Solid-State Chemistry of Organic Polyvalent Iodine Compounds. 10. Sequential, Competitive, and Reversible Topotactic Transformations

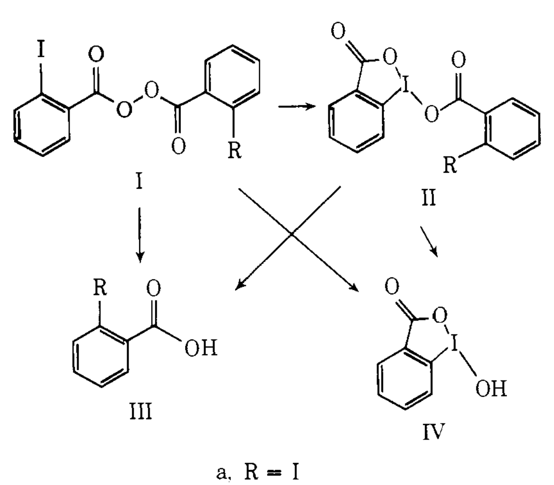
J. Z. Gougoutas

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received March 22, 1976*

Abstract: Single crystals of the 2′-I, -Br, and -F derivatives of 2-iododibenzoyl peroxide, I, undergo several competitive and consecutive topotactic transformations, yielding pseudomorphs containing more than two single-crystal lattices; I → A + B + C (products are benzoxiodole isomers of I, *o*-iodosobenzoic acid, and *o*-halobenzoic acids). The absence of conservative twinning of a particular product lattice, B, relative to the crystal structure of A, suggests that A does not control the preferred topotactic alignment of B in I. Independent studies of the topotactic formation of B in single crystals of A lend support to this conclusion, for the preferred mode of mutual phase alignment of B in pure A differs from that observed when the other lattices are present. Some possible consequences of conservative twinning during successive cycles of reversible topotactic transformations are considered.

The solid-state chemistry of organic polyvalent iodine compounds[1] has provided several examples of sequential topotactic transformations in which an oriented product of the initial transformation may be degraded further to other products which also crystallize in preferred orientations within the original solid. In many cases, several aligned crystal structures are simultaneously present at intermediate stages and it is of interest to identify those which influence the crystallization of the subsequently formed product(s). We have suggested that important clues for the identification may be evident in the symmetry of transformation twinning during the crystallization of product.[2] In this manner we reasoned that the oriented structure of *o*-iodobenzoic acid, IIIa (formed predominantly through subsequent photochemical reductions of the initial transformation product IIa), crystallized on nucleation sites previously established relative to the parent Ia, since the observed multiplicity of orientations (twin members) of IIIa was consistent with the point group symmetry of the parent crystal structure, Ia, but not with the point group symmetry of the intermediate structure, IIa.

Similarly, *o*-iodosobenzoic acid, IV, another, relatively minor topotactic product which chemically may originate from either Ia or IIa, or both, orients uniquely relative to Ia (unique *b* axes of monoclinic Ia and IV are parallel) and not in accord with the point group symmetry of IIa. The topotaxies for both IIIa and IV, therefore, appeared to be established relative to Ia.



a, R = I
b, R = Br
c, R = F

In order to test these ideas, we have studied the topotactic transformations of the intermediate product, IIa, *in the absence of the initial parent structure Ia,* and its other products. The results of these studies of the solid-state chemistry of pure IIa, which was independently synthesized and crystallized from solvents, are presented in this paper. The observed topotactic transformations of pure IIa to IIIa and IV verify the underlying hypothesis and previous prediction that entirely different twinning modes should be observed for topotaxy established solely relative to IIa. Further, they provide independent evidence in support of the above conclusions: (a) the topotaxy between IV and IIa in pure IIa differs from the formal arrangement of their crystal structures in decomposed pseudomorphs of Ia; (b) the directional specificity of alignment of IIIa in pure IIa is considerably lower than that observed in crystalline Ia.

Some competitive and sequential topotactic transformations of 2-iodo-2′-bromodibenzoyl peroxide (Ib) and its 2′-fluoro analogue Ic also are considered below in light of the twinning criterion.

Finally, we explore some implications of the "memory effect" of conservative twinning for reversible topotactic transformations.

Experimental Methods

The synthesis and crystallization of compounds I and II have been described in previous reports of the corresponding crystal structure determinations.[2-5] Weissenberg, Laue, rotation, and precession x-ray photography of crystals having dimensions in the range 0.05–0.2 mm were used to study the various topotactic transformations. Cu Kα x-ray wavelengths (50 kV; 20 mA) were used for most studies, including the photochemical transformations II → III; the occasional use of Mo Kα wavelengths and different power settings gave similar results. Crystals were mounted on glass fibers with DUCO cement; unless otherwise noted, they were continually exposed to the ambient atmospheric and thermal conditions of the laboratory.

The mutual angular orientations of parent and product crystal axes were readily derived from x-ray photographs of partially transformed single crystals. Although some variation in the specificity of alignment, as estimated from the breadth of product reflections on Weissenberg and rotation photographs, was noted for different specimens from the same crop of reactant crystals, the *average* topotactic alignment, derived from the maximum or center of reflection intensities, was constant for each particular chemical parent and product.

