaturation [22,23]), it was thought that since any kind of defect in some way leads to the accumulation of energy in the system and hence to the departure of the system from equilibrium, accumulation of any kind of defect in the crystal must always result in its increased reactivity. This is the reason for using integral quantities, such as heats of dissolution, degree of amorphization of structure, to estimate "activity".

However, the studies which we carried out at the end of the 1950 established that this was not true and that the character of the effect of defects on the rate of topochemical reactions depended strongly upon the mechanism of the process [24–28]. In particular, for the reactions of thermal decomposition of solids, it was shown that they can be conventionally divided into two groups. The first group includes reactions in which the rupture of a chemical bond occurs locally, within one molecular group, or in terms of structure, one crystalline cell. Examples of such reactions may be, for instance, the decomposition of carbonates, nitrates and oxalates of alkali and alkali earth ions. The second group includes those reactions in which the process of thermal decomposition is accompanied by charge or mass transfer over distances much longer than inter-atomic ones. This is the case in the decomposition of azides and oxalates of heavy metals.

It can readily be seen that the classification of the reactions of thermal decomposition is based not on purely external criteria, but the most general peculiarities of the mechanisms of thermal decomposition are assumed as its basis [28]. According to it, the first group includes reactions whose potential centres are situated on the surface, whereas the second group of reactions are those whose progress is associated in some way with the bulk of the crystal. In accordance with this, the rate of reactions of the first group is influenced by crystal defects that give rise to a change in the interrelations between the bulk and the surface of the crystal (for example, the change of crystal habitus or the presence of vicinal forms, figures of growth, macro-cracks, the boundaries of blocks [29–33]).

This can be exemplified by data on the correlation between the habitus variation of magnesium sulphate heptahydrate and the rate of its thermolysis [29], data on the influence of the size of fresh and aged crystals of lead oxalate on the kinetics of their thermal decomposition [30–35].

If a reaction belongs to the second group the rate is mostly influenced by lattice defects — ionic vacancies, interstitial ions and impurity ions. Examples of these reactions are the decomposition of silver oxalate, in which one of the most important stages is the migration of silver ions over interstitial sites, or the decomposition of potassium permanganate, in which the most important stage is the electron transfer from one anion site to another [36].

Thus, it was not essential to accumulate defects in general but, knowing the peculiarities of the reaction mechanism, to try to discern those crystal defects to which the reaction is most sensitive. This conclusion seems to be trivial now, but at that time, in the 1950s, when we started our investigations, it was not obvious.

This also meant that new approaches to the study of the mechanism of the reactions of thermal decomposition were required, namely, it was necessary to apply physical methods independent of kinetics to the study of elementary stages. Before conclusions on the mechanism might be drawn, a new approach required the knowledge of the substance itself and the nature of defects in it.

Hence, possibilities arise in controlling the rate of a reaction, at least in the initial stage, i.e. the stage where the localization of the process is of considerable significance. Strategy of control is restricted to a study of the mechanism of the thermal decomposition reaction, to finding the rate-determining stage of the process and then searches for a method of preparation, storage and treatment of the crystals which would lead to formation in the crystal of those defects to which the reaction is most sensitive.

The dehydration of crystalline hydrates may be cited as an example. It has been known since Faraday that the dehydration of crystalline hydrates starts first of all at sites where the crystal or its surface is damaged. This appears to be associated with the peculiarities of the dehydration mechanism of crystalline hydrates. The point is that the dehydration of crystalline hydrates is especially sensitive, on the one hand, to various kinds of strain in the lattice, the site of concentration of which usually coincides with the site of localization of the dehydration process. Also, at the sites of disturbances in the crystalline hydrate the "cage effect" abruptly decreases, which is essential for dehydration processes where reverse reactions play an important role. Therefore, if a crystalline hydrate has a block structure, the topography of the sites at which the centres of dehydration arise is determined by the arrangement of the boundaries between blocks. In the case of ferroelectrics, for example, it will be the domain's walls, as shown [37] in the instance of Rochelle salt dehydration. This effect may be increased if at the moment of dehydration the surface of Rochelle salt crystals is treated with surface acoustic waves. It is interesting to note that the action of these acoustic waves is selective: the centres of dehydration are formed only on those domains whose direction is perpendicular to the direction of propagation of the surface acoustic waves [37].

