

CRYSTALLOGRAPHY OF TOPOTACTIC REACTIONS*

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ABSTRACT

Many reactions in solids are known to be governed purely by structural considerations. In these reactions one generally finds that a single crystal of the starting material is converted into a pseudomorph containing one or more products in a definite crystallographic orientation and the conversion takes place throughout the volume of the crystal. These observations can be made with the help of suitable diffraction techniques. The reason why there is no breakup of the lattice in such cases is because the crystal structures are to a large extent preserved. These reactions, known as topotactic reactions, can therefore be adequately explained only if the relevant structures are taken into consideration. Topotaxy has been observed in a variety of reactions, such as polymorphic transformations, oxidations, dehydrations, decompositions, isomerisations, etc., both in organic and inorganic systems. The interest in these studies, the experimental techniques employed and some examples in this field are discussed.

Key words: Topotaxy; topotactic reactions; pseudomorph; hybrid crystal; orientation relationships; mechanism.

I. INTRODUCTION

Many reactions in solids are studied by chemists using a variety of experimental techniques. Spectroscopic methods such as i.r., n.m.r., Mossbauer thermal techniques such as D.T.A. and T.G.A., electrical conductivity, microscopy, both optical and electron, X-ray diffraction, kinetic measurement are a few that can be mentioned. Generally these reactions take place in powdered or microcrystalline specimens. However many solid state reactions are known to occur in single crystals; i.e., a single crystal of the starting material is converted into the product(s) as a pseudomorph (without an change in the external shape), the conversion taking place in the entire volume of the crystal. Further there exist certain definite three-dimensional orientation relationships between the respective lattices. Such reactions, termed as topotactic reactions [1, 2], can be studied by suitable single crystal diffraction techniques.

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niques. The reason why there is no break-up of the lattice in such cases is because of some three-dimensional correspondence or similarity between the respective structures. For these reasons, topotactic reactions should be of considerable interest to the X-ray crystallographer. Differing views have been expressed [3-7] as to how exactly Topotaxy has to be defined, but we shall not go into this question. We shall also not be concerned here with the closely related but more general theme of Topochemical reactions [8]. Topotaxy has been observed in a variety of reactions such as polymorphic transformations, oxidations, dehydrations, decompositions, isomerisations, exsolution phenomena, etc., in organic and inorganic compounds, especially minerals.

The importance of a study of these reactions should be mentioned. With a knowledge of the orientation relationships and the crystal structures of the reactant and product (and intermediate phases, if any), the relationship between the structures can be deduced. One thus gains an insight into how atomic re-arrangement takes place during the reaction. This information is of considerable value in trying to understand the detailed mechanism of the reaction at the atomic level, particularly when supplemented by some of the physico-chemical techniques mentioned earlier. The study of topotaxy also provides a powerful tool, in certain cases, for predicting unknown crystal structures.

2. EXPERIMENTAL METHODS

Although some studies have been done using optical microscopy [9], the most powerful tools for the study of topotactic reactions are single crystal X-ray and electron diffraction techniques, the latter having the advantage that very small crystals of dimensions 10^{-8} to 10^{-4} mm could be employed. Some crystals decompose in the electron beam and topotactic reactions occurring in this manner have been effectively studied by electron diffraction combined with electron microscopy [10-13].

To study a typical topotactic reaction, a single crystal with well-defined morphology is mounted in appropriate orientations on the camera and diffraction patterns taken before and after the reaction. By comparing the positions of the spots due to the reactant and product(s) on the photographs, the orientation relationships between the respective lattices can be deduced. The accuracy of the result will, of course, depend on the ease with which the outlines of the crystal could be identified and the accuracy with which it can be reset on the camera. If it is of considerable advantage if the reaction can be temporarily halted before completion. The 'hybrid' crystal thus obtained will contain the lattices of the reactant and product phases in the appropriate

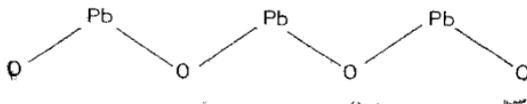
orientation. Therefore it is possible to obtain photographs of the two interpenetrating reciprocal lattices on the same film and thus eliminate errors due to crystal setting.

In thermal transformations, which are the most common, if the reaction is irreversible, the crystal can be heated separately in a furnace and studied at room temperature in the camera. However, for reversible reactions, a high-temperature attachment will have to be employed so that the crystal can be heated *in situ*. There are cases [14, 15] where the products have not given diffraction spots, but powder lines with non-uniform intensity distribution in each line. This means that the product is not exactly a single crystal but an aggregate of microcrystallites oriented in certain preferred directions. However, even in such cases, it has been possible to determine the orientation relationships. In many of these reactions, differing degrees of crystallinity of the reactant and product, short range order, etc., are encountered. These can be deduced from characteristic diffraction effects, such as broadening of spots, streaks and other extended regions of scattering. It should also be added that in some reactions, for example, the polymorphic transformations in *p*-dichlorobenzene [16] and silver nitrate [17], no orientation or crystallographic relationships have been found between the two phases even though the reactions take place in single crystals.

