Special Review

TOPOCHEMICAL REACTIONS.

PARTICULARITIES OF THEIR MECHANISM AND OUTLOOK ON THEIR RESEARCH, PART II*

V. V. BOLDYREV

Institute of Chemical Kinetics and Combustion,
Siberian Department of the Academy of Sciences of the U. S. S. R.

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A survey of topochemical reactions is given and the theory of their kinetics is discussed.

The first part of this study [1] deal with the autolocalization, now the factors leading the autolocalization are under consideration.

I. Causes of autolocalization in topochemical reactions

The factors in thermal decomposition may be divided into three groups:

(i) crystallochemical properties of the starting material,

(ii) separation of a solid reaction product,

(iii) change in the reactivity of the starting solid, owing to the gaseous reaction products evolved in the reaction.

Let us investigate these causes in more detail.

1. *Autolocalization of topochemical reactions caused by crystallochemical properties of the starting material*

One of the causes of the autolocalization of topochemical processes may be the anisotropy of crystal properties. If, in the course of the topochemical process, those crystal faces develop that are characterized by increased reactivity, this may be a cause of autolocalization. The possibility of this type of autolocalization has been considered among others by Pavlyuchenko [2, 3]. His work is based on the known fact that different sites on the crystal surface have different reactivities. Thus, in cubic crystals, for example, the particles at the apices are characterized by higher reactivity than particles situated on the edges, etc.

It may be expected, therefore, that the topochemical reaction will start at the most reactive sites of the crystal, viz. at its apices.

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If, as a result of the first act, a particle is removed from an apex of the crystal, this will involve the appearance of three new particles equivalent to the disappearing particle with respect to reactivity. If, at the next moment, these three particles are also removed, six such particles will appear in the following layer, and so on (Fig. 1). When a face having higher reactivity develops in the described manner in the course of the topochemical reaction, this will lead as a result to preferential development of the process in the vicinity of the site where the process has started, i.e. to autolocalization of the process.

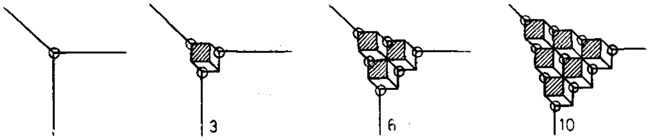


Fig. 1. Anisotropy as a cause for localization

The general mechanism of autolocalization in topochemical reactions proceeding in this way clearly indicates that the theory of phase transformations cannot, in principle, describe their course, since the stage of solid product formation is not involved at all, while interest is concentrated on the breakdown of the crystals of the starting material. Accordingly, analogies of such topochemical reactions with phase transformations, if any, should not be sought with crystallization and condensation processes, i.e. the main model systems in the theory of phase transformations, but rather with processes opposed to the former, viz. processes involving the breakdown of crystals (e.g. sublimation or dissolution) [4–6]. Further, as is the case with crystal dissolution processes, it is to be expected that after initial development of the reaction zones these zones will finally fuse. As a result, the rate of the process will reach a maximum and the rate will be described by relatively simple topokinetic equations.

With the simplest topochemical reactions, such as for instance topochemical decomposition reactions the above-described autolocalization mechanism is to be expected when no solid reaction product is formed, or when neither the solid nor the gaseous products formed in the reaction exert a catalytic effect on the process.

Autolocalization in the thermal decomposition of mercury oxide, studied by Prodan and co-workers [7, 8], appears to belong to the above-discussed type. It was found, that at low temperature the process starts at the defect sites of the crystal and then develops at different rates in different directions of the crystal. As a result, similarly to the dissolution of ionic crystals, decomposition figures are observable. The shapes of these figures are similar to those of etch patterns and resemble the formation of negative crystals.

In thermal decomposition at higher temperatures, the localization of the process at defect sites ceases and decomposition starts to proceed uniformly over the whole surface.

The thermal dissociation of silver cyanamide [9, 10] and zinc oxide [11 – 13] and the sublimation of some ammonium salts [14] occur in an analogous manner.

2. *Autolocalization due to the solid reaction product (autocatalysis by the solid product)*

Several authors [15 – 18] have pointed out the possibility of autolocalization in topochemical processes as a result of the catalytic action of the solid reaction product. The starting point in these cases was usually the postulation of an analogy between topochemical reactions and other, simpler types of phase transformations. We have demonstrated above, however, that this analogy by no means holds true in all cases. In solid-state chemical reactions and particularly in topochemical reactions, nuclei of the new phase are formed and will grow in the interior of the crystal or on its surface; this defines the specific features of nucleus formation and growth, in contrast to the processes usually considered in the theory of phase transformations. This may also occur when the chemical and phase stages are not separated in time and space, but the solid product formed in the reaction affects the rate of the process.

Let us consider the formation and growth of nuclei in topochemical reactions in more detail.

a) *Product nucleus formation in topochemical reactions*

Recent studies [19 – 22] have indicated that nucleus formation is a more complex process than would follow from the Gibbs – Volmer theory. The essential feature is that in the early stages of the reaction the product atoms or the crystal defects are not statistically distributed over the lattice, as assumed earlier, but – owing to their interaction – form clusters. This should obviously affect the process of nucleus formation.