Another example is the thermal decomposition of ammonium perchlorate. In studies of the thermal decomposition of this compound we started with the mechanism of the reaction. It was essential at first to determine which of the three possible stages in the thermal decomposition of ammonium perchlorate is primary: the electron transfer from an anion to a cation, the rupture of the chlorine–oxygen bond or the transfer of a proton from a cation to an anion.

Examining the thermolysis of ammonium perchlorate directly in the ion source of a time-of-flight mass spectrometer and using pulse calorimetry, we established that ammonia and perchloric acid are the primary products of the thermal decomposition of ammonium perchlorate from very low temperatures (180°C) and to rather high ones (400°C) [38]. Approximately at the same time, Jacobs and Russel-Jones [39] came to a similar result. Hence, the conclusion was drawn that the primary stage of the thermal decomposition is the transfer of a proton and this mechanism is true over the whole temperature range.

The proton transfer was shown [40–42] to proceed through several successive stages:
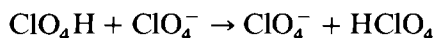
(a) the transfer of a proton from an ammonium ion and its addition to a perchlorate ion

$$NH_4^+ ClO_4^- \rightarrow NH_3 + HClO_4$$
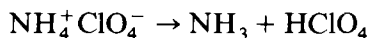
(b) reorientation of the protonated anion

$$HClO_4 \rightarrow ClO_4H$$
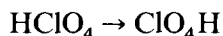
(c) jump of the proton to the next anion

$$ClO_4H + ClO_4^- \rightarrow ClO_4^- + HClO_4$$

From this scheme it follows that the transport of a proton in the lattice takes place at the stages (b) and (c) and it is these stages that are responsible for long-range interaction effects.

A measurement of the temperature dependence of dielectric relaxation and a comparison of the results obtained with the temperature dependence of conductivity showed that the process of reorientation of the protonated anion made the main contribution to the activation energy value.

The proton migrates in the lattice until it is caught by an acceptor, for example, by a perchlorate ion situated at a defect site where better conditions are available for decay of the molecule of perchloric acid formed at every proton jump.

Impurity ions of chlorate must be particularly effective traps for protons: chloric acid resulting from the addition of a proton to a chlorate ion is unstable and decomposes to give chlorine dioxide. Since chlorine dioxide can interact with unreacted ammonium perchlorate, new chlorate ions are constantly being regenerated as a result of this reaction and thus potential centres of the reaction responsible for localization of the process of thermal decomposition renew all the time.

On the basis of this scheme of mechanism, methods for control of the thermal decomposition of this salt can be proposed. In order to stabilize ammonium perchlorate, it is necessary to reduce the concentration of chlorate ions, defects and impurity ions which might be proton donors. It is also possible to introduce into the lattice additives of ions which might be proton traps and compete with chlorate and perchlorate ions. Indeed, the addition of PO_4^{3-} and SO_4^{2-} ions introduced into the lattice impedes the thermal decomposition of ammonium perchlorate whereas doping of perchlorate with ClO_3^- ions leads to an abrupt decrease in its stability [42].

The approach that we proposed allowed us to reach the solution of the reverse problem: to establish the mechanism of a reaction using the knowledge of how one defect or another influences its rate.

Thus, important conclusions were drawn about elementary stages of the thermal decomposition of silver oxalate [34–36]. In studies of the thermal decomposition of silver oxalate, an extremely high sensitivity of the initial stage of this process to divalent impurity cations capable of substituting

silver ions in the lattice was found [34]. The properties of silver oxalate thus doped, in particular, its conductivity, were studied in more detail. The experimental results showed that silver oxalate is mainly an ionic conductor. The electron component of conduction is absent. As the concentration of dopant introduced into the lattice is increased, both conductivity and the coefficient of self-diffusion of silver [36] pass through a minimum value and are well described by the Koch–Wagner isotherm [43]. This, and an examination of luminescence spectra of doped and pure oxalate [44], suggested Frenkel disordering in it and the presence of interstitial ions in the crystal of silver oxalate, and also allowed the mobility and concentration of the interstitial silver ions to be measured [36].