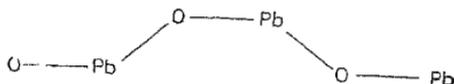
A few representative examples of studies in the field will be described in the following pages, wherein the crystallographic aspects will be highlighted. However, this review is not intended to be exhaustive. Excellent reviews on the subject are available in the literature [2, 3, 18-23].

3. POLYMORPHIC TRANSFORMATION IN LEAD MONOXIDE [24]

PbO exists in two crystalline forms, the yellow orthorhombic high-temperature form and the red tetragonal low-temperature form, with a transition temperature of 491° C. Both modifications have layer structures parallel to (001) with the oxygens sandwiched between the lead atoms, which have an approximately cubic close-packed arrangement. The layers in tetragonal PbO can, in the (100) and (010) planes, be considered to be made up of simple zigzags with all the leads in any one zigzag on the same surface of the layer.



These layers interlock at right angles in the oxygen atoms. In a layer of orthorhombic PbO, however, the chains are made up of corrugated units



running along [100] but in antiparallel directions in neighbouring (010) planes. Here both lead and oxygen atoms are present on both surfaces of the layer. The structures of the two modifications are shown in projection in Figs. 1 and 2.

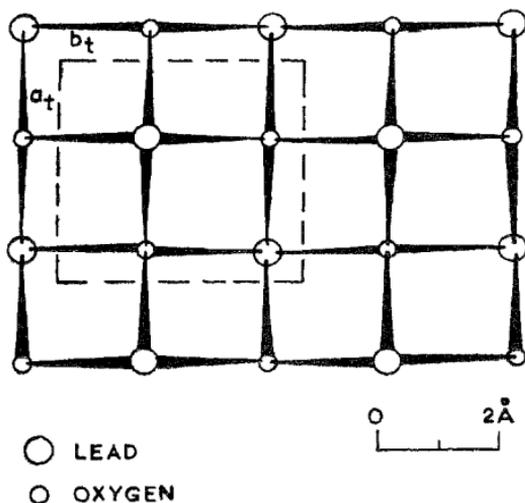


Fig. 1. Projection along [001], of a layer of the structure of tetragonal PbO. (From Soderquist and Dickens [24].)

The high-temperature orthorhombic form could be prepared at room temperature as a metastable phase, which transforms spontaneously to the stable tetragonal modification. Since the transformation takes a few hours for completion, it was possible to obtain a hybrid crystal whose diffraction patterns could be recorded by X-ray techniques. The crystal data for the two phases, as well as the orientation and dimensional relationships that were obtained, are given in Table I.

TABLE I

Crystal data for the two modifications of lead oxide, orientation and dimensional relationships. Note approximate halving of a_0

	Crystal data		Orientation and dimensional relationships
	PbO (<i>o</i>)	PbO (<i>t</i>)	
Symmetry	Orthorhombic	Tetragonal	$(001)_o \parallel (001)_t$
Space group	Pbma	P4/nmm	$[001]_o \parallel [001]_t$
a (Å)	5.489	3.976	$[100]_o \parallel [110]_t$
b (Å)	4.755	3.976	$d_{(100)_o} = 5.89, d_{(001)_t} = 5.02 \text{ Å}$
c (Å)	5.891	5.023	$d_{(200)_o} = 5.49, d_{(110)_t} = 2.81 \text{ Å}$
Z	4	2	

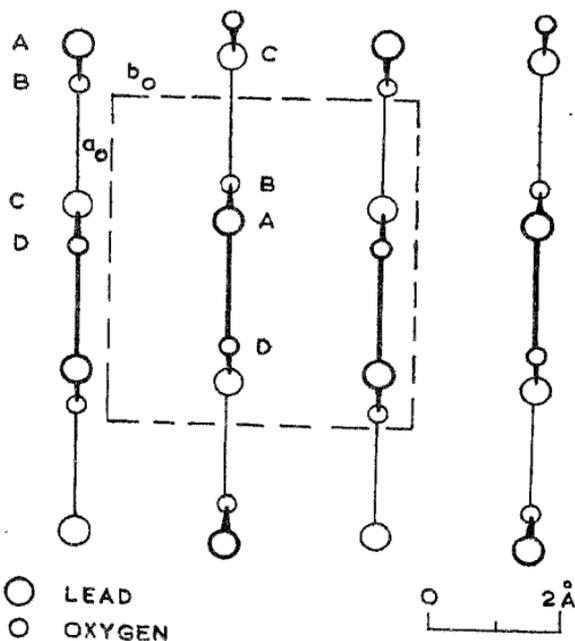


FIG. 2. Projection along $[001]_o$ of a layer of orthorhombic PbO. (From Söderquist and Dickens [24].)

