

Review

Attempt to a Systematic Classification of Topotactic Reactions

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I. INTRODUCTION

The term "topochemistry" was first used by V. Kohlschütter¹⁾ to describe reactions occurring in or at the surface of a solid, which often show specific influences of the nature of the substrate on the kinetics and mechanism of the reaction and on properties of the product (*e.g.* on its porosity, particle size, shape, surface structure, crystal structure or even chemical composition). Such reactions have extensively been studied by V. Kohlschütter and later by W. Feitknecht²⁾ and by H. W. Kohlschütter.³⁾ The growing field of applications of X-ray and electron diffraction revealed a great number of topochemical reactions, in which the property influenced most strikingly by the substrate is the product crystal structure orientation. The necessity of introducing a special term for this type of topochemical reaction was met by F. K. Lotgering (influenced by E. W. Gorter)⁴⁾ in 1959. He denoted by "topotaxy" "all chemical solid state reactions that lead to a material with crystal orientations which are correlated with crystal orientations in the initial product". At about the same time, J. D. Bernal introduced the term "metataxy" for the same kind of reaction, but Lotgering's expression gained general acceptance. Bernal reduced the wide range of Lotgering's definition in 1960⁵⁾ by requiring a three-dimensional accord between original and product crystals for a reaction to be called topotactic. He stated that in general the main directions of symmetry of the reacting crystal remain intact in topotactic reactions. This definition was extended by A. L. Mackay⁶⁾ to include structural transformations. Furthermore, the term should only be applied, if the majority of the atomic positions remain fixed, according to Mackay. This was again altered by L. S. Dent-Glasser, F. P. Glasser, and H. F. W. Taylor,⁷⁾ who adopted an intermediate position with respect to the requirements of structural accord between the strict requests of Bernal and Mackay and the rather diffuse statement of Lotgering. In 1964, Bernal and Mackay⁸⁾ again stressed the importance of dimensional and structural correspondence in the three axial directions. R. D. Shannon and R. C. Rossi⁹⁾ attempted a new definition of topotaxy by reducing the requirements of Bernal and Mackay and introducing different degrees of topotaxy, corresponding to the extent of perfection of the preferred orientation found in the product crystallites. They ask for a clear separation of topotaxy from epitaxy, the latter term being used only for oriented overgrowths and

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not for transformations. W. Kleber¹⁰⁾ pointed out that most topotactic reactions do not yield single crystal products, but "topotactic reaction fabrics", assuming only "a structural relation" between parent and product crystals, which may be one-, two- or three-dimensional. In a review of topotactic reactions, A. Deschanvres and B. Raveau¹¹⁾ cover only phenomena included in Bernal and Mackay's concept, treating phase transformations as well. Their classification is according to supposed reaction mechanisms (homogeneous, heterogeneous and others), which, however, are often not established definitely. The most recent paper on questions of terminology for crystallographic orientation relations by I. Bonev¹²⁾ defines topotactic reactions as chemical reactions of a solid leading to a product with defined crystallographic orientation with respect to the original crystal. This orientation need not be three-, but may be only two- or even one-dimensional. An additional requirement is the exchange of components with the surroundings, separating topotaxy from endotaxy (in Bonev's terminology), in which only energy, but no components may be exchanged. This definition is supported by a number of observations by Kleber¹⁰⁾ and mainly based on work of Oswald and Günter,¹³⁻¹⁵⁾ who have expressed similar views earlier.

Taking into account the ideas put forward in this field up to now and trying not to create any artificial boundaries between closely related processes, we have arrived at the following working definition, which includes a clear separation from endotaxy on one and from epitaxy on the other hand:

A chemical reaction of a solid is called topotactic, if the product is formed in one or several crystallographically equivalent orientations relative to the parent crystal, if there has been an exchange of components with the surroundings, and if the reaction can proceed throughout the entire volume of the parent crystal.

If the product is formed in a small number of defined, but not equivalent orientations, the reaction is treated as a case of several different topotactic reactions occurring simultaneously.

II. ATTEMPT TO A SYSTEMATIC CLASSIFICATION

Considering the vast number of experimental data on topotactic reactions available in literature (partly reviewed in^{5,7,8,10,11,16-18)}), it seems to be appropriate to discuss them from a common point of view. To make this possible, a consistent system of classification must be found. In the present communication, we shall not attempt to give a literature review, but shall only mention a few examples considered suitable to illustrate the various classes of reactions proposed.