In general, the angular specificity of alignment (±2°) observed for topotactic isomerization (I → II) is higher than observed for the more extensive solid-state reorganization required for the topotactic crystallization of III and IV in I and II (±4°). In any case, the specificity of alignment usually is not isotropic; partially transformed crystals

Table I. Crystal Data

Structure	a, Å	b, Å	c, Å	β, deg	Z	Space group	V, Å^3	Ref
Ia	13.02	4.22	15.43	121.1	2	Pc	726	a
Ib	12.96	4.12	15.38	121.2	2	Pc	700	5
Ic	21.41	4.20	15.46	93.7	4	$P2_1/c$	1387	3
IIa	4.09	30.75	22.47	93.3	8	Cc	2821	a
IIb	3.99	26.55	26.01	90	8	$Pbc2_1$	2756	5
IIc	4.08	12.00	26.25	90.5	4	$P2_1/c$	1283	3
IIIa	4.32	15.08	11.29	91.5	4	$P2_1/c$	735	2
IIIb	14.82	4.10	25.90	118.3	8	$C2/c$	1352	2
IIIc	6.55	3.81	24.75	100.7	4	$P2_1/c$	617	11
IV	12.89	4.10	14.05	96.7	4	$P2_1/c$	737	12

[a] These cell constants differ slightly from values reported in previous papers in this series. The revised values were obtained from least-squares analyses of aluminum-calibrated Weissenberg photographs.

Table II. Topotactic Matrices (Φ) and Their Elements

Matrix[a]	φ_{11}	φ_{12}	φ_{13}	φ_{21}	φ_{22}	φ_{23}	φ_{31}	φ_{32}	φ_{33}	Det Φ	Ref
1	0	0.972	0	−2.506	0	−1.915	−0.831	−0.307	0.958	3.878	2[b]
2	0	1.024	0	−0.097	0	0.931	1.008	−0.070	0.491	1.009	2[b]
3	1.054	0	0	0.199	−0.171	0.631	−0.128	−0.344	−0.175	0.260	[c]
4	1.054	0	0	−0.199	0.171	−0.631	−0.017	0.344	0.175	0.260	[c]
5	−0.082	−0.374	−0.261	−1.002	0	0	−0.165	0.253	−0.521	0.261	[d]
6	−0.098	−0.353	−0.310	1.002	0	0	0.178	−0.200	0.563	0.261	[c]
7	1.142	0	0.378	0	0.973	0	0.033	0	0.923	1.013	2[b]
8	0	−0.968	0	2.346	0	0.677	0.473	0	1.862	3.919	[d]
9a	0.035	0	0.978	0	−0.995	0	2.029	0	0.052	1.973	[d]
9b	−0.262	0	0.830	0	0.995	0	−1.803	0	−1.859	1.974	[d]
10	0	0	0.570	1.028	0	0	0	0.859	−0.471	0.503	[d]
11	0	0.971	0	−0.246	0	0.676	1.104	−0.055	0.843	0.926019	
12	0	0.971	0	−0.562	0	−0.054	0	−0.055	1.698	0.926	9
13a	0.599	0	−0.044	0	0.976	0	0	0	0.909	0.532	9
13b	−0.599	0	−0.151	0	−0.976	0	0	0	0.909	0.532	9
14	0.027	−0.126	0.488	1.005	0	0	0	1.171	0	0.574	3

[a] Key to matrices: (1) Ia → IIa; (2) Ia → IIIa; (3) IIIa relative to IIa; (4) IIIa relative to IIa; (5) IIa → IV; (6) IV relative to IIa in Ia; (7) Ia → IV; (8) Ib → IIb; (9a) Ib → IIIb (major); (9b) Ib → IIIb (minor); (10) IIb → IIIb; (11) Ic → IIc; (12) Ic → IIc; (13a) Ic → IV (major); (13b) Ic → IV (minor); (14) IIc → IV. [b] Previously reported matrices have been recalculated using the revised cell parameters in Table I. [c] See text. [d] Determined from Weissenberg and precession photographs of partially transformed crystals.

displaying relatively sharp layer lines (rotation and Laue photographs) corresponding to well aligned, short 4-Å axes of parent and product phases tend to be less specifically aligned along other (longer) lattice repeats. An exception was found in the photochemical transformation IIa → IIIa, where [100] rotation and Laue photographs suggest considerable misalignment of the short 4-Å axes as well.

Quantitative considerations of these effects and their relationship to the degree of perfection of the parent crystal are beyond the scope and intent of this paper. We are here concerned primarily with the measured *average* topotactic alignment and possible twinning of a product phase.