The manner in which the transformation takes place can be understood by examining Fig. 3, which is the projection down the common axis (c) of the structure of a hybrid crystal formed from the two structures in the appropriate orientation. Here A and C, which are leads on the upper and lower surfaces of a layer respectively, are assumed to be in approximately the same positions in the two modifications. This condition would also conserve the lead packing which is similar in both structures. To accomplish the transformation there are two alternate but equivalent directions of motion of the oxygen atoms indicated by solid and dotted arrows. If we consider moving

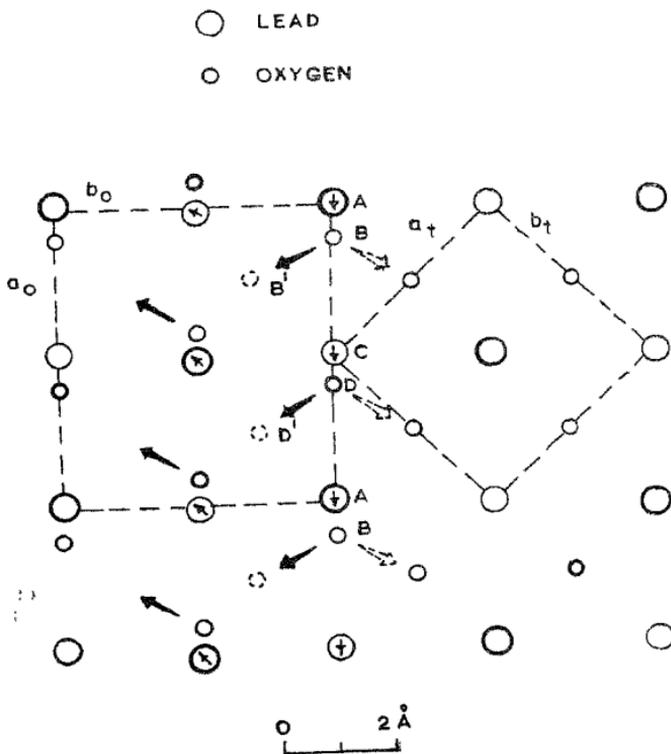


FIG. 3. Projection along [001] of the structure of a hybrid crystal composed of PbO (\circ), left and PbO (\circ), right. (From Söderquist and Dickens [24].)

the oxygens B and D to their new positions B' and D', in the process they, are moved alternately upwards and downwards respectively along [001] thus flattening the puckered oxygen layers of the orthorhombic form. This is an interesting example where the structural change appears to be brought about by movement of the anions through a relatively unchanged cation framework. This is not unexpected in view of the comparatively large size and mass of lead.

However, in most of the topotactic reactions in inorganic oxycompounds such as oxides, oxide hydroxides, silicates, etc., containing small cations such as Mg^{2+} , Al^{3+} , Fe^{3+} , Si^{4+} , the oxygen framework, which approximates a close-packed arrangement to varying degrees, remains relatively unchanged while the cations migrate. The type of oxygen packing may, however, change. Mention should be made in this connection of the pioneering work in the iron oxide hydroxide system by Bernal and coworkers [25, 26].

4. DEHYDRATION OF MAGNESIUM HYDROXIDE

The above ideas are exemplified in the dehydration of brucite, $Mg(OH)_2$ to periclase, MgO which takes place at 250–300° C. Apart from X-ray studies, an electron beam has been used to effect the dehydration in single crystals at room temperature and electron micrographs and electron diffraction patterns have also been obtained [27]. These studies indicate that the product is an aggregate of microcrystallites highly oriented with respect to the initial crystal. Further, additional weak reflections were observed on the X-ray photographs indicating the existence of an intermediate spinel-like phase.

MgO has the cubic rock-salt structure, while $Mg(OH)_2$ has the hexagonal CdI_2 layer structure. The experimental results showed that the close-packed (111) planes of oxygens in the oxide are oriented parallel to the close-packed (0001) planes of hydroxyl ions in the reactant. The crystal data for the compounds, orientation and dimensional relationships are given in Table II. Thus the main feature of the reaction is the maintenance of the close-packed arrangement of anions and the octahedral coordination of Mg ions.

The mechanism earlier proposed [27] was that adjacent pairs of hydroxyl ions in brucite react to give oxygen ions and water, thus leading to the alternating sequence of Mg^{2+} and O^{2-} found in the structure of periclase (Fig. 4 a). The water molecules migrate between the planes to the surface and are removed. This 'homogeneous' mechanism in which water is lost more or less uniformly from all parts of the crystal could not, however, explain

the formation of the intermediate spinel-like structure in which Mg ions have both tetrahedral and octahedral coordination.

TABLE II

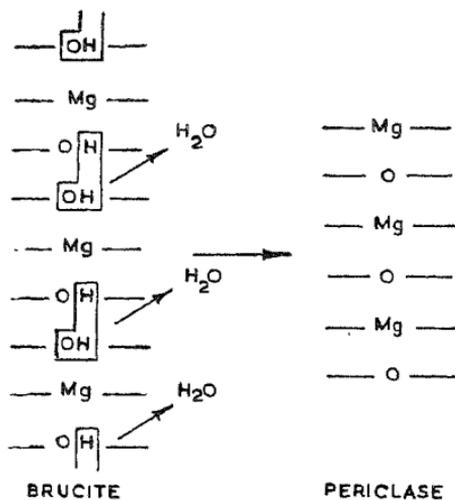
Crystal data for brucite and periclase, and orientation and dimensional relationships between them. Note approximate halving of c_B .