Further, in contrast to crystallization from a solution or a melt, where heterophase fluctuations are the result of the translational movement of individual atoms and molecules, in the case of solid-phase nucleus formation the presence of the periodic field of the crystal lattice is of fundamental importance. As a result, fluctuations give rise to fluctuation waves in the lattice, their nodal points being able to serve as sites for various phase transformations, including chemical reactions [23 – 28]. A comparison of nucleus formation according to the classical theory of phase transformations and in solid-state processes indicates that in the classical theory nucleus formation is the result of configurational fluctuations of irregularly moving particles, whereas in solid-state transformations nucleus formation is the result of the combined movement of the lattice elements.

By way of example (which has by now become classical) we shall cite the work of Roth [26] on the formation of magnetite nuclei in the decomposition of wuestite.

This decomposition

$$3FeO \rightarrow Fe + Fe_2O_3$$

consists of several elementary steps. Initially, oxidation of some of the bivalent iron ions takes place. As a result, iron(III) ions and associated cation vacancies will appear in the octahedral lattice of the iron(II)oxide. Since a trivalent iron-ion is much smaller than a bivalent iron ion, its position in the octahedral lattice is unstable and it will tend towards an interstitial position with a tetrahedral environment. Due to this transition, a cluster complex consisting of two cation vacancies and an Fe^{3+} ion will be formed. The essential feature is that the Fe^{3+} ion immediately occupies the position which it must take in the lattice of the reaction product, magnetite.

Later studies [27, 28] led to a further refinement of this model and demonstrated that the stable cluster is formed as a result of the aggregation of four interstitial iron(III) ions and thirteen cation vacancies. The general conclusion, however, remains unchanged: the cluster formed as a result of the interaction between defects in the lattice is simultaneously the nucleus of the reaction product.

A similar situation is observed in the oxydation of uranium dioxide [29].

The effect of structure on the mechanism of the initial stage can also be demonstrated for more complex chemical reactions. By way of example, the formation of the intermediate compound $K_3(MnO_4)_2$ in the course of the thermal transformation of potassium permanganate into manganate [30–32] may be mentioned.

If the molecular volume of the product is larger than that of the starting material, another specific features of nucleus formation in the solid phase will appear, distinguishing this process from nucleus formation from the gas or liquid phases. The volume of the nucleus formed being greater in this case than the volume of the starting material in which the nucleus is being formed, a deformation of the neighbouring lattice will result. An additional term Δg_e must therefore be introduced into the equation describing the change of the thermodynamic potential on the formation of the new phase:

$$\Delta g = \Delta g_v + \Delta g_s + \Delta g_e$$

The term Δg_e characterizes the deformation work done by the nucleus on the surrounding lattice. Similarly to Δg_s, Δg_e also means energy consumption, and hence the ratio between these terms will define the shape of the nucleus being formed [33]. If $\Delta g_s \gg \Delta g_e$ and the medium is isotropic, the nucleus will be spherical, this shape yielding minimum interphase energy. If $\Delta g_s \ll \Delta g_e$, however, the nucleus will tend towards a flat shape that will decrease volume deformation. [35]

b) *Growth of the nucleus.* The process of growth of the nucleus in topochemical reactions also involves many specific features.

The effect of the solid product formed in the reaction will vary, depending on the continuance of coherence, on a molecular level, between the lattices of the initial material and the reaction product.

If the lattices of the starting material and the reaction product are not in contact, and the phase stage and chemical stage of the process are separated, then – with the exception of some special cases that will be discussed – later the solid product does not affect the reactivity of the starting material and no autocatalysis by the solid product takes place.

In this case the situation will be identical to that when no solid product is formed in the topochemical reaction, or when the solid product formed does not possess catalytic activity. Hence, the causes for autolocalization of the process (if such causes exist) must be related to the particular structure of the starting solid, or to the catalytic activity of the gaseous product.

If correspondence exists in the orientation of the lattices of the starting material and the reaction product, enabling topotaxial transition from the former to the latter, the catalytic activity of the product is to be expected.

Depending on the mechanism of the topochemical reaction, it may be of importance whether all bonds in the lattice of the initial material will weaken on the boundary surface, or only the bonds of some elements constituting the lattice.

In the first case the topotaxial transition of the lattice of the initial material into the lattice of the reaction product will result in a decrease of the activation energy of the transition. In the absence of topotaxy this activation energy will be higher than or equal to the heat of transition.

If more information of the process in question is available, if it is known, for instance, that the reactivity is determined by the bond strength of a certain component in the lattice of the starting material, the action of the solid product can be considered with respect not to the whole lattice, but only to the bond energy of this component.

This will be illustrated with the reduction of metal oxides. It is known that the reductivity of oxides generally changes in the opposite direction to the bond energy of oxygen in the oxide. Hence, to decide in an actual case whether the metal product formed on reduction will catalyze the reduction reaction, so that autocatalysis is to be expected, it is necessary to estimate the bond energy of oxygen on the surface of the oxide in vacuum, and on the contact interface with the metal.

The results of such calculations made by Bulgakov [36], using a method developed by him and based on the model of interacting bonds [37], are presented in Table 1.