Results

Matrices (Φ) defining the topotactic relationship between the unit cell *vectors* of the parent crystal structure ($\mathbf{a}$) and the unit cell vectors of a particular product ($\mathbf{A}$) (Table I) according to $(\mathbf{A}) = \Phi(\mathbf{a})$ are given in Table II. Multiple orientations of the product phase are formed whenever the directions of point group symmetry axes of parent and product are not coincident (conservative twinning). The cell vectors for the nth symmetry equivalent orientation (nth twin member) of product are given by $(\mathbf{A})_n = \Psi_n(\mathbf{a})$ with $\Psi_n = \Phi C_n$, where the C_n are matrices representing the point group symmetry of the parent crystal structure. For triclinic, monoclinic, and orthorhombic point groups, corresponding elements of the group of matrices Ψ_n differ in sign, but not numerical value. (Only one matrix and the crystallographic symmetry of the reactant are given for each topotaxy represented in Table II.)

The formal relationship between the nth oriented member of the initial product, IIa, and the mth oriented member of the subsequent product IIIa may be obtained from the tabulated relationships between Ia and IIa (matrix Φ_1 for $(\mathbf{A}_{\mathrm{IIa}})_n = \Phi_1 C_n(\mathbf{a}_{\mathrm{Ia}})$), and between Ia and IIIa (matrix Φ_2 for $(\mathbf{A}_{\mathrm{IIIa}})_m = \Phi_2 C_m(\mathbf{a}_{\mathrm{Ia}})$):

$$(\mathbf{A}_{\mathrm{IIIa}})_m = \Phi_2 C_m C_n^{-1} \Phi_1^{-1} (\mathbf{A}_{\mathrm{IIa}})_n \ldots \quad (1)$$

Two distinguishable orientations of IIIa relative to IIa, therefore, are present in decomposed pseudomorphs of Ia: $\Phi_3 = \Phi_2 \Phi_1^{-1}$ and $\Phi_4 = \Phi_2 C_2 \Phi_1^{-1}$, where C_2 is the matrix representing a twofold rotation about b ($c_{11} = c_{33} = -1$, $c_{22} = 1$, $c_{ij} = 0$). However, there is no detectable ordering in orientations expected for *conservative twinning relative to IIa:*

$$(\mathbf{A}_{\mathrm{IIIa}})_n = \Phi_{(3 \text{ or } 4)} C_n (\mathbf{a}_{\mathrm{IIa}}) \ldots \quad (2)$$

The situation is clearly different for pure crystals of IIa which have been photochemically reduced[1] to IIIa during continuous exposure to X radiation (Cu Kα; 50 kV, 20 mA) and atmospheric moisture over a period of several months at ~22 °C. Reflections from the sole crystalline product IIIa are very extensively elongated, suggesting a severe mosaic with

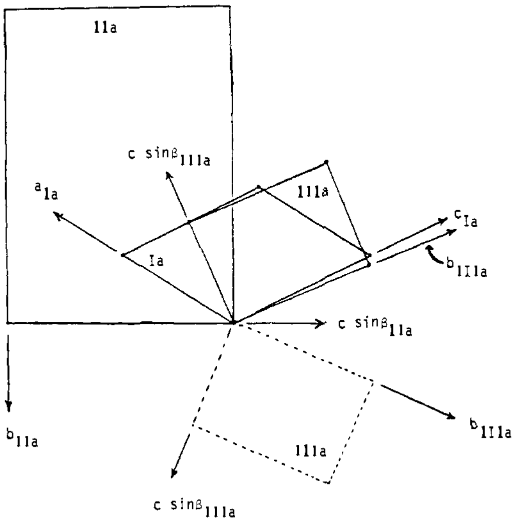


Figure 1. The relative angular alignments of Ia, IIa, and IIIa in Ia and pure IIa. The aligned 4-Å axes of all structures are perpendicular to the plane of the drawing. The unit cells delineated by solid lines represent the observed orientations of IIa and IIIa in Ia. Each of these two products consists of two conservative twin members related through reflections across (010) of Ia, which is parallel to the plane of the drawing. Equal amounts of two conservative twin orientations of IIIa (solid and dashed unit cells) crystallize during the topotactic reduction of pure IIa. (The lattice of Ia is not present in pure IIa.)

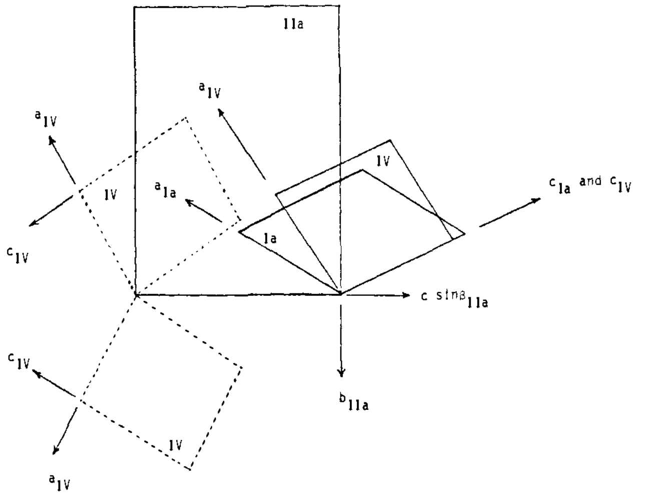


Figure 2. The relative angular alignments of Ia, IIa, and IV in Ia and pure IIa. The aligned 4-Å axes of all structures are perpendicular to the plane of the drawing. The unit cells delineated by solid lines represent the observed orientations of IIa and IV in Ia. Equal amounts of two conservative twin orientations of IV (dashed unit cells) crystallize during the topotactic hydrolysis of pure IIa.