	Crystal data		Orientation and dimensional relationships
	Brucite	Periclase	
Formula	Mg(OH) ₂	MgO	(0001) _B (111) _P
Symmetry	Hexagonal	Cubic	{001} _B {111} _P
Structure type	CdI ₂	NaCl	[100] _B [110] _P
a (Å)	3.11	4.20	$d_{(001)B} = 4.74$, $d_{(111)P} = 2.42$ Å
c (Å)	4.74		$d_{(100)B} = 3.11$, $d_{(110)P} = 2.97$ Å

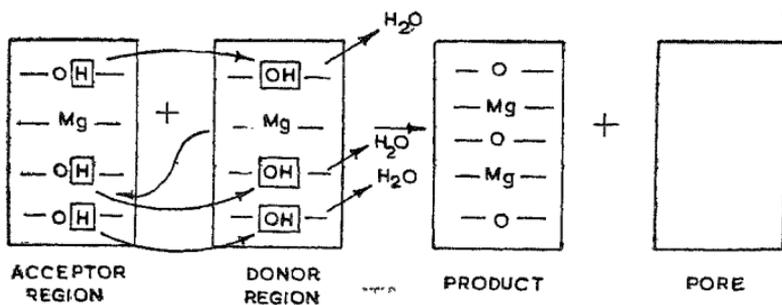
An alternate 'inhomogeneous' mechanism, (Fig. 4 *b*), was therefore proposed [28, 29] in terms of donor and acceptor regions with respect to Mg ions. The acceptor regions in brucite are converted to periclase by gain of Mg²⁺ from the donor regions and loss of protons. These protons combine with hydroxyl ions of donor regions and are removed as water molecules. Thus the donor regions are completely depleted of both cations and anions and become the pores which are experimentally observed in electron micrographs. Since in this mechanism, the migration of Mg²⁺ is postulated, the formation of the intermediate phase could be explained by saying that during the reaction some of the cations occupy temporarily the tetrahedral sites.

5. DEHYDRATION OF MOLYBDENUM TRIOXIDE HYDRATES

The following is an interesting example in which a crystal structure has been proposed purely based on considerations of topotaxy [30]. It has been shown by thermogravimetry that the dehydration of molybdenum trioxide dihydrate in air takes place in two distinct steps. The first step to the monohydrate (yellow monoclinic form) occurs at 60–80° C and the second to the anhydrous trioxide at 110–125° C. This has made possible the isolation and characterisation of the pure monohydrate phase, for which no structural information was available earlier.



(a)



(b)

FIG. 4. Schematic representation of (a) homogeneous and (b) inhomogeneous mechanisms in the dehydration of brucite to periclase. (From Dent Glasser, Glasser and Taylor [3].)

The structure of the dihydrate and anhydrous oxide are known. The structure of the former is built up of slightly deformed layers parallel to (010) of strongly distorted octahedra $\text{MoO}_5 \cdot \text{H}_2\text{O}$ sharing corners. These layers are stacked over each other with layers of crystal waters in between. The anhydrous oxide also has a layer structure parallel to (010) with Mo having an octahedral coordination. However, the octahedra partly share edges in addition to corners. Schematic diagrams of the structures are shown in Fig. 5.

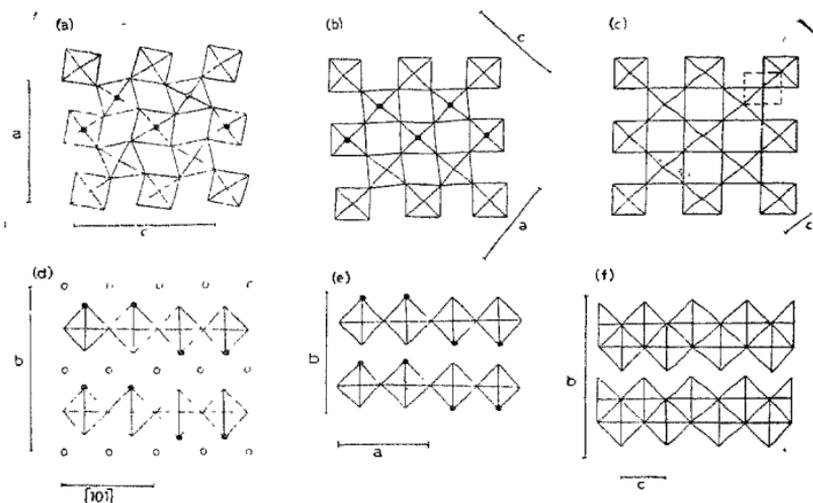


FIG 5. Comparison of schematic structures involved in the topotactic dehydration of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$. Filled circles denote coordinated waters and open circles interlayer waters.

(a) Layer (010) of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$; Octahedra $[\text{MoO}_5 \cdot \text{H}_2\text{O}]$. (b) Layer (010) of $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (proposed structure); Octahedra $[\text{MoO}_5 \cdot \text{H}_2\text{O}]$. (c) Layer (010) of MoO_3 ; Octahedra $[\text{MoO}_6]$. (d) Projection (101) of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$. (e) Projection (001) of $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (proposed structure). (f) Projection (100) of MoO_3 . (From Günter [30]).