Table 1

Oxygen bond energies on the free surface of oxides and on their interface with the metal formed in their reduction

Oxide	Bond energy on the oxide-vacuum boundary surface, kcal/mole	Bond energy on the oxide-metal interface, kcal/mole
CoO	226	140
NiO	180	130
ZnO	136	156

These data indicate that the bond energy of oxygen at the interface with the metal is less than on the oxide surface in vacuum for nickel and cobalt oxides, whereas for zinc oxide it is higher.

These calculated results are in good agreement with experimental findings. In fact, the reductions of nickel and cobalt oxides are autocatalytic in character [38, 39], while no catalytic action of the reduced metal was observed in the case of zinc oxide [38, 40].

If the elementary steps of the process are known, the catalytic action of the solid product on the individual steps can be studied separately.

This is the case when the solid undergoing topochemical transformation is a semiconductor, and the topochemical reaction is an oxidation – reduction reaction, that is it includes an electrontransfer step. The existence of an interface between the starting material and the solid reaction product can then lead to a change in the reactivity of the unreacted material in the neighbourhood of the contact, owing to a change in the electron-electron hole equilibrium in this part of the crystal.

The thermal decomposition of potassium permanganate is an example of this type of topochemical reaction. Its mechanism has been studied in detail in our laboratory.

The results of these studies indicated that the thermal decomposition of potassium permanganate, a semiconductor of the p type [41, 42], takes place as the result of electron-transfer from one anionic lattice point to an other:

$$\begin{array}{l} MnO_4^- + MnO_4^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} MnO_4^0 + MnO_4^{2-} \\ \qquad\qquad\qquad\qquad\quad \downarrow k_3 \\ \qquad\qquad\qquad\qquad\quad MnO_2 + O_2 \end{array}$$

Electron-transfer leads to the formation of the unstable radical MnO_4^0, which subsequently decomposes to MnO_2 and O_2. Assuming that electron-transfer takes place rapidly enough, that the rate-controlling step is decomposition of MnO_4^0 radicals, and further that the steady-state is established in the system, the rate of reaction can be written as follows:

$$v = \frac{k_1 \cdot k_3}{k_2[e] + k_3}.$$

Here $[e]$ is the number of anionic lattice points where an excess electron is situated. When $k_3 \ll k_2[e]$, $v = k_1 \cdot k_3/k_2[e]$.

It follows from what has been said that the overall rate of the reaction will increase when the electron-electron hole equilibrium is shifted towards the right hand side, and will decrease when the equilibrium is shifted towards the left hand side.

The conditions for such shifts of the equilibrium may arise, for example, when the electron work functions for the starting material and for the solid reaction product differ, so that a contact potential difference results at the boundary surface which is the interface of two semiconductors.

We have measured the electron work functions for potassium permanganate and for its solid decomposition products, viz. manganese dioxide and the double salt. $K_3(MnO_4)_2$, that can be conceived as the salt of MnO_4^{2-} associated with the MnO_4^{1-}-ion. The data presented in Fig. 2 demonstrate that under conditions close to those of the thermal decomposition of potassium permanganate, the electron work function for manganese dioxide is higher, and that for the double salt $K_3(MnO_4)_2$ is lower than that for permanganate. According to these findings and to the suggested thermal decomposition scheme, manganese dioxide, should be the electron acceptor and must therefore catalyze the thermal decomposition of permanganate, whereas manganate or the double salt should be the electron donor and must therefore inhibit thermal decomposition.

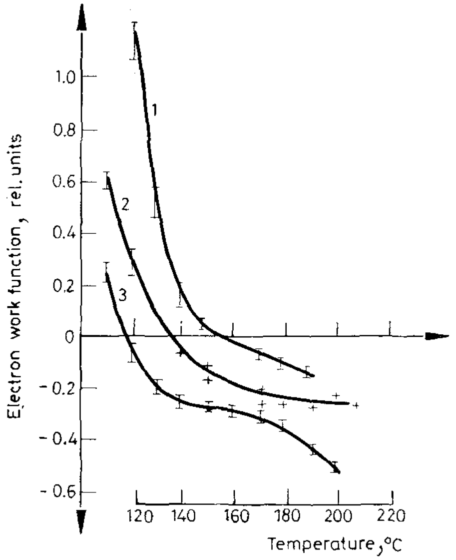


Fig. 2. Contact potential difference of $KMnO_4$ and its decomposition products
1 — MnO_2, 2 — $KMnO_4$, 3 — $K_3(MnO_4)_2$

Experimental data shown in Fig. 3 confirm this assumption. In fact, addition of manganese dioxide exerts a catalytic effect on the thermal decomposition of permanganate (in agreement with data in the literature, cf., for example, [43]). On the other hand, addition of the manganate retards the reaction. Thus, the well-known phenomenon of autocatalysis in the thermal decomposition of potassium permanganate is in fact the result of the superposition of the catalytic activity of one of the solid reaction products on the inhibiting activity of another reaction product.

The particular feature of autocatalysis in this case is that the effect of the solid reaction product is not limited to the surface layer of the starting material in contact with the product, but extends deep into the initial solid phase over the screening length of the charge. Therefore the formation of MnO_4 radicals may also occur in the interior of the crystals, at some distance from the surface. Since the decomposition of this radical to MnO_2 and O_2 is practically irreversible, gas evolution in the interior of the crystal will finally lead to cracking of the crystal during its thermal decomposition, and to its dispersion. This is obviously the true cause of the self-comminution taking place in the course of the thermal decomposition of alkali permanganate crystals, and not – as assumed earlier – the difference between the lattice parameters of the starting material and the reaction product. Judging by the results of studies already cited [30–31], this difference could hardly be of essential importance.