~25° randomness in all directions. The *average* topotaxy, in fact, corresponds to the above derived relationships between IIa and IIIa in decomposed Ia. However, the topotaxy in pure IIa is augmented by conservative twinning according to expression 2 such that two distinguishable modes of alignment are established with *equal frequency* relative to IIa (Figure 1).

The topotactic hydrolysis of pure IIa to IV is slow under ambient laboratory conditions of temperature and humidity. However, partial hydrolysis was evident in crystals which had been stored for ~6 weeks in air saturated with water vapor at ~40 °C. Infrared spectra of the partially hydrolyzed crystals of IIa show absorption from both of the expected hydrolysis products, IIIa and IV. The fact that very little, if any, preferentially oriented IIIa is evident in the x-ray photographs is consistent with the previously noted absence of a strongly favored mode of topotactic alignment of IIIa relative to IIa.

As expected, conservative twinning augments the topotaxy, Φ_5, resulting in two equally present though distinct orientations of IV relative to IIa: $(\mathbf{a}_{\mathrm{IV}})_n = \Phi_5 C_n(\mathbf{a}_{\mathrm{IIa}})$. Moreover, it is clear that no one of these symmetry-equivalent modes of mutual alignment is equivalent to either of the two arrangements of IV and IIa present in decomposing pseudomorphs of Ia (compare Φ_5 and $\Phi_5 C_2$ with the derived matrix $\Phi_6 = \Phi_7 \Phi_{\mathrm{I}}^{-1}$ (and $\Phi_7 C_2 \Phi_{\mathrm{I}}^{-1}$) defining the relative orientation of IIa and IV in the parent Ia). Φ_7 defines the unique relationship observed between Ia and IV in decomposing Ia (see Table II and Figure 2).

Competitive Topotactic Transformations of 2-Iodo-2′-bromodibenzoyl Peroxide (Ib). The topotactic transformations of the unsymmetrical peroxide Ib are considerably more complex than those of Ia. The benzoxiodole isomer IIb[4] is dimorphic and both forms crystallize during *thermal*[6] topotactic isomerization of Ib. Under humid conditions, topotactic transformation of Ib to IV and IIIb competes with topotactic isomerization, and not uncommonly, five different single crystal phases—Ib, both forms of IIb, IV, and IIIb—are simultaneously present in the pseudomorph at intermediate stages. For present purposes we consider only the topotaxies between Ib and the acicular form of IIb, $(\mathbf{a}_{\mathrm{IIb}})_n = \Phi_8 C_n(\mathbf{a}_{\mathrm{Ib}})$, and between Ib and IIIb. In the latter transformation, conservative twinning does not occur, since the symmetry axes of Ib and IIIb are aligned; however, two different topotaxies, $\Phi_{9\mathrm{a,b}}$, are evident. The preferred mode of alignment is defined by $\Phi_{9\mathrm{a}}$. The two orientations of IIIb at least formally are related through twinning about $(20\bar{2})_{\mathrm{IIIb}}$, but it is not clear whether this is another example of Lonsdale twinning[8] or whether such twinning also occurs in independently crystallized samples of IIIb.

Independently prepared crystals of the acicular IIb are slowly reduced by x rays. The transformation is more rapid than IIa → IIIa, yielding detectable amounts of oriented IIIb after ~6 days of continuous exposure to x rays at room temperature. Although the mechanism of photochemical reduction of structures II is not known, it is clear from several related studies that halobenzoic acids derived from both halobenzoate groups are present among the products. However, in the reduction of IIb, the acid IIIa does not crystallize as its conventional structure; probably it is present in solid solution in the structure of IIIb.[6]

The topotaxy between IIIb and IIb includes the alignment of 4-Å axes, and a parallel alignment of $(001)_{\mathrm{IIIb}}$ and $(010)_{\mathrm{IIb}}$ for both conservative twin members of IIIb: $(\mathbf{a}_{\mathrm{IIIb}})_n = \Phi_{10} C_n(\mathbf{a}_{\mathrm{IIb}})$. Neither of these two symmetry-equivalent modes of mutual alignment is equivalent to either of the two arrangements of IIb and IIIb in the parent Ib (Figure 3). Therefore, we conclude that, during decomposition of Ib, both product lattices IIb and IIIb orient relative to the parent Ib and not with respect to each other.