A single crystal of the dihydrate oriented along its b axis could be dehydrated topotactically to the monohydrate by heating in air at 80°C without the orientation on the goniometer being altered. From an analysis of the single crystal patterns the cell dimensions for the monohydrate as well as the orientation relationships between the two hydrates (Table III) could be deduced. Further dehydration at 200°C yielded the anhydrous oxide also as a pseudomorph. The approximate relationships between the respective

$I, I, \text{Sc} - 5$

axes are also given in Table III. It is seen that in both the steps the orientation of (010) remains virtually unchanged, while the interlayer separation decreases in the first step and increases in the second. Note also the approximate halving of the a and c axes of the monohydrate in the second step.

TABLE III

Crystal data for $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, yellow $\text{MoO}_3 \cdot \text{H}_2\text{O}$ and MoO_3 , and orientation and dimensional relationships between them

	Crystal data		
	$\text{MoO}_3 \cdot 2\text{H}_2\text{O}$	Yellow $\text{MoO}_3 \cdot \text{H}_2\text{O}$	MoO_3
Symmetry	Monoclinic	Monoclinic	Orthorhombic
Space group	$\text{P2}_1/\mu$	Probably $\text{P2}_1/c$	Pbcm
a (Å)	10.476	7.55	3.963
b (Å)	13.822	10.69	13.855
c (Å)	10.606	7.28	3.696
β (°)	91.62	91	90
<i>Orientation and dimensional relationships</i>			
$(010)_{\text{di}} \parallel (010)_{\text{mono}}$			$(010)_{\text{mono}} \parallel (010)_{\text{anhy}}$
$[101]_{\text{di}} \parallel [001]_{\text{mono}}$			$[100]_{\text{mono}} \parallel [001]_{\text{anhy}}$
$[101]_{\text{di}} \parallel [100]_{\text{mono}}$			$[001]_{\text{mono}} \parallel [100]_{\text{anhy}}$
$d_{(101)\text{di}} = 7.37$, $d_{(001)\text{mono}} = 7.28$ Å			
$d_{(101)\text{di}} = 7.58$, $d_{(100)\text{mono}} = 7.55$ Å			

From the close relation in lattice constants and orientation of molybdenum trioxide monohydrate both to the dihydrate and the anhydrous salt, it is reasonable to expect that all the three structures are closely similar. Thus based on considerations of topotaxy a crystal structure was proposed for the monohydrate (Fig. 5). It consists of $\text{MoO}_5 \cdot \text{H}_2\text{O}$ octahedra, sharing corners similar to the layers of the dihydrate structure. These layers are stacked on top of each other parallel to (010). Information derived from scanning electron micrographs of the final product is in good agreement with the crystallographic results. The postulated structure has not yet been independently confirmed by structure analysis.

However, more recently, workers from the same group have reported [31] the topotactic relationships between another modification (triclinic white form) of the monohydrate and the anhydrous salt, on the basis of which a model for the so far unknown crystal structure of this hydrate has been proposed. The results of an independent structure analysis are in excellent agreement with the proposed structure.

6. OXIDATION OF ORTHORHOMBIC ANTIMONY TRIOXIDE

It has recently been shown [32] in our laboratory that the oxidation of orthorhombic valentinite, Sb_2O_3 , to orthorhombic cervantite, Sb_2O_4 , is a topotactic reaction. Valentinite belongs to the space group Pccn with $a = 4.911$, $b = 12.464$, $c = 5.412$ Å and $Z = 4$. Its structure [33] consists of infinite chains of Sb_4O_6 groups extending along (001), with empty channels in between. Within the chains, each Sb III is bonded to three O atoms and each O to two Sb atoms. Cervantite belongs to the space group $\text{Pc}2_1n$ with $a = 4.810$, $b = 11.76$, $c = 5.436$ Å and $Z = 4$. The structure [34] is

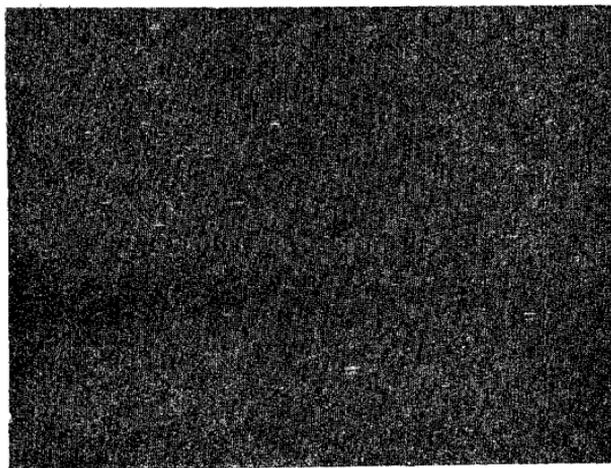


FIG. 6. Zero layer Weissenberg photograph of a hybrid crystal of valentinite and cervantite rotated about the common c axis. Note the twin festoons of spots, of which these at slightly higher angles are due to cervantite. From photographs such as this, the orientation relationships between the axes of the reactant and product are determined. (From Gopalakrishnan and Manohar [32].)

made up of corrugated sheets, parallel to (010), of $\text{Sb}^{\text{V}}\text{O}_6$ octahedra sharing edges. Adjacent sheets are joined through Sb^{III} atoms which have an irregular four-fold coordination of oxygens.