A correlation of the relative change of the rate constant of the process in the initial stages of thermal decomposition of silver oxalate and the concentration of interstitial ions in the lattice showed a linear dependence between them. Thus, a model of the thermal decomposition of oxalate was proposed [45] in which concurrently with the rupture of the $-C-C$ bond the transfer of an electron to an interstitial silver ion occurs either from an excited oxalate ion or from CO_2^- radicals formed during the rupture of the bond. The alternation of the migration of interstitial silver cations to trapped electrons and electron transfer from oxalate ions which surround silver nuclei in the lattice enable this process to proceed. Since the concentration and mobility of interstitial silver ions are low, soon after the start of nuclei growth, it stops and the process proceeds due to the formation of new nuclei situated near the site of the start of reaction. This accounted for the formation of clusters observed in the initial stages of the thermal decomposition of silver oxalate [46,47], and also various characteristic features of the thermal decomposition of silver oxalate including the effect of an external electric field on the rate of the thermal decomposition [48–50], the influence of dyes, etc. [51].

A number of scientists studying different aspects of the thermolysis of silver oxalate [50–53] used the mechanism that we proposed.

Analogously, from analysis of data on the physical properties of potassium permanganate, important conclusions were drawn concerning the mechanism of this reaction, which was one of the first reactions studied in the field of topochemistry of thermal decompositions [2,54–56]. A lot of data have remained unclear until recently. The thermal decomposition of potassium permanganate, which occurs in the temperature range 205–280°C, is a typical redox reaction following the scheme:

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$
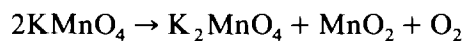
Two solid products are formed, manganese dioxide and potassium manganate, and one gaseous, oxygen. Since electron transfer occurs during this reaction, it is essential to discover exactly where this transfer takes place and what role it plays in the thermal decomposition.

To answer the first of these questions, the nature of majority carriers in permanganate crystals was studied by measuring their conductivity, electromotive force and transport numbers [57,58]. It appeared that in the temperature range 170–210°C the conductivity of permanganate is between 10^{-6} and 10^{-8} ohm^{-1} cm^{-1} (depending on the subject of investigation — a single crystal or a pressed pellet). The measurement of transport numbers showed no anionic component of the conductivity and cationic component (if it exists at all, it does not exceed 5% of the overall conductivity value).

The measurement of thermoelectromotive force indicated that the majority carriers in potassium permanganate are characterized by negative charge. All these results make it possible to conclude that potassium permanganate is an n-type conductor. Then it was necessary to find where the electron transition takes place in the permanganate lattice. Bearing in mind the high values of energetic barriers, it is difficult to imagine that electron transfer occurs from an anion to a cation. Besides, if this mechanism of thermal decomposition were true, the composition of the product formed would differ from that observed in experiments.

We supposed that the electron transfer occurs not between an anion and a cation as it is the case, for example, in azides of heavy metals or silver oxalates, but within the anion sublattice from one permanganate anion to another [59]. As a result of this transition, anion sites exist with an excess electron captured on them, along with those that have lost an electron. Whereas the first of them, according to estimation made in ref. 60, are chemically stable, the second must be unstable and decompose to give manganese dioxide and oxygen (the same conclusions were drawn from other viewpoints by the authors of a recent study [61]). The validity of this assumption was supported by our experiments on the thermal decomposition of solid solutions of potassium permanganate and potassium perchlorate [59]. We observed that on heating the system up to 235–240°C, not all of the permanganate ions contained in the solid solution decomposed, but only those which had at least one permanganate ion as a neighbour. Isolated permanganate ions did not decompose. According to this, the scheme of the initial stages of the thermal decomposition may be written as follows:

$$2MnO_4^- \underset{K_2}{\overset{K_1}{\rightleftarrows}} MnO_4^0 + e \rightarrow \left(MnO_4^{2-}\right)$$
$$\downarrow$$
$$MnO_2 + O_2$$
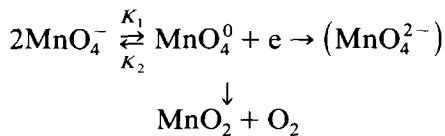
It can readily be seen that the products of the reaction formed according to this scheme are the same as those obtained experimentally. When it is assumed that in the course of the process a stationary state is attained in the system very rapidly, the rate of this process may be written as follows:

$$\omega = \frac{K_1 K_3}{K_2 \, |e| + K_3} C$$

where C is the reticular density of the ion MnO_4^- at the interface. If K_3 is the rate-determining stage and $K_2 |e] \gg K_3$, the rate equation becomes

$$\omega = \frac{K_1 K_3}{K_2 |e]} C$$

Thus, changing the electron–hole equilibrium in the lattice, one can effect the rate of the thermal decomposition of potassium permanganate in the initial stage. This explains two things: (1) why the thermal decomposition of potassium permanganate is sensitive to the effect of various kinds of defects which might be traps for electrons [62,63] and especially to the action of heterogeneous additives [59–64]; and (2) why one of the solid products of the reaction, potassium manganate or its binary salt, characterized by a lower electronic work function as compared with permanganate, impedes the thermal decomposition, and the other solid product, manganese dioxide, the electronic work function of which is larger, catalyzes it.

Based on these facts we accounted for [65,66] the well-known phenomenon of the effect of preliminary irradiation on the rate of the thermal decomposition of permanganate as a result of superposition of the effects of these two products (manganate and manganese dioxide), which are also formed during radiolysis [67].

Though the detailed mechanism of the thermal decomposition of potassium permanganate has not been yet revealed, especially at the level of chemical and structural stages following the electron transition and the decomposition of a hole, the approach to an understanding of the initial stages of decomposition that we proposed turned out to be useful for scientists working in this field [68–72].

The same strategy of investigation: accumulation of data on the defect structure of substance and effect of various kinds of defects on the rate of reaction, was used in our studies on the mechanism of the thermal decomposition of copper hypophosphite [73,74] and aluminium hydride [75,76]. In the same manner, important data were obtained on the mechanism of the processes similar to thermal decomposition: chemical changes in crystals under the action of a shock wave [77] and in the tracks of heavy, high-energy particles [78].

Thirty years later, this approach to the study of thermal decomposition reactions can hardly be argued with, and the details of the mechanism of the reactions which have been studied seem apparent and usual. But at that time, just at the very beginning, it was new, unusual and unclear for many chemists. It should not be forgotten that solid-state physics, upon which our work was based, was also making its first steps at that time. Therefore, there were many unclear things, not only concerning the effect of defects on the rate of chemical reactions in general and the reactions of thermal decomposition in particular, but also with respect to the nature of defects and methods of their study. The first attempts at doping with the aim of

changing the electronic and ionic properties of a crystal were made at that time mainly in semiconductor technology and for the modification of optical properties of alkaline halogen crystals, the term of dislocation was still achieving the right for life in the brains of average physicists. Modern concepts and fundamentals, such as the concept of the nature of chemical bond, the structural nature of metastability in crystals, modern methods of investigation of defects in crystal with the use of radiospectroscopy, electron microscopy, the methods of computer simulations, the methods of direct study of the surface properties, which are used so much now and without which nobody can carry out this kind of study, were not available at that time. It was very difficult to speak to the chemists of that time about the effect of any particular defect on the rate of chemical reactions. The books by Garner [79], Bowden and Yoffe [80], Rees [81], Hauffe [82], Budnikov and Ginstling [83], and ours [84] (to say nothing of more recent manuals and guides [85–87]) which brought up a generation of solid-state chemists and which are now considered by many people to be hopelessly old-fashioned, were not yet published.