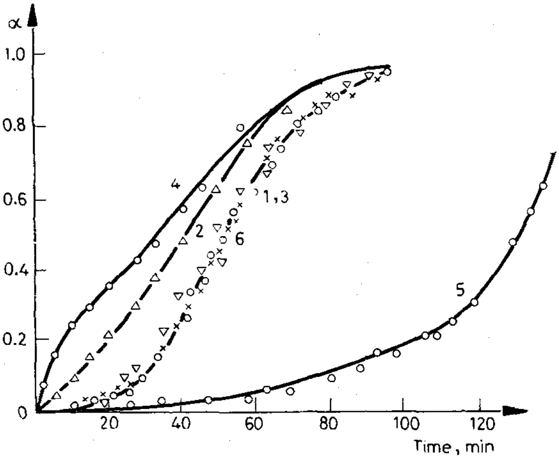


Fig. 3. Effect of additives on the thermal decomposition of $KMnO_4$

3. *Autolocalization of thermal decomposition caused by gaseous reaction products*

Gaseous products formed in topochemical reactions may also result in autolocalization of the process. One of the various possible variants will take place when the gaseous product is subsequently submitted to further chemical transformation (e.g. decomposition) and the products of this transformation are capable of reacting with as yet unreacted solid.

This type of autolocalization will be illustrated by nucleus formation and growth in the low-temperature thermal decomposition of ammonium perchlorate. As early as in 1954, Birkemshaw [44] demonstrated that cigar-shaped nuclei are formed in the low-temperature thermal decomposition of ammonium perchlorate. More detailed electron microscopic studies revealed that each of these nuclei is an aggregate of smaller nuclei, and the visually observed growth involves the formation of new nuclei at the borders of this aggregate [45–47]. The physical-chemical causes of autolocalization were not clear. Since ammonium perchlorate is decomposed without any solid product being formed, the formation of active nuclei cannot be attributed to the catalytic activity of a solid product. Further, since the formation of reactive nuclei is not related to crystal sites having particular geometric properties, autolocalization due to the anisotropy of the crystal appears improbable.

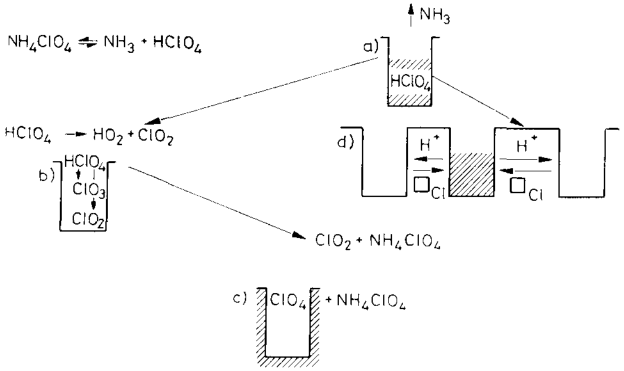


Fig. 4. Schematic representation of the thermal decomposition of ammonium perchlorate. a) Separation of ammonia and perchloric acid in the pore, owing to the difference in their rates of diffusion. b) Decomposition of perchloric acid. c) Interaction of the decomposition products of perchloric acid with unreacted perchlorate on the wall of the pore. d) Migration of perchloric acid into an "unfilled" pore. Stages *a* and *b* are responsible for nucleus formation, stages *a*, *c* and *d* for nucleus growth

To explain the mechanism of autolocalization in this case, we made the assumption that autolocalization is caused by the action of the products formed in the thermal decomposition of perchloric acid, the latter being formed in the thermal dissociation of ammonium perchlorate (Fig. 4).

It is well-known now that the primary step in the thermal decomposition of ammonium perchlorate, at both high and low temperatures, is proton-transfer [48, 49] leading to the formation of ammonia and perchloric acid. If the crystal contains no pores, both dissociation products will leave the crystal, i.e. ammonium perchlorate will undergo sublimation.

However, if the crystal does contain pores (e.g. groupings of dislocations at the boundaries of blocks, etc.), and the dimensions of these pores are sufficiently small, it may be expected that from these domains of the crystal, ammonia and perchloric acid will be removed at different velocities, defined by the expression [50].

$$v = \frac{8\pi}{3}\sqrt{\frac{1}{2\pi \mathrm{RTM}}}\cdot\frac{r^3}{l}\cdot\Delta P$$

Since the molecular weight of perchloric acid is 100, while that of ammonia is 17, the latter will obviously escape from the pore at a velocity 2.5 times as high as that of perchloric acid.

As a result, perchloric acid will accumulate in the pore. This has been confirmed experimentally [51]. Perchloric acid accumulated in the pore may be consumed by means of two processes:

(i) migration of the acid into a neighbouring pore, as a result of proton conductivity and counter-diffusion either of proton holes or of anion vacancies formed after protons on the wall of the neighbouring pore have associated with perchlorate ions;

(ii) decomposition of perchloric acid into chlorine oxides, particularly ClO_2. Chlorine dioxide (and also ClO_3 and ClO if they are formed in larger amounts) are capable of reacting with still unreacted ammonium perchlorate on the wall of the pore. The mechanism of this interaction can include the reaction of chlorine oxides with both the anionic and cationic constituents of the lattice [52, 53].