By heating a single crystal of valentinite in air around 490°C for about 4 hours a hybrid crystal containing both phases could be obtained. Rotation and Weissenberg photographs (Fig. 6) of the latter revealed that the three crystallographic axes of the reactant and product are individually parallel. That is, $a_{\text{val}} \parallel a_{\text{cerv}}$, $b_{\text{val}} \parallel b_{\text{cerv}}$, $c_{\text{val}} \parallel c_{\text{cerv}}$. Note the near equality of corresponding cell dimensions.

The close relationship between the two structures could be deduced by comparing the projections down a and c axes in the appropriate orientations as shown in Figs. 7 and 8. It can be seen that the relative positions of the atoms belonging to the Sb_4O_6 groups of valentinite are almost preserved in cervantite. The only additional atoms in cervantite are $0(11)$, $0(12)$, $0(11')$ and $0(12')$. As Fig. 8 clearly shows, these oxygens have entered the lattice of Sb_2O_3 , taken up positions along the empty channels present in the structure and linked up Sb atoms of neighbouring chains along $[100]$. This, along with a closing up of chains along $[010]$, has resulted in the chain structure of valentinite being converted into the three-dimensional structure of cervantite. The reduction of cervantite to valentinite has also been shown to be a case of topotaxy.

The structural work has been supplemented by kinetic studies in a single crystal using a hot stage microscope [35]. The combined results from these two types of studies lead to the interesting conclusion that the diffusion mechanism for this oxidation is governed purely by structural considerations.

7. TRANSFORMATION OF LINARITE TO ANGLESITE

The transformation of linarite, a basic sulphate of copper and lead with the composition $\text{PbCu}(\text{SO}_4)(\text{OH})_2$ to anglesite, PbSO_4 by heat treatment as been found [36] to take place in a single crystal. The reaction has been studied in detail by Dasgupta using X-ray diffraction methods and the orientation and dimensional relationships have been established (Table IV). The presence of tenorite (CuO) crystals in random orientation was also observed in the photographs. It can be seen from the orientation relationships that (100) of linarite becomes (001) of anglesite and (010) remains unchanged.

Schematically the structure of linarite can be considered as made up of blocks of $\text{Cu}(\text{OH})_4$ and PbSO_4 arranged in such a way that a $\text{Cu}(\text{OH})_4$

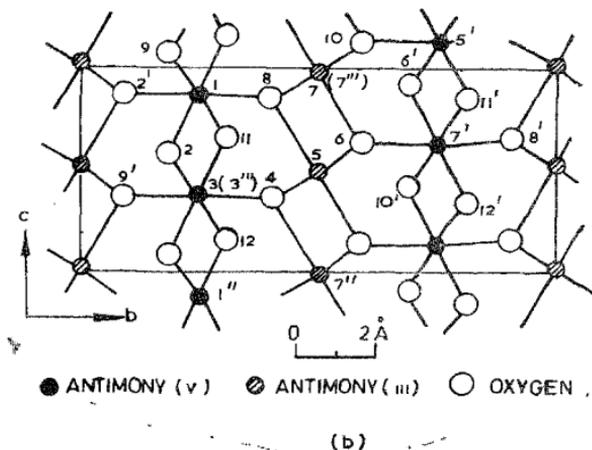
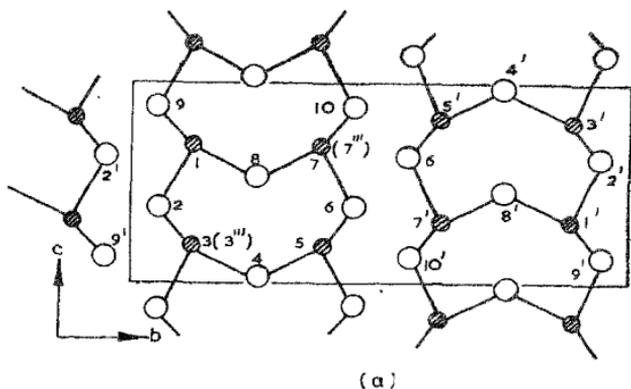


FIG. 7. [100] projections of the structures of (a) valentinite and (b) cervantite. Note that the relative positions of the atoms numbered 1-10, 2' and 9' are nearly the same in the two structures. (From Gopalakrishnan and Manohar [32].)

block is sandwiched between two PbSO_4 blocks. The units of $\text{PbSO}_4\text{-Cu}(\text{OH})_2\text{-PbSO}_4$ are arranged parallel to each other along the a^* direction of linarite. It has been suggested that during the reaction each $\text{Cu}(\text{OH})_2$ block comes out of the linarite structure and the PbSO_4 blocks close up to

