383. Topochemistry. Part I. A Survey.

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A survey is presented of the chemistry of solid-state reactions of organic compounds. Three tests are discussed which indicate that one of the controlling factors in such reactions is the geometry of the crystal structure of the reactant species: (1) chemically closely-related compounds show significant differences in chemical behaviour in the solid state; (2) a given compound reacts differently in the solid and dispersed phases; (3) polymorphic modifications of a given compound show significant differences in chemical behaviour. The evidence is interpreted in terms of the " topochemical " postulate that reaction in the solid state occurs with a minimum of atomic or molecular movement.

Possible experimental approaches to the problem of topochemistry are outlined.

The analysis of the mechanism of solid-state reactions has for some time now centred around the study of lattice imperfections; in particular, the number and nature of these imperfections have been shown [1,2] to determine the mobility of the reactant species and hence the reaction rate. This focus on lattice irregularities has tended to ignore the major feature of the crystalline state, namely three-dimensional regularity and its effect on reaction mechanism, rate, and products. The work in progress here [3-7] is intended to analyse the role of lattice geometry and thereby to extend our understanding of solid-state chemistry.

The following Papers are mainly concerned with the thesis that the course of certain types of solid-state reactions are determined by the geometry of the reactant lattice, or in Hertel's phrase [8] by " topochemical " factors. This thesis may be formulated as the postulate that *reaction in the solid state occurs with a minimum amount of atomic or molecular movement.* This postulate implies that solid-state reactions are controlled by the relatively fixed distances and orientations, determined by the crystal structure, between potentially reactive centres. It follows that for each reaction type there should exist an upper limit for such distances beyond which reaction can no longer occur. Furthermore, bimolecular reactions are expected to take place between nearest neighbours, which in turn suggests that the molecular structure of the product might be a function of the geometric relation in the crystal lattice of reactant molecules. Finally, the postulate places restrictions on types and mechanism of solid-phase reactions, such as *cis–trans*-isomerisation which as a unimolecular process appears to be associated with large-scale atomic movement. Topochemical influences are expected to be dominant only in certain types of reaction: they are probably of minor importance when the reaction mechanism involves long-distance migration of electrons or of excitation energy, and are unlikely to operate in ionic systems of high symmetry (inorganic compounds); they will become effective where both the molecule and the crystal lattice are of low symmetry as in organic compounds.

A number of experimental techniques are relevant to these problems, and their applicability illustrates some of the unique features of solid-phase reactions: first, the initial state of the system, before reaction, can be defined to any reasonable accuracy by the methods of *X*-ray crystallography; secondly, the rigid matrix of the crystal lattice stabilises, in favourable cases, intermediate reaction products which can be studied by

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[1] " The Chemistry of the Solid State," ed. Garner, Butterworths, London, 1955.

[2] Stone in " Reactivity of Solids," ed. de Boer, Elsevier, Amsterdam, 1961, p. 7.

[3] Schmidt, *Acta Cryst.*, 1957, **10**, 793.

[4] Cohen, Hirshberg, and Schmidt, *Bull. Res. Council Israel*, 1957, **6***A*, 167.

[5] Cohen, Hirshberg, and Schmidt in " Hydrogen Bonding," ed. Hadži, Pergamon, London, 1959, p. 293.

[6] Cohen and Schmidt, ref. 2, p. 556.

[7] Cohen and Schmidt, Proc. Durham Symposium on Reversible Photochemical Processes, *J. Phys. Chem.*, 1962, **66**, 2442.

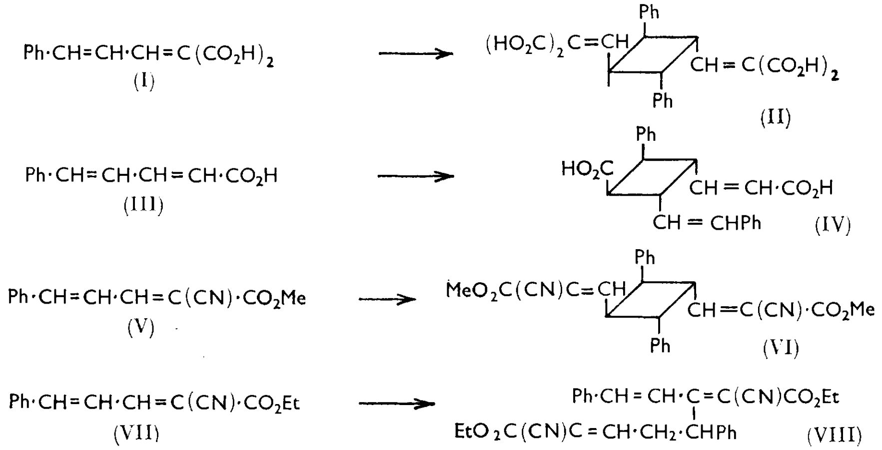
[8] Hertel, *Z. Elektrochem.*, 1931, **37**, 536.

spectroscopic, electron spin resonance, or proton spin resonance methods; and thirdly, relationships may be sought between the course of the reaction, and hence the chemical, and even stereochemical, structure of the reaction product and the crystal structure of the reactants. A combination of these three points may provide insight into, and even lead to the formulation of, reaction mechanisms and their geometries in a quantitative manner not usually possible for