I remember very well how one professor at the Chemical Department of Tomsk State University, who taught me and to whom I am obliged since solid-state chemistry became my speciality for life, gave me rather pressing advice not to study this problem: "It is better for you to go in for chemistry", he insisted, "the chemistry which all of us have already got used to, where we ourselves can do something. For what are those defects to you, in which physicists themselves did not gain an understanding? If you, nevertheless, want something unusual, concerned with physics, go in for thermal analysis". Since that time, perhaps, I associate the notion of thermal analysis with the boundaries of understanding the role of physics by certain representatives of the classical trends of inorganic chemistry. Of course, it was very difficult as the majority of my colleagues simply did not understand me. And what about physicists? Physicists were busy with their own chemical problems: primarily the problems of determining microimpurities, purification, growing crystals needed for conducting special physical studies. Since the research that I carried out was not within their field of interest, I did not receive much notice from physicists. Nevertheless, the choice was done and the work was started. The main support and enthusiasts in it were students, the only representatives of our scientific association ready to do any new job without hesitation (provided, of course, that they will pass a test). We were the first in the country and probably in the world to start studies on the role of dislocations in thermal decomposition. The same may be also said about the use of electrophysical methods in thermal decomposition processes.

AUTOLOCALIZATION IN THERMAL DECOMPOSITION

In spite of the successful application of our approach to studying the thermal decomposition of solids at the stage of localization, it remained

unclear what occurred after the reaction had started. The method success-fully applied in the initial stage becomes ineffective for the subsequent steps of the process. Therefore, along with factors concerning the localization of the process of thermal decomposition, one should study and take into account factors leading to its autolocalization, i.e. the capacity of a reaction to change the reactivity of the crystal near the sites where it has already started. The classical theory of phase transformations is commonly used as a model for describing the course of a thermal decomposition reaction. According to this theory, the appearance of nuclei of a new phase may be considered as a result of heterophase configuration fluctuations in the system. And their growth, on reaching a critical value by the nucleus, when the increase in energy of the system resulting from the formation of the new phase exceeds energy consumptions necessary for the new surface to be formed, is considered as the formation and evolution of two-dimensional nuclei on the surface. However, a more careful consideration shows that a simple transfer of the classical theory of phase transformations on topochemical processes and on thermal decomposition reactions in particu-lar is not correct [88–90].

Firstly, not one factor (a decrease in activation energy of the formation of the new phase) but several factors act at the interface in topochemical processes. Among these factors are those which are not usually considered in the classical theory of phase transformations, for example, the change of electron–hole equilibrium [91,92] and ion–vacancy distribution [93] at an interface, elastic stresses, etc.

Secondly, the formation of the solid product is considered as a rate-de-termining step in the classical theory of phase transformations and when strictly following the canons of the classical theory, the product is expected to be a single crystal.

However, experimental results show that it is not true. In reality, the formation of the solid product is a complex system of successive and concurrent stages in which, other than in simple phase transitions, steps of the process may be also rate-determining (for example, the destruction of the lattice of the starting crystal). If a thermal decomposition is accompa-nied by topotactical transformation of one structure into another, the stages of destruction of the old phase and formation of the new one cannot be separated.

Besides, in the case of simple phase transformations, changes in structure and composition occur simultaneously. That is why the reaction zone is represented as a planar boundary separating the starting substance and the reaction product. This model is generally accepted in classical topokinetics. Actually, the changes in composition and structure of a solid during the course of the reaction may be separated in both time and space.

Moreover, instances are known of the formation of nuclei during thermal decomposition (e.g. perchlorate [94], bicarbonate ammonium [95,96] and

mercury oxide [97]), when no solid product is formed in the reaction at all.

All these points taken together made us revise the common traditional method of simply transferring the fundamentals of the classical theory of phase transformations onto more complicated topochemical systems, including thermal decomposition. We understood the necessity of this revision in the fifties. It was just then that the question of the nature of the catalytic effect of solid products in topochemical reactions was put for the first time [98–102]. The first attempts were made to prove this catalytic effect by direct experiments [101] rather than by referring to the f-shape form of a kinetic curve as previously [99,103–105]. The question of the specific state of the layer of the starting substance adjacent to the layer of the product at the interface was put at that time.

A strong deformation effect of the lattice of the product on the lattice of the starting substance was pointed out. Finally, the question of the change in degree of localization with the course of the process in thermal decomposition because of superposition of two activation components: thermal and crystallochemical was made [106]. Whereas the thermal component is equally probable for all crystal sites, the crystallochemical one, which is the consequence of the lattice disturbance existing before a chemical act, leads to a change in reactivity of particles neighbouring the site at which the reaction has just occurred. The following development of this idea [88] led to consideration of possible physical causes for manifestation of the crystallochemical component and finally to the concepts of localization of the reaction now adopted in solid-state chemistry [107]. It appeared that, besides purely crystallochemical causes leading to autolocalization of the process, other causes are possible, relative to the catalytic effect of the solid product formed, to the chemical effect of gaseous products liberated in the reaction of the initial substance, etc.