Competitive Topotactic Transformations of 2-Iodo-2′-fluorodibenzoyl Peroxide (Ic). Topotactic isomerization of Ic at ~22 °C yields two preferred orientations (Φ_{11} and Φ_{12}) of the known crystal structure of IIc. Again, each preferred mode consists of two conservative twin members: $(\mathbf{a}_{\mathrm{IIc}})_n = \Phi_{(11\text{ or }12)} C_n(\mathbf{a}_{\mathrm{Ic}})$. Variable amounts of oriented IV (matrix 13a) are formed together with IIc when single crystals of Ic decompose during storage in a moist atmosphere.[9] As is commonly observed for the topotactic crystallization of IV in many of the peroxide crystal structures in this series, minor amounts of IV also crystallize in another topotactic orientation (matrix 13b), which is related at least formally to the major orientation, matrix 13a, through twinning about (100) of IV. *o*-Fluorobenzoic acid, IIIc, the other hydrolysis product, has

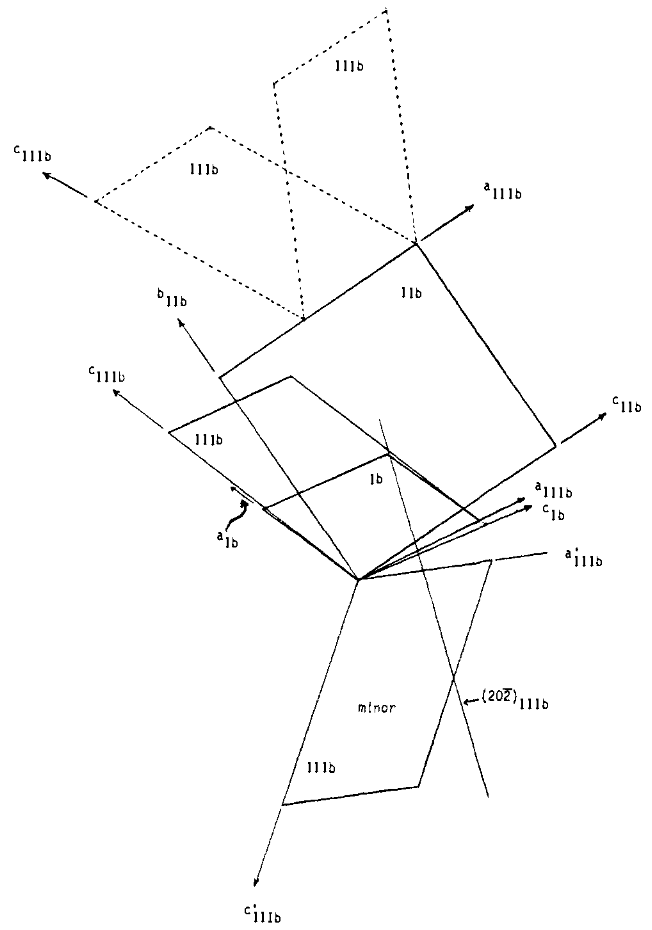


Figure 3. The relative angular alignments of Ib, IIb, and IIIb in Ib and pure IIb. The aligned 4-Å axes of all structures are perpendicular to the plane of the drawing. Unit cells delineated by solid lines represent the observed orientations of IIb and IIIb in Ib. The lower of the two orientations of IIIb in IIb is the minor member. Equal amounts of two conservative twin members of IIIb (dashed unit cells) crystallize during the topotactic reduction of pure acicular IIb.

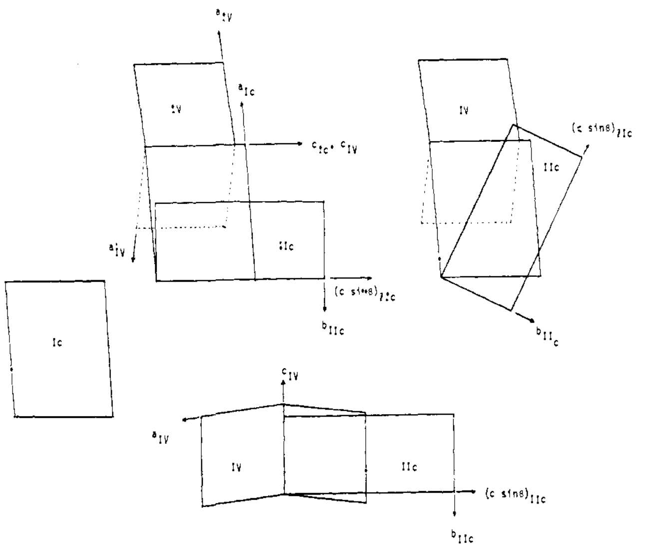


Figure 4. The relative angular alignments of Ic, IIc, and IV in Ic and pure IIc. The aligned 4-Å axes of all structures are perpendicular to the plane of the drawing. (Top left and right) topotactic isomerization of Ic yields two different arrangements of IIc (shown separately for clarity). Each consists of two conservative twin members related through reflection across (010) of Ic, which is parallel to the drawing. Concurrent hydrolysis in Ic yields a major (solid) and a minor (dashed) orientation of IV. (Bottom) Equal amounts of two conservative twin members of IV crystallize during the independent topotactic hydrolysis of pure IIc. (Other relatively minor orientations of IV in IIc are not shown.[3])

not been observed to crystallize in the pseudomorph. The relative angular alignments of Ic, IIc, and IV defined by these matrices are shown in Figure 4.

If IV had oriented relative to IIc, we would have expected its multiple orientations to be distributed with equal frequency in a conservatively twinned arrangement about (010) of IIc. This is clearly not the case for any of the relative arrangements of IIc and IV in Ic. Although the two orientations of IV defined by matrices 13a,b are symmetrically arranged about (010) of one of the oriented members of IIc, they are not equally present. At most, only a small fraction of crystalline IV may have oriented relative to IIc. The bulk appears to have crystallized under the control of the parent Ic.