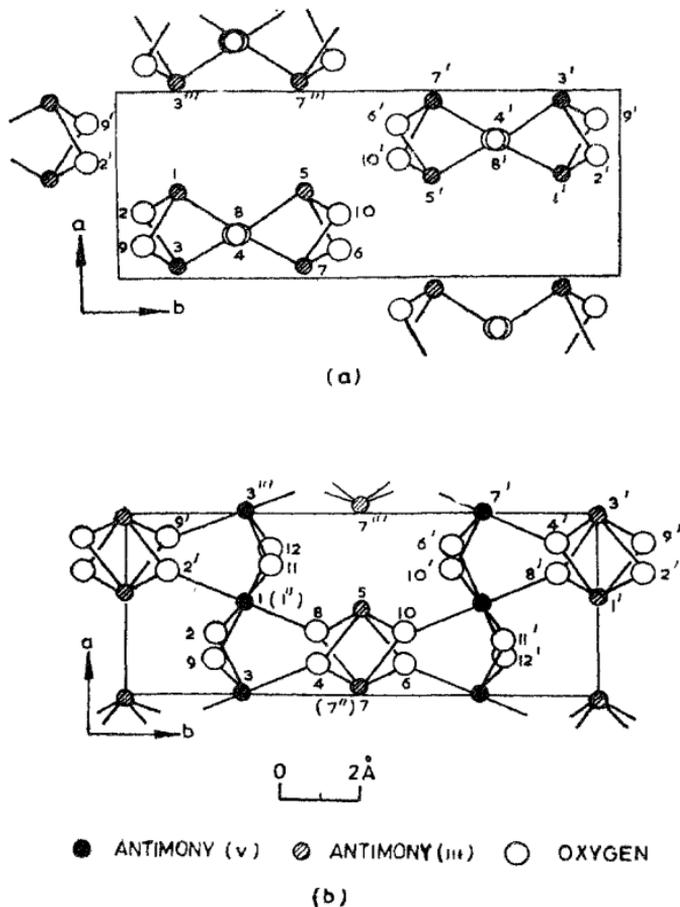


FIG. 8 [001] projections of the structures of (a) valentinite and (b) cervantite. Note that the relative positions of the atoms numbered 1-10, 2' and 9' are almost the same in the two structures. (From Gopalakrishnan and Manohar [32].)

form the product lattice. A slight reorientation of the sulphate tetrahedra with respect to the lead atoms also takes place. It is indeed remarkable that a group of molecules can be removed *en bloc* from the original structure

without disrupting the single crystal character of the product. A similar mechanism [37] has been observed in the decomposition of ankerite, $\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2$.

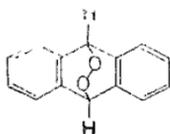
TABLE IV

Crystal data for linarite and anglesite, orientation and dimensional relationships

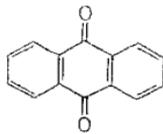
	Crystal data		Orientation and dimensional relationships	
	Linarite	Anglesite		
Formula	$\text{PbCu}(\text{SO}_4)(\text{OH})_2$	PbSO_4	$a_{\text{lin}}^* \parallel c_{\text{ang}}$	$2a_{\text{lin}} \approx 3c_{\text{ang}}$
Symmetry	Monoclinic	Orthorhombic	$b_{\text{lin}} \parallel b_{\text{ang}}$	$b_{\text{lin}} \approx b_{\text{ang}}$
Space group	$\text{P}2_1/\text{m}$	Pnma	$c_{\text{lin}} \parallel a_{\text{ang}}$	$2c_{\text{lin}} \approx a_{\text{ang}}$
a (Å)	9.68	8.480		
b (Å)	5.65	5.398		
c (Å)	4.685	6.958		
β (°)	102.6	90		
Z	2	4		

8. DECOMPOSITION OF ANTHRACENE PEROXIDE [21, 38]

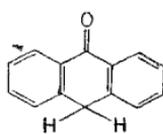
Single crystals of anthracene peroxide (I) upon moderate heating or continuous irradiation by X-rays are transformed into mixed crystals of anthraquinone (II) and anthrone (III).



I



II



III

The decomposition has been studied by X-ray diffraction methods and detailed structural information of the different stages of the reaction has been derived. Anthracene peroxide is a bent molecule with a bridge of two oxygens between the central aliphatic carbon atoms. Anthrone, on the basis of a disordered

structure, is found to be pseudo-centrosymmetric with the oxygen and two hydrogens statistically distributed between two positions. Anthrone and anthraquinone, both planar molecules, are thus isomorphous with very close unit cell dimensions and the two can form mixed crystals. Crystal data for the three compounds are given in Table V.