Thus, the necessity of a more detailed and consistent study of causes leading to autolocalization of the process was obvious long ago. This stimulated studies directed towards revealing possible physico-chemical causes of autolocalization, and towards a more detailed understanding of the structure of the reaction zone.

Taking into account experience accumulated in our laboratory and laboratories of other scientists, we considered the possible reasons leading to autolocalization in a survey [107]. In brief, they are the following:

(a) Autolocalization may be a consequence of the anisotropy of the crystal properties. If, during the course of the process the evolution of the edges takes place with high reactivity, the rate of the chemical reaction will initially increase and then, reaching a maximum, fall off. As a result, the transformation–time curve will take on a f shape. The possibility of this kind of autolocalization was first pointed out in ref. 108, and this viewpoint was developed in ref. 109.

(b) Autolocalization may be due to deformation of the starting substance

by the solid product formed in the reaction on account of both interfacial energy and difference in molecular volumes, as is the case in the recrystallization of metallic alloys [110,111]. The occurrence of the deformation of the lattice near a nucleus may lead to a change in reactivity of the crystal in this region. Examples of this kind of autolocalization for the case of thermal decomposition are given in ref. 107. In more recent papers this question was specifically studied on various solid-state transformations and it was shown that the reactivity of the starting solid substance may be changed due to the occurrence and the subsequent relaxation of stresses at the interface between the starting substance and the reaction product [112].

(c) Autolocalization may be due to a change in electron–hole equilibrium at the interface between the reaction product and the starting substance [91,92]. This kind of autolocalization manifests itelf primarily in redox reactions, i.e. reactions concerned with electron transfer. The solid product formed in the reaction can change the conditions for electron transfer in the layer of the starting substance at the interface. As an example, the work of Torkar and Spath [113] may be cited in which they showed this phenomenon in the thermal decomposition of barium azide. When the substance being decomposed and the reaction product are semiconductors, a change in the electron–hole equilibrium near the contact region and, hence, the reactivity of the starting substance can take place as a result of a contact potential difference. We have shown this for the thermal decomposition of potassium permanganate [59,64].

(d) If the gaseous reaction products formed during thermal decomposition undergo subsequent chemical transformations and the products thus evolved interact with unreacted substance to give new potential centres of the reaction, this may also cause autolocalization of the process. The thermal decomposition of ammonium perchlorate can be cited as an example. As mentioned above, the primary products of the thermal decomposition are ammonia and perchloric acid. Since there are no solid products, the formation of nuclei and their growth may not be attributed to the deformation or catalytic effect of the reaction products. Similarly, the absence of correlation between the crystallochemical structure of ammonium perchlorate and the shape of nuclei, and their formation mainly at the faces rather than at corner edges, make it clear that autolocalization is not associated with crystallographic causes.

In order to explain the formation of nuclei in the thermal decomposition of ammonium perchlorate and their subsequent growth, we supposed [114] that the autolocalization of the process is due to the accumulation of perchloric acid in the micropores of the crystal and its subsequent decomposition with the formation of chlorine dioxide. The interaction of chlorine dioxide and unreacted perchlorate leads to the formation of chlorate ions which are known to play the role of potential centres of the reaction and are reproducible with the course of the process. On the other hand a fraction of

perchloric acid can migrate to the neighbouring pores of the crystal and contaminate them. Recently, the availability of the increased concentration of protons in the layer of starting perchlorate adjacent to the growing nucleus was supported by direct experiments [115]. At the same time, it was shown in refs. 116 and 117 that the region round the nucleus in the thermal decomposition of perchlorate is the region of concentration of stresses occurring in the lattice under action of the bubbles of the gas formed in the process. This resulted in an increased concentration of dislocations in this region.

The superposition of all the above factors appears to be the cause of autolocalization in this very interesting case of thermal decomposition where there are no solid products. The viewpoint on the nature of autolocalization developed in our works provoked interest and found support in the papers of other investigators [118–120].