Studies[3] of the hydrolysis of independently prepared single crystals of IIc lend support to this conclusion, for the preferred topotaxy between IV and IIc in pure IIc, $(\mathbf{a}_{IV})_n = \Phi_{14}C_n(\mathbf{a}_{IIc})$, corresponds to an arrangement which is entirely different from any in Ic (Figure 4).

Discussion

Studies of numerous examples of topotactic transformations uniquely involving one parent and one product phase have led us to expect conservative twinning, leading to equally present, multiple orientations of the product arranged about symmetry elements of the parent phase whenever the specific topotaxy favors a divergent arrangement of parent and product axes of point group symmetry. This generalization has been extended to transformations which result in pseudomorphs containing several simultaneously present phases. We thus may conclude that crystallization of an incipient product phase B is not controlled by another phase, A, in the pseudomorph if the orientations and relative amounts of single-crystal domains of B are not distributed in accord with the point group symmetry of A.

For most of the topotactic transformations described in this paper, such conclusions based on the absence of conservative twinning have now been corroborated through independent studies of the topotactic crystallization of B in pure A. The expected twinning of B in pure A has been observed in all cases, and indeed the preferred mode of mutual phase alignment of A and B in most cases has been found to be entirely different in the absence of the other lattices.

The twinning criterion cannot be invoked for transformations in which the "intermediate" phase A has crystallized topotactically in a manner which introduces no *new* directions of symmetry in the original pseudomorph. (This of course will never be the case when the point group symmetry of the crystal structure of A contains more symmetry elements than originally present in the parent crystal structure.) Thus, a topotactic transformation P → A, involving two structures of point group symmetry $2/m$, in which the specific topotaxy favors an alignment of their unique symmetry axes, will not exhibit conservative twinning. In this case, the criterion cannot be used to decide which lattice, P or A, serves to orient another phase, B, which also crystallizes in the pseudomorph. However, this particular ambiguity raises an interesting alternative to some of the above conclusions regarding the topotactic behavior of peroxides Ia-c: the monoclinic acid IV crystallizes in the various monoclinic peroxide structures without conservative twinning and, therefore, it is not possible rigorously to exclude the possibility that its oriented structure, and not those of the parent peroxides, directs the topotactic alignment of the respective benzoxiodole products, II, which crystallize at a subsequent stage of the decompositions. That being the case, the corresponding matrix relationships would have to be re-

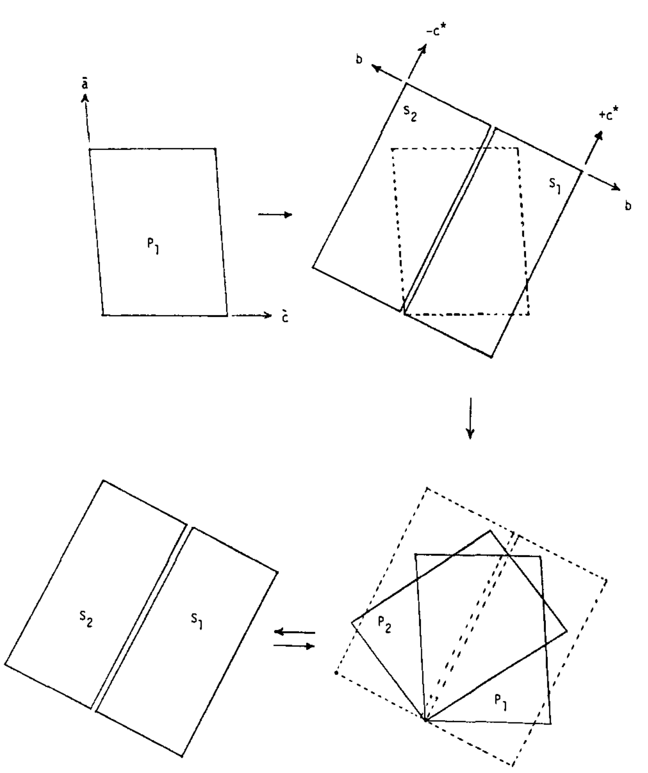


Figure 5. A hypothetical reversible topotactic transformation involving two monoclinic crystal structures of C_2 point group symmetry. The specific topotaxy has been assumed to favor a perpendicular arrangement of the unique *b* axis of parent P (top left; *b* axis is normal to drawing) and the unique *b* axis of product S (*b* axis in the plane of the drawing). The initial forward transformation P → S (top) yields two conservative twin members, S_1 and S_2, related through a 180° rotation about *b* of P. Conservative twinning relative to S during the reverse transformation (right) yields the original P_1 and a new orientation P_2 of the parent. Subsequent cycles (bottom) yield no new orientation of either phase.