Our attempt to a classification is based on the great importance of oriented nucleation for topotaxy. The actual cause of topotaxy is the reduced energy of nucleus formation in specific orientations compared to random nucleation. The following main possibilities for such a lowering of the nucleation energy exist:

- Conservation of certain structural elements of the parent structure in the nucleus of the new phase, reducing the necessity of diffusion for some of the participating atoms. The structural elements conserved may be three-dimensional, two-dimensional (layers) or one-dimensional (chains).

The conservation of structural elements not extended further than a few atomic

distances in any direction, *e.g.* of single coordination polyhedra, does not induce topotaxy in general.

—Epitactic nucleation, due to some metrical accord between parent and product structure in certain lattice planes. Such a nucleation may occur either on inner lattice planes or on outer surfaces.

Further details of the reaction mechanisms shall not be discussed here, being of minor importance for the classification scheme presented.

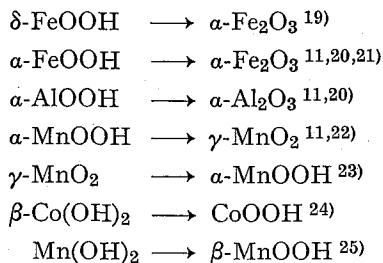
II.1. Conservation of Structural Elements

II.1.1. Three-Dimensional Structural Elements

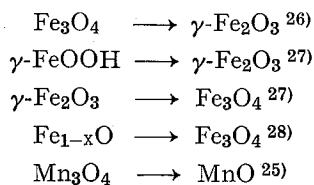
This group of reactions is the one included in all, even the most restricting definitions of topotaxy. Accordingly, classical examples are cited in most of the review articles.

Very obvious is the conservation of a three-dimensional element in reactions of natural and synthetic zeolites and of ion exchange resins.

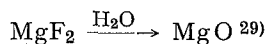
Of particular chemical interest, however, are processes of this group, in which close packed arrangements of ions remain unchanged during a reaction, with counterions only changing their sites. Most well known are the cases, where oxygen anions (O^{2-} and/or OH^-) remain in their approximate close packed arrangements with the cations diffusing. For the case of hexagonal close packed structures, the following reactions may be named as examples:



Similarly, approximately cubic close packed structures may be conserved during topotactic reactions:



In rather rare cases, it has been suggested that the close packed cation sublattice is the element conserved:



Rather more complex cases, where the conserved three-dimensional element includes both cations and anions have also occasionally been reported.

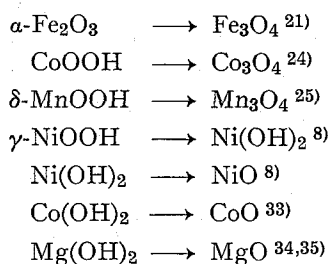
The conversion of chlorapatite into hydroxyapatite³⁰⁾ may be considered as an ion exchange reaction in a more or less rigid lattice of calcium ions and phosphate.

In the oxidation of Sb_2O_3 to Sb_2O_4 ,³¹⁾ virtually the whole lattice of Sb_2O_3 remains intact, with oxide ions diffusing along open channels in the structure to their appropriate positions in the Sb_2O_4 structure.

Similarly, in thin crystalline films of 7,7,8,8-tetracyanoquinodimethane, cesium ions can diffuse through channels to produce a charge transfer complex,³²⁾ without any major change in the spacial arrangement of the organic molecules.

II.1.2. Two-Dimensional Structural Elements

In the transition metaloxide systems, not only reactions with conservation of cubic or hexagonal close packed anion sublattices occur, but also transitions from one of these types to the other. In this case, the three-dimensional arrangement is not conserved, as the dense packed layers are shifted with respect to each other. Therefore, these reactions only show conservation of structural elements in two directions, in this case of close packed oxygen layers:



Similarly, many compounds crystallizing in actual layer lattices react chemically by preserving the prominent layers, the reaction taking place in between these planar elements:

- intercalation of various substances in graphite, *e.g.*,³⁶⁾
- intercalation of various substances in clay minerals, *e.g.*,^{37,38)}
- dehydration of layer silicates,¹⁸⁾ *e.g.* of kaolinite,³⁹⁾
- interlayer ion exchange in layer silicates, *e.g.*,⁴⁰⁾

More complex cases, where the layers themselves are conserved, but at least slightly altered by participating in the reaction, are of crystal chemical interest, *e.g.*:

- transformation of aragonite into hydroxyapatite,⁴¹⁾
- numerous reactions of layered hydroxide salts, as the reaction of zinc hydroxide nitrate with various metal chloride solutions,⁴²⁾
- dehydration of molybdenum trioxide dihydrate in two separate topotactic steps.⁴³⁾

II.1.3. One-Dimensional Structural Elements

Reactions, in which the conservation of a one-dimensional structural element (chain) is the determining factor of nucleation are frequently found in cases, where educt, product or both have pronounced chain structures. Very often this is illustrated by a fibrous appearance of the primary particles in the product pseudomorphs.