The particular feature of these reactions is that they can result in the regeneration of the acid or of the chlorine oxides, and hence the rate of reaction is independent of the equilibrium pressure of the acid.

In the course of the reaction between chlorine oxides and ammonium perchlorate on the wall of the pore, the pore size will increase until it surpasses the free path length of the molecules under the given conditions. This moment will correspond to transition from Knudsen diffusion to diffusion in a non-porous medium, where no separation of ammonia and perchloric acid will occur. Apparently this moment coincides with that of the decrease in reaction rate usually observed in the low-temperature thermal decomposition of ammonium perchlorate, when conversions of 20 to 40% have been reached. A subsequent mechanical treatment of the residue (leading presumably to the formation of new pores) restores the reactivity of the material [54–56].

Thus, according to the discussed scheme of autolocalization in the thermal decomposition of ammonium perchlorate, nucleus formation is the result of the dissociation of ammonium perchlorate into ammonia and perchloric acid, accumulation of the acid in the pore and thermal decomposition of the acid.

Nucleus growth is the result of the reaction between the decomposition products of perchloric acid and unreacted ammonium perchlorate on the wall of the pore. Nucleus growth, in addition, also includes the migration of perchloric acid into the neighbouring pore, "filling" this. Since the rate of thermal dissociation of ammonium perchlorate is small at low temperatures, it may be said that the low-temperature decomposition of ammonium perchlorate is in fact a gas + solid reaction involving the regeneration of active molecules, this reaction being the cause of autolocalization.

The difference in the mechanisms of nucleus formation and nucleus growth is reflected in the difference of the activation energies of these processes; 50 ± 5 kcal/mole and 30 ± 2 kcal/mole, respectively.

A study of the low-temperature thermal decompositions of other ammonium salts indicated that when an oxidizing acid or an acid whose decomposition yields an oxidizing product is involved, the thermal decomposition of the salt – similarly to that of ammonium perchlorate – is accompanied by autolocalization [58, 59]. Data for ammonium halates are shown in Table 2. The p_s values of the corresponding acids are given as a measure of the proton affinity, and the maximum numbers of nuclei formed under identical conditions on analogous faces as a measure of the rate of nucleus formation. A comparison of the data indicates that the rate of nucleus formation is proportional to the proton affinity of the anion. This finding is in good agreement with the mechanism suggested above.

Table 2

Dependence of maximum number of nuclei per unit surface area on the strength of the acid in the thermal decomposition of ammonium halates

Salt	p_S of acid	δ_{max}	1/cm²
NH_4ClO_3	0.3	644	± 190* ± 82
NH_4BrO_3	0.7	950	± 280 ± 120
NH_4IO_3	0.8	195,000	±4500 ±1400

* To the right side of the δ_{max} values, confidence intervals are given (the upper value corresponds to 95%, the lower value to 70%).

No reactive nuclei are formed in the thermal decomposition of ammonium salts containing non-oxidizing acids (e.g. ammonium carbonate, sulphate, chloride, etc.).

4. *Autolocalization of thermal decomposition, caused by the simultaneous effects of several factors*

In some cases autolocalization is the result not of only one, but of two or more of the above factors. This is so, for example, in the dehydration of crystalline hydrates. According to the concepts of the mechanism of this process developed in our laboratory by Lyakhow, increased reactivity at those sites of the crystal surface where dehydration has already started is due to the weakening of the bonds of the water molecules under the effect of the electrostatic field of water molecules released in the course of the reaction in the form of vapour and adsorbed on the surface of the initial crystalline hydrate. A similar action is also brought about by the solid product of the dehydration reaction. Hence, the reactivity of the crystalline hydrate will increase at a site where the reaction has already started and nuclei will be formed.

By varying the external conditions, it is possible to influence dehydration so that one of these two factors should exert the major effect on the rate of the process. Thus, when dehydration is carried out in vacuum or at a low partial pressure of water vapour, the main effect of autolocalization will be due to the action of the gaseous reaction product, and therefore the shape of the nucleus will be defined by the anisotropy of the lattice of the initial crystalline hydrate. When the water vapour pressure is increased, catalysis of the reaction by the solid product will become predominant. Under these conditions, the shape of the nucleus will be defined not only by the structure of the initial material, but also by the structure of the solid reaction product, and must consequently be different from that in the previous case. This was experimentally confirmed, for instance, in studies on the dehydration of zinc sulphate heptahydrate [60].

II. Prospects of research in the field of localization and autolocalization of solid-state chemical reactions

We have shown above that the systematization of existing experimental results and concepts already allows one (though at the present only on a qualitative level) to specify the factors defining localization and autolocalization and autolocalization in topochemical reactions.

The major factors responsible for localization and autolocalization are assembled in Table 3.

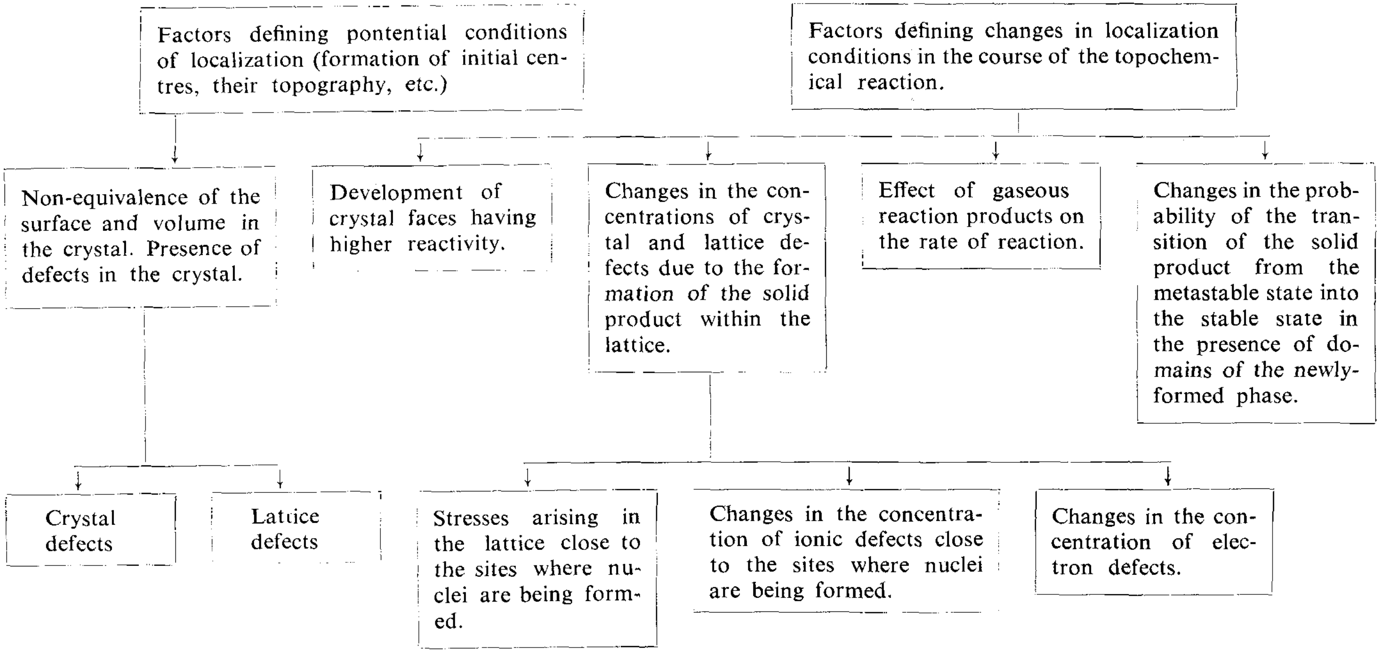
In the knowledge of these factors, we can now pass to the second stage of our investigations, namely to research into the quantitative relationships and the interrelation between the physico-chemical properties of the system and the tendency of the process to autolocalization.

The main difficulty that is immediately met in this field is that in contrast to simple phase transformations, in topochemical processes the simultaneous effects of several factors on the boundary surface must be taken into account, each of these affecting the reactivity to a different extent. This is illustrated in Table 4. Whereas in classical phase transformations such as vapour condensation and melt solidification only one parameter (composition or structure) changes at the boundary surface, in crystallization from solution and in polymorphic transitions two parameters undergo change, while in topochemical reactions, particularly those belonging to the second group into our classification, several factors change simultaneously. The situation is further complicated in that these factors may differ not only with regard to the strength and efficiency of their effect on the reactivity of the solid, but also with regard to the sign of this effect. Hence, it can happen that some of the factors enhance the reactivity, while other factors simultaneously retard the process.

The problem to be solved can be formulated as follows: for any given system the resultant of the actions of different factors must be found, these factors changing the reactivity of the solid in the reaction zone, and thereby affecting the extent

Table 3

Factors leading to localization in solid-state thermal decomposition reactions



Factors defining pontential conditions of localization (formation of initial centres, their topography, etc.)

Factors defining changes in localization conditions in the course of the topochemical reaction.

Non-equivalence of the surface and volume in the crystal. Presence of defects in the crystal.

Development of crystal faces having higher reactivity.

Changes in the concentrations of crystal and lattice defects due to the formation of the solid product within the lattice.

Effect of gaseous reaction products on the rate of reaction.

Changes in the probability of the transition of the solid product from the metastable state into the stable state in the presence of domains of the newly-formed phase.

Crystal defects

Lattice defects

Stresses arising in the lattice close to the sites where nuclei are being formed.

Changes in the concentration of ionic defects close to the sites where nuclei are being formed.

Changes in the concentration of electron defects.

Table 4

Parameters changing on the boundary surface of the phases in the course of nucleus formation

Changing parameter	Process involving nucleus formation
Structure	Vapour condensation, crystallization of supercooled liquid (melt)
Structure and composition	Crystallization from solutions
Structure and deformation	Allotropic transformations
Structure, composition and deformation	Topochemical reactions (first group)
Structure, composition, deformation, ionic and electron properties	Topochemical reactions (second group)

of localization of the thermal process. This is obviously a very difficult problem, and its definitive solution is complicated in many cases for a very simple reason: insufficient information and understanding as to what physico-chemical factors may cause autolocalization in the actual case.