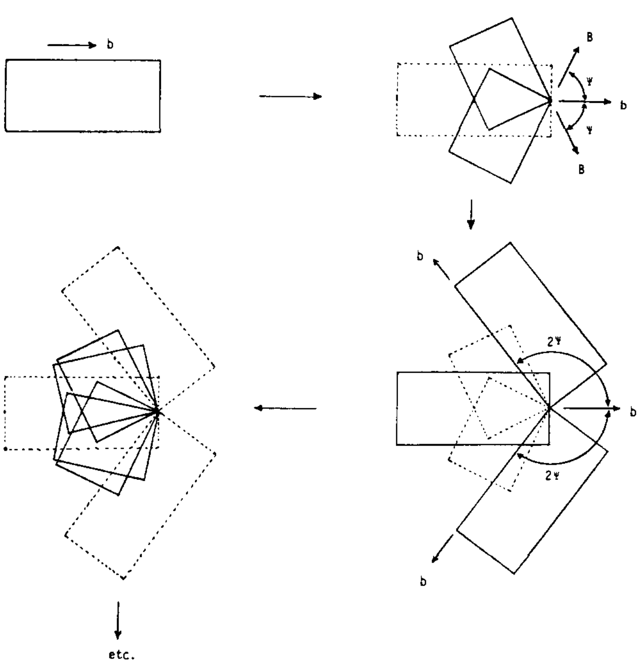


Figure 6. A hypothetical reversible topotactic transformation involving two monoclinic crystal structures for which the specific topotaxy favors an angle of $\Psi < 90°$ between the *b* symmetry axis of the parent and the *B* symmetry axis of the product. An increasing number of orientations of both phases are formed through conservative twinning during successive cycles of the reversible transformations.

formulated as $(\mathbf{a}_{\mathrm{II}})_n = \Phi C_n(\mathbf{a}_{\mathrm{IV}})$. This expression, which above was shown to assume the form $(\mathbf{a}_{\mathrm{IIa}})_n = \Phi_6{}^{-1} C_n(\mathbf{a}_{\mathrm{IV}})$ for the transformations in Ia, formally corresponds to the *reverse* of the independently studied topotactic hydrolysis of *pure* IIa: $(\mathbf{a}_{\mathrm{IV}})_n = \Phi_5 C_n(\mathbf{a}_{\mathrm{IIa}})$. Yet $\Phi_5 \neq \Phi_6$, and the two matrices clearly represent physically different modes of relative alignment of IIa and IV.

Unfortunately this alternative interpretation cannot be examined directly, for it is chemically not possible to convert crystalline IV to IIa. More generally, however, it raises the interesting possibility that *a chemically reversible topotactic transformation may exhibit different modes of mutual alignment of parent and product crystal structures for the forward and reverse directions of transformation.* We would expect this not to be the case if the topotaxy simply reflects a thermodynamically favorable geometrical fit of the two lattices.

Reversible Topotactic Transformations. It is of interest to consider some possible consequences of conservative twinning during a *reversible* topotactic transformation, P ⇄ S, exhibiting identical modes of mutual phase alignment for the forward and reverse direction (i.e., the matrix for the reverse transformation is simply the inverse of the matrix for the forward transformation). The behavior of such a system should depend on the particular angular alignment of point group symmetry axes of the parent and product crystal structures.

Conservative twinning during the reversible topotactic interconversion of two monoclinic structures (point group 2), in which the specific topotaxy favors a *perpendicular* arrangement of their unique axes (Figure 5), would be expected to lead to two distinguishable orientations of product during the forward transformation: $(\mathrm{S})_1 = \Phi(\mathrm{P})_1$ and $(\mathrm{S})_2 = \Phi C_2(\mathrm{P})_1$. During the reverse transformation, each orientation of S could yield two conservatively twinned orientations of P: $\Phi^{-1}(\mathrm{S})_1 = (\mathrm{P})_1$ and $\Phi^{-1}C_2(\mathrm{S})_1 = \Phi^{-1}C_2\Phi(\mathrm{P})_1 = (\mathrm{P})_2$ from S_1; $\Phi^{-1}(\mathrm{S})_2 = \Phi^{-1}\Phi C_2(\mathrm{P})_1 \equiv (\mathrm{P})_1$ and $\Phi^{-1}C_2(\mathrm{S})_2 = \Phi^{-1}C_2\Phi C_2(\mathrm{P})_1 \equiv (\mathrm{P})_2$ from S_2. The net result of one complete cyle would be a redistribution or "twinning" of half of the originally single-crystal structure of P into a new orientation related to the first through a 180° rotation about the symmetry axis of S. If this "twinning" of P did not affect the specific topotaxy (i.e., if the product in the next transformation crystallizes relative to single-crystal domains of P which are distant from the potentially perturbing effects of a twin interphase), no other new orientations of either phase would be generated during succeeding cycles of the transformations. The two orientations of P would transform to the two previous orientation of S, and vice versa.

Similar considerations suggest that a *continuously increasing* number of multiple orientations of the two phases may be expected during successive cycles of other chemically reversible transformations in which the specific topotaxy favors angles less than 90° between symmetry axes of reactant and product phases (Figure 6). In principle, the history of such a pseudomorph (the number of previous reversible cycles of transformation) should be reflected in the total number of multiple twin orientations of either phase which are present at a given stage. We would further expect that repeated cycling of a reversible topotactic transformation would progressively transform an initial single crystal into a polycrystalline pseudomorph in cases where the angular mosaic spread of topotactic alignment is comparable to the angle of divergence of symmetry axes.