Well known structures of this class are gypsum, the dehydration of which^{7,44,45)} is such a one-dimensionally controlled reaction, and copper (II) hydroxide, which can be decomposed to copper(II)oxide and further to copper(I)oxide,^{35,46)} or which may be formed on the other hand from copper hydroxide salts by decomposing crystals of a number of such salts with different anions in sodium hydroxide solutions.⁴⁷⁾ The chain

elements conserved are linear arrays of edge linked distorted coordination octahedra around copper(II)ions. The transformations of the mineral malachite into azurite and copper(II)oxide¹⁰⁾ follow a similar principle.

Less well known structures, the dehydrations of which also belong into this class, are γ -Zn(OH)₂³⁵⁾ and white molybdenum trioxide monohydrate, MoO₃·H₂O.⁴⁸⁾

II.2. Epitactic Nucleation

A number of reactions appear to be two-dimensionally controlled when investigated both by morphological and diffraction techniques, but an exact study of the crystal structures involved shows no structural elements whatsoever being conserved in the product. However, at least a metrical accord between certain lattice planes of educt and product has been found to exist in these cases. Therefore, it may be concluded that epitactic nucleation on these planes leads to reactions, the appearance of which cannot be distinguished from the one of the reactions discussed under II.1.2. without detailed structural studies. Two cases can be postulated and both have actually been observed:

- epitactic nucleation on inner lattice planes of decomposing crystals, and
- epitactic nucleation on outer surfaces of the educt.

II.2.1. Epitactic Nucleation on Inner Lattice Planes

In cases where the reaction produces voids inside the reacting crystals, inner surfaces become free to act as substrates for epitactic nucleation. This kind of topotactic reactions has mainly been found in decompositions of inorganic substances under the influence of the beam of an electron microscope.³⁵⁾ The following substances have been shown to react by this mechanism:

- lead iodide, PbI₂⁴⁹⁾
- cadmium iodide, CdI₂⁵⁰⁾
- tin(IV)sulfide, SnS₂⁵¹⁾
- titanium(IV)sulfide, TiS₂³⁵⁾

II.2.2. Epitactic Nucleation on Outer Surfaces

This borderline case might also be called "reactive epitaxy" instead of topotaxy, but for the sake of a uniform classification, reactions with epitactic nucleation on outer surfaces are considered to be topotactic, if the reaction can proceed throughout the initial substrate crystal. Such processes are of great practical importance in the corrosion science (reactions of solids with gases or liquids). A typical example is the formation of silver selenide from thin silver films and selenium vapour.⁵²⁾

Also for the oriented hydration of magnesium oxide to the hydroxide with water vapour,⁵³⁾ nucleation has been shown to occur at the surface. For certain organic polymerizations, a similar reaction mechanism has been suggested.⁵⁴⁾ From a comparison of the crystal structures involved and their mutual orientation, the recently described formation of an anthracene-TCNQ (1 : 1) complex⁵⁵⁾ seems to belong to this class of topotactic reactions as well.

III. SUMMARY AND DISCUSSION

Based on a review of earlier conceptions on topotaxy, a clear definition of this term has been worked out, separating it from endotaxy and epitaxy. Stressing the fact that

oriented nucleation is the most important step in a topotactic reaction, the possibilities of such an oriented nucleus formation in a solid state reaction have been sought. These, in turn, yield the basis for a first attempt to a consistent and systematic classification of all topotactic processes. Specific reactions can easily be classified in most cases, if the crystal structures of educt and product, as well as their mutual orientations, are known.

The purpose of the present communication is to establish such a scheme of classification. No detailed arguments have been given for the classification of specific examples cited, and also the various possible applications of topotaxy, such as preparation of new compounds, prediction of crystal structures or interpretation of reaction mechanisms, have not been discussed. These points will be treated in detail in our future work. In the course of further refined discussions, it might well be possible that small changes in the classification system proposed here will have to be made, without, however, affecting the principal idea it is based on.

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