TABLE V

Comparison of unit cell data for anthracene peroxide and its decomposition products, anthraquinone and anthrone

	Anthracene peroxide	Anthraquinone	Anthrone
Formula	$C_{14}H_{10}O_2$	$C_{14}H_8O_2$	$C_{14}H_{10}O$
Symmetry	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$	$P2_1/a$
a (Å)	15.94	15.83	15.80
b (Å)	5.86	3.97	4.00
c (Å)	11.43	7.89	7.86
β (°)	108.2	102.5	101.7
Z	4	2	2
Molecular Volume (Å ³)	254	242	242

The following different stages of the reaction were observed :

1. Before irradiation the Bragg or Laue spots were sharp and apparently normal.
2. After a relatively brief period of irradiation well-defined continuous lines were observed connecting spots on k -constant festoons on Weissenberg photographs or k -constant layer lines on rotation photographs. The interpretation of this is that rows or chains of molecules parallel to b are behaving as if isolated and are not diffracting in phase with their neighbours. They may be rotated about the chain axis or shifted in the b direction relative to one another, etc. Thus the first stage is a separating out of isolated b -parallel chains of molecules within the original structure.
3. As time goes on, the above continuous lines grow weaker and new X-ray diffraction festoons characteristic of the final product appear (Fig 9). This means that individually the chains of anthracene peroxide molecules become chains of anthraquinone or anthrone or of the two mixed. This stage corresponds to the actual chemical reaction.

4. The new lines do not continue to intensify but tend to break up into new, slightly diffuse spots typical of the product unit cell. As these spots grow in intensity, those of the original peroxide weaken, but the intensities never completely disappear. This step corresponds to crystallisation of the final product in three dimensions into very small mixed crystals or a mixture of crystals, still within the anthracene peroxide matrix. The crystallites are twinned, sometimes double-twinned, and there is a definite topotactic relationship between the original unit cell and all the individuals of the final twinned product.

5. Finally the change-over is complete except for the surface layer of the original crystal, which retains its exact shape.

Many other interesting decompositions, dimerisations, and isomerisation which are topotactic in behaviour have been studied in organic systems [19, 21, 22, 39].

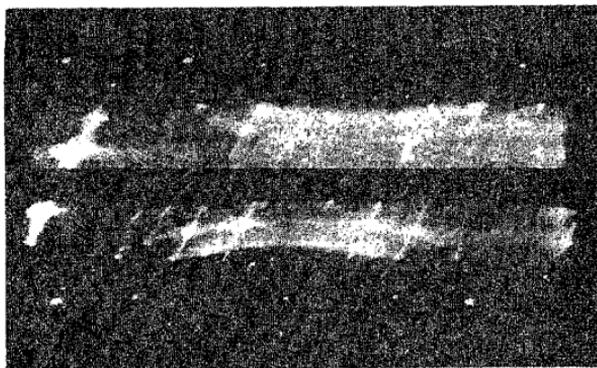


FIG. 9. $\{hko\}$ Weissenberg photograph of anthracene peroxide in an early stage of decomposition showing k -constant festoons (at lower angles) due to isolated strings of peroxide molecules. Also seen are new k -constant festoons (at higher angles) due to strings of anthraquinone or anthrone molecules into which some of the former strings have changed, retaining their original direction but altering their identity distance along the string from 5.6 Å to 4.0 Å. (From Lonsdale [21].)

9. GROWTH OF SINGLE CRYSTALS OF SPINELS [40, 41]

Upto now we have considered cases in which one compound has topotactically reacted to give one or more products. The following is an example of topotaxy in reactions between two solids giving rise to a third. Single crystals of spinels have been grown by heating together single crystals of

MgO with crystals of Al_2O_3 , Fe_2O_3 and TiO_2 , both components being placed in specific crystallographic orientations. It has been shown that the reaction occurs across the interface in a topotactic manner. In every case the axes of the product spinel (cubic) were found to be oriented parallel to those of MgO (cubic). Studies of this type are obviously of technological importance for growing single crystals.

10. CONCLUSION

The examples cited in the preceding pages are an illustration of the wide variety of structural changes which take place in topotaxy and they emphasise the role of X-ray crystallography in understanding these reactions. One general conclusion that can be drawn from the studies done so far is that topotactic processes are probably quite commonplace and many more systems will have to be carefully examined from this point of view.

A pertinent question which can be posed is what type of reactions are suitable for such studies. A clear-cut answer to this question obviously cannot be given. Considerations such as structural similarities between the starting phase and product, existence of voids, channels or similar vacant regions in a structure, which could be occupied by other atoms, would appear to be useful criteria in choosing the systems. Inorganic oxycompounds with small cations and having close-packed arrangements of the anions, salt hydrates in which the water molecules could be easily removed under appropriate conditions, may prove suitable subjects of investigation. In this task, the crystallographic intuition and chemical ingenuity of the worker will, of course, be called into play.

On the other hand, it has been shown [7, 13] that topotaxy does not necessarily need a three-dimensional similarity between the structures of the compounds involved and that a two-dimensional and even one-dimensional relationship is sufficient to induce topotaxy. Examples have also been given (Section 7) in which whole blocks of molecules are removed from a structure and yet the crystal lattice is preserved. Again, several studies in organic systems [22] suggest that surprisingly large molecular migrations and conformational changes may occur without randomizing the final arrangement of the product molecules. Thus the general basis for the occurrence of topotaxy is far from clearly understood. This is all the more reason why the subject should attract the attention of more Indian crystallographers who could make valuable contributions in this fascinating field.

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