Conservative twinning and the associated consequences described in this paper normally are to be expected only when *many* nucleation sites for topotactic crystallization develop within the pseudomorph. Although this appears to be the case in all of the ~50 topotactic chemical transformations which have been examined in this series, exceptions may be found in polymorphic phase transformations in which topotaxy is established relative to a very limited number of nucleation centers.

Kitaigorodskii's study of the topotactic, reversible polymorphic phase transformation of *p*-dichlorobenzene [10]exemplifies a failure of the "memory effect" of conservative twinning. The low-temperature (α) monoclinic phase ($P2_1/a$) and high-temperature (β) triclinic phase ($P\bar{1}$) reversibly interconvert at temperatures approximately 20 °C below the melting points of the separate phases (53 °C). A single crystal of either phase may be repeatedly cycled topotactically through both phases. Whereas an *initial* transformation $\beta \rightarrow \alpha$ should occur without conservative twinning, the reverse change would be expected to yield two conservative twin orientations of the β phase, if many nucleation centers develop within the pseudomorph. This appears not to be the case, for Laue photographs of the β phase no longer display the mirror symmetry of the prior α phase. It is also of interest that the mutual phase alignment, from cycle to cycle, is variable in both directions of the transformation. Accordingly, the successive reverse transformations do not imply simple inverse topotactic matrix relationships. An intriguing memory effect of a different sort, nevertheless, is manifest in the observed invariant orientation of the monoclinic α phase relative to some external reference coordinate system.

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References and Notes

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Catalysis in Oxidation Reactions. 3. The Oxalic Acid Catalyzed Chromic Acid Oxidation of Tris(1,10-phenanthroline)iron(II)[1,2]

Ray E. Hintze and Jan Roček*

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680.
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Abstract: Oxalic acid accelerates the chromic acid oxidation of tris(1,10-phenanthroline)iron(II), $Fe(phen)_3{}^{2+}$, by factors up to 4×10^4. The reaction is first order in $Fe(phen)_3{}^{2+}$, $HCrO_4{}^-$, H^+, and $(CO_2H)_2$. The proposed mechanism involves formation of an oxalic acid–chromic acid complex, followed by its rate-limiting one-electron outer sphere reduction by $Fe(phen)_3{}^{2+}$. The chromic acid–oxalic acid complex is about 3000 times more reactive than H_2CrO_4. The reaction provides evidence that oxalic acid can accelerate the one-electron reduction of chromium(VI) to chromium(V). It is postulated that the rate acceleration results from a substantial increase in the Cr(VI)/Cr(V) reduction potential in the presence of oxalic acid due to the high stability of the Cr(V)–oxalic acid complex relative to the Cr(VI) complex. At high concentrations of $Fe(phen)_3{}^{2+}$ the reaction between $HCrO_4{}^-$ and $(CO_2H)_2$ tends toward becoming rate limiting ($k = 9.1 \times 10^3$ M^{-1} s^{-1}).

Oxalic acid accelerates the rates of many chromic acid oxidations. For example, in the presence of oxalic acid alcohols react with Cr(VI) in a rapid cooxidation reaction yielding a ketone, CO_2, and $CO_2{}^-$ (or $\cdot CO_2H$), with Cr(VI) being reduced directly to Cr(III) in the rate-limiting step.[3,4] A similar rapid three-electron cooxidation reaction has been reported for oxalic acid acceleration of oxidation of malachite green.[5]

On the other hand, oxalic acid can also increase the rate of chromic acid oxidations without undergoing oxidation itself; it thus can act as an oxidation catalyst.[6] The most thoroughly investigated example within this class is the chromic acid oxidation of iodide.[2,8,9] However, because of the number of known and relatively stable valence states of iodine, it is difficult to determine whether oxalic acid accelerates a one-electron reduction of chromium(VI) to chromium(V), or a two-electron reduction to chromium(IV). A similar problem is encountered in the interpretation of the results of the oxalic acid catalyzed chromic acid oxidation of thiocyanate.[10]

It is therefore of interest to examine the mechanism of an oxalic acid catalyzed chromic acid oxidation reaction of a compound which exists in only two stable oxidation states. Eswara Dutt and Mottola[7] recently observed that oxalic acid greatly accelerates the redox reaction of chromic acid and tris(1,10-phenanthroline)iron(II), $Fe(phen)_3{}^{2+}$. However, their study was concerned primarily with the analytical utility of the rate enhancement, and kinetic measurements were confined to initial rates. The uncatalyzed reaction has been studied by Espenson and King,[11] who found that the reaction was highly complex with first- and second-order dependencies in $Fe(phen)_3{}^{2+}$, $HCrO_4{}^-$ as well as in H^+, and with the reaction going via four transition states of different composition with respect to numbers of chromium and iron atoms. Since they found that the oxidation product, $Fe(phen)_3{}^{3+}$, had no