Since this article has the characteristics of a memoirs, I cannot help remembering an instructive story relative to the selection of reagents for etching dislocations in ammonium perchlorate, the selection being done by one of the co-workers of my papers [116] (L.A.V.) at the end of the fifties in our laboratory.

The selection of etchants for revealing the emergence points of dislocations was not a new method but it was used at that time mainly on metals and semiconductors. For ionic crystals, the methods of detecting dislocations were well developed mainly on alkaline halogenides. Therefore, in the same manner as others did it, first, we tested as etching agents aqueous and then alcoholic solutions with additions of different inorganic salts. But we failed to obtain good results. Days and months passed, about a hundred additives were tried, but success was far away. Being an honest and conscientious co-workers, L.A.V. began to despair and I suspected that during the last weeks of this work, which was carried out for ten months, some woman's tears were added to the etchant. As the superviser of the work, I began worrying and even thought about a cessation of this Sisyphean work. A chance helped the matter, and once, obviously very tired of this chemical marathon, L.A.V. forgot to put an additive into an alcohol and hence performed the etching with pure alcohol. Excellent etch pits were obtained on both the faces of the perchlorate crystals and their cleavage surfaces. We were proud of the result obtained and found the explanation at once — we needed to take a very dilute solution of the etchant–water in the liquid that poorly dissolved perchlorate–alcohol. But all this became clear later, when the etchant was found. We were near the solution of the problem and needed only to think. Instead of this, we followed other investigators and wasted a lot of time in finding the etching reagent, thereby supporting the known thesis that it is better to think once rather than to try many times.

After this work, alcohols as etchants for ammonium perchlorate crystals were commonly used both in our studies and in the studies of other scientists [121–123].

The results of studies on more complex systems [124–127] show that the examples mentioned above do not cover the variety of physico-chemical factors and causes that may lead to autolocalization of the thermal decomposition of solids.

Moreover, as we have already written [128,129], the combined effect of several factors is usually the case. These factors may differ not only in efficiency of change in reactivity but also generally in sign of action (i.e. whereas some factors accelerate, others impede). All this makes the problem essentially more complicated, hinders the study of autolocalization phenomena and requires the development of principally new experimental methods. An experimental procedure for measuring the rate of advance of the interface elaborated in our institute for the dehydration of crystalline hydrates [130] can be referred to as an example.

In this procedure, the process on a preset crystal face is isolated, the plane reaction front is formed artificially and the reaction is carried out under such conditions that the effect of the secondary processes is prevented as much as possible.

It allows one to obtain conditions which enable the process to be carried out in kinetic regime and the interface advance to be measured in a given crystallographic direction. As a result, for the dehydration of $Li_2SO_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$, data were obtained on the temperature dependence of the rate of the process, concerning the elementary stages of the thermal decomposition process [131], and for gypsum dehydration, anisotropy of the reaction rate connected with crystallochemical peculiarities of the arrangement of water molecules in the crystal were revealed [132,133].

Another method for carrying out studies in this direction appears to be the method of computer simulation, which enables one to estimate the effect of each individual factor on autolocalization when it is impossible to separate the action of factors by experimental methods [134].

Besides the knowledge of possible causes capable of describing the autolocalization of the process, it is necessary to know the topography of the process in the crystal, i.e. the structure of the reaction zone. As it was shown above, the ideas of topokinetics on a plane interface separating the solid product and the starting substance in many instances turned out to disagree with experiment. First of all, it was found in the earliest works [135,136] on topochemistry of thermal decompositions that the chemical and phase stages of the processes did not coincide. Subsequent works confirmed the results of these observations for a wide range of thermal decomposition reactions [137–144]. This turned out to be due mainly to the different mobilities of different structural elements of the substance being decomposed. Therefore, in the course of thermal decomposition the reaction product, being in metastable state, retains for some time the structure of the starting substance. This and other factors make the interface diffuse from the side of the product of the reaction [5,6,79,144].

But the part of the interface that is adjacent to the starting substance also diffuses. The causes of this may be connected with the deformation of the lattice of the starting substance by the reaction product due to either their different structures or the difference in their molecular volumes [98,110].