However, even when only generalities are available regarding the physico-chemical parameters affecting localization, essential conclusions on the character of the spatial development of topochemical reactions can be arrived at.

Let us consider, for example, the case when active potential centres are not regenerated in the course of the process, i.e. neither the gaseous nor the solid reaction product catalyzes the reaction. Further, the anisotropy of the properties has a very slight effect on the reactivity, and therefore cannot be the cause of autolocalization. Let us now assume that the change in reactivity is characterized by some parameter ΔR (in the general case the relative or absolute change in the rate constant of the chemical reaction can be used for this purpose).

A plot of ΔR versus the distance r from the potential centre where the reaction has already started will then characterize the tendency of the process to autolocalization.

In the above case where the reaction, having started at some site in the crystal, does not change the reactivity in neighbouring, as yet unreacted domains on the surface or in the interior of the crystal, the curve reflecting the absence of a relationship will obviously coincide with the horizontal axis (Fig. 5a).

The potential centres of the reaction will be scattered over the surface at the initial moment, and further development of the process will take place from the total surface of the crystal (or from a layer adjoining the surface, its thickness being defined by the ratio of the rate of diffusion of the product in the solid phase and the linear velocity of the reaction zone in the interior of the crystal, owing to the chemical reaction), and the rate of reaction will be described by one of the variants of the equation of the "contracting sphere" or "contracting parallelepiped".

Let us now consider another case. Let us assume that active centres will be regenerated in the course of the reaction. This can happen, as has already been discussed, either because the reaction process leads to the development of more reactive faces on the crystal surface, or as a result of autocatalysis by the solid product, or owing to the catalytic action of the gaseous product evolved in the reaction. All these causes increase the probability of the reaction developing above all in the vicinity of that site where it has already started.

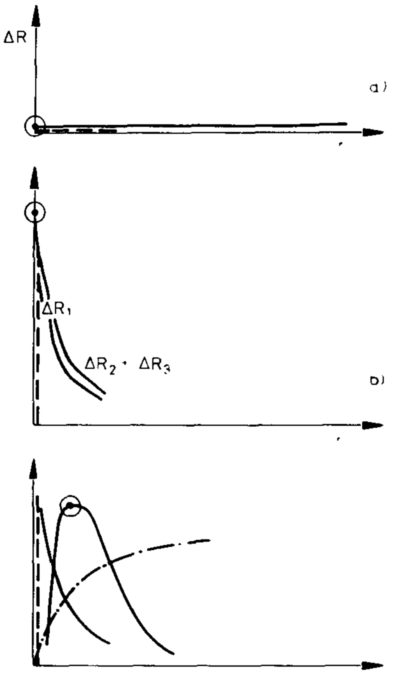


Fig. 5. Different cases of autolocalization in topochemical reactions. a) Reactivity of unreacted domains in the neighbourhood of the potential centre where reaction has already started is unchanged by the reaction. b) Reactivity of unreacted domains is changed by the simultaneous effect of several factors acting in one and the same direction. c) Reactivity of unreacted domains is changed by the simultaneous effects of several factors acting in opposing directions

Let us assume some chemical reaction proceeding in the solid phase, in the course of which the reactivity of the solid initial material will change on its boundary surface with the reaction product.

(i) owing to the non-correspondence in orientation between the lattices of the initial material and the reaction product, that will result in the weakening of the bonds between the components of the initial lattice;

(ii) owing to the non-correspondence of the molecular volumes of the reaction product and the starting material. This will result in the deformation of the initial lattice in the crystal domains surrounding the nuclei of the product. As a final result of stress relaxation, new dislocations may by created;

(iii) owing to the potential difference on the starting material – reaction product interface, leading to a shift of the electron – electron hole equilibrium in the vicinity of the interface.

Let us assume in addition that all these factors lead to the increased reactivity of the starting material. The action radius, however, will be different for each factor.

The action radius of the first factor is limited to a few interatomic distances. In contrast, the second factor acts over substantially greater depths. The stress field around the initial centre created in the course of the reaction can be dealt with in an analogous way as for the stress field around helical dislocations [59, 61]. If not the Burgers vector, but the difference between the molecular volumes of the starting material and the reaction product is utilized, the stress in one direction will be given by the formula

$$\varepsilon = \frac{\Delta V \cdot g}{r}$$

where g is Young's modulus and r is the distance from the active centre, i.e.

$$\Delta R_2 = K''/r \quad \text{where} \quad K'' = \Delta V \cdot g.$$

The action radius of the third factor may be estimated if the values of the electron work function for the starting material and the reaction product are known. The action radius will be equal to the screening length, which can be estimated by the formula [62]

$$r = \sqrt{\frac{V_0 \varepsilon}{2\pi \rho}}$$

where V_0 is the difference between the electron work functions, ε is the dielectric constant, and ρ is the charge per unit volume.

It may be assumed that R, connected with electron transfer in the course of the topochemical reaction, is proportional to the charge per unit volume, i.e. to the change in electron or electron hole concentration. This will be expressed by

$$\Delta R_3 = \frac{K'''}{r^2}$$

If both the second and the third factors affect one and the same kinetic stage, i.e

$$\Delta R_s = \Delta R_2 + \Delta R_3,$$

the overall curve will be expressed by

$$\Sigma\, \Delta R_s = \frac{K''}{r} + \frac{K'''}{r^2}$$

Depending on the signs of K'' and K''', the plot ΔR vs. r will assume different shapes.

In the present case, when both factors accelerate the reaction, i.e. $K'' > 0$ and $K''' > 0$, the overall curve will assume the shape shown in Fig. 5b. As regards the relationship between ΔR_1 and r, all we know is that ΔR_1 rapidly decreases with increasing distance from the reaction site.

As may be seen from Fig. 5b, maximum change in reactivity owing to the superposition of the effects of these three factors corresponds to the point located on the vertical axis. Hence it is to be expected that the topochemical reaction will develop mainly as a result of the growth of nuclei previously formed.

Let us now consider the third possibility. Let us assume that, as in the previous case, several factors act simultaneously on the interface between the initial material and the product. However, the directions of their effects are *different*: while some factors increase the reactivity, others decelerate the reaction.

By way of example for a system where this situation exists, the thermal decomposition of silver oxalate may be mentioned. In the decomposition of silver oxalate, the formation of metallic silver nuclei is the result of yet another cause, in addition to those discussed in the previous example. It is obvious that the silver concentration in the metallic nuclei is much higher than that of the silver ion in the oxalate lattice. To maintain coherence in the initial lattice and the reaction product lattice as the reaction proceeds, therefore, the diffusion of silver ions from the surrounding oxalate lattice to the place of contact is necessary. This diffusion takes place by means of interstitial silver ions.

If the migration of interstitial silver ions and their fusion with the growing silver nucleus proceeds more rapidly than the restoration of the equilibrium concentration of interstitial ions in the lattice, and thereby the conditions described by Scholz [64] and Rogalla and Schmalsried [65] are realized for the solid-state reaction, the interstitial ion concentration in the vicinity of the growing nucleus will fall, and consequently the reactivity too will decrease. In fact, the rate of growth of the metallic silver nucleus changes parabolically with its growth.

The superposition of all the effects on the reactivity will then yield a curve (Fig. 5c) whose maximum is not located on the vertical axis, but is shifted to its right side, reflecting that the topochemical reaction develops in this case not on account of nucleus growth, but on account of the formation of new nuclei. Autolocalization then takes place as a result of the preferential formation of new nuclei close to already-formed nuclei, this leading to the "clustering" of the nuclei.

It is clear from what has been said that even qualitative information on the factors that can cause autolocalization in the course of the process may be of great use in predicting the character of the space development in topochemical reactions.

When the absolute (or relative) values of ΔR due to each of the factors affecting the reactivity are known, we shall be able to predict the development of the process on a quantitative level, and also to outline the general strategy of governed control. For this reason, further expansion of studies in this direction is indispensable.

Up to now, we have utilized – as a first approach – the assumption that different factors affect the autolocalization independently of each other, so that their resultant effect is obtained by simple summation. Actually, however, this assumption is not true. The following task of great importance, therefore is the consideration of non-additivity for some of these factors.

Finally, the medium in which the process develops is not isotropic, as has tacitly been stipulated above, but anisotropic. For a closer and more rigorous approach, we must therefore pass from the one-dimensional concept used so far to three-dimensional concepts in order to express the change in reactivity on the boundary surface that gives rise to autolocalization. This change will then be described by a set of tensors written in matrix form. This is another important task for the future.

What can be expected from research into the physico-chemical causes of autolocalization? The great significance of such studies, as regards both pure and applied science, can hardly be overestimated.

In fact, if we were able to understand these causes and to predict the characteristics of steric development in topochemical processes, this would permit the solution of a number of problems:

(i) In kinetic analyses, instead of dealing with hypothetic models and testing the applicability of different kinetic equations for the description of the development of the topochemical reaction, as is usually done at present, it should become possible to predict realistic physical models for topochemical reactions.

(ii) The true physical sense of topokinetic constants could be found. Up to the present these constants have been outlined in a largely generalized and undefined form only.

(iii) New prospects could open up concerning the governed control of the rate of topochemical reactions. So far, governed control is accessible on a qualitative level only, and is usually limited to the initial stage of the process.

(iv) Conditions for governed control not only in time, but also in space, could be created. This would allow the control of the morphologic properties of the solid product being formed in the reaction. Such potentialities would be of the greatest importance when thermal decomposition reactions are used to prepare catalysts, highly-active oxides utilized in the metallurgy of rare and non-ferrous metals, ceramic materials of the ferrite type, etc. It may well be expected that success in this field would lead to the development of fundamentally new technologies, uniting the stages of material production and forming of the material to the shape required in the end use.

(v) It should become possible to predict the applicability of various rapid methods of kinetic analysis including methods based on experimental data obtained under non-isothermal conditions.

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Résumé — On présente une étude d'ensemble sur les réactions topochimiques en discutant la théorie de la cinétique.

Zusammenfassung — Eine Übersicht über die topochemische Reaktion wird gegeben und die Theorie ihrer Kinetik erörtert.

Резюме — Сделан обсор теоретических воззрений на механизм топохимическх реакций.