In the simplest way this effect may be traced in the instance of polymorphous transitions. Its mechanisms have been recently studied in detail in refs. 145 and 146. It was shown that in the case of the polymorphous transformation of ammonium perchlorate, for example, the relaxation of stresses occurs by the formation and slip of dislocation semi-loops and in the case of ammonium rhodanide by domain representation. The above-mentioned cases of autolocalization on account of change in electron–hole and ion–vacancy equilibria in the layer of the starting substance adjacent to the reaction zone also result in diffusion of the reaction front.

Since it appeared that a reaction zone is a layer rather than a surface, the question arises of determining the exact site where the reaction occurs and where the structure changes. The method of optical observations used until recently cannot precisely answer this question. It is rough and simply characterizes an interface where changes in refraction and reflection of light by a crystal take place and this interface does not always coincide with the zone of chemical reaction or structural change.

Therefore, in our laboratory experimental studies have been undertaken concerning the state of the starting substance and the reaction product on the interface between them.

The use of local X-ray diffraction analysis [16,147] showed that the layer on the crystal boundary adjacent in the dehydration to the boundary of the growing nucleus is strongly deformed and contains a large amount of water molecule vacancies. French scientists independently obtained similar results and called this state "vacancy phase" [138,148].

The use of synchrotron radiation for diffraction studies allowed us to advance considerably in this direction since the possibilities of both space and time resolution of the method were appreciably increased. Thus, for example, a diffractometer SI that we used made it possible to shorten the time of exposure from several hours in a common X-ray experiment to several seconds in the collimation of a beam of 5–10 μm [149,150]. This allowed the strained–deformed state in the reaction zone and its depth to be determined for dehydration reactions. The depth of the zone turned out to be about a hundred micrometres [151]. The same value of the deformed layer was obtained by another method — by using changes in the EPR spectrum of Cr^{3+} used as a mark when the arrangement of surrounding ions in the lattice changes because of deformation [151].

The data obtained made it possible to propose a diffusion-kinetic model of moving reaction fronts based on the positive feedback that arises during the course of reaction due to the relaxation of stresses occurring in the vacancy structure and the formation of the porous reaction product [152].

Besides complications in determining the structure and composition, the situation in the reaction zone may be strongly complicated by various secondary physical and chemical processes, the role of which is not always taken into account. An example of this is the formation of a liquid or a melt as an intermediate product. In studies of potassium perchlorate decomposition, the authors of ref. 153, from the fact that the rate passed through maximum, concluded that the reaction was topochemical and proceeded in the solid state. But a detailed study performed in ref. 154 showed that in reality, the ∫-shaped character of the curve of the decomposition results from the formation of a eutectic mixture of potassium perchlorate and the reaction product (chloride) and the formation of a melt. Therefore, the rate increases at the beginning of the process. The subsequent accumulation of chloride leads to solidification of the melt and the rate falls off.

In recent years, several similar cases of the formation of an intermediate liquid phase in the dehydration of a crystalline hydrate were revealed by Galwey et al. [155] and in our laboratory [156,157]. The reasons for liquid phase formation may be quite different: incongruent melting, kinetic hindrance for water removal from reaction zone, etc.

In the reaction zone a change in composition of the gaseous products can take place due to secondary processes catalyzed by the solid product formed in the reaction [158–160] and also by the secondary processes (for example, reaction with the solid phase [161,162]). Finally, the phase composition of the reaction zone depends upon conditions of the reaction course and can change even if the rate of heating of the substance is changed [163,164].

CONCLUSION

In spite of successes achieved, the problems concerning the mechanism of autolocalization processes are far from being solved. It is probably more correct to say that they are just raised now.

The number of publications concerning the topochemistry of thermal decomposition of solids is steadily increasing. It is difficult, if at all possible, to cover all the available experimental data in a review. My aim was not to write such an exhaustive survey. I rather tried to give a brief introduction into this very interesting and very important field of thermochemistry. For illustration I used mainly my own results and results of my colleagues. I hope that our first steps in this field will be followed by others, made by the younger generation, beginning their scientific studies today. I wish them good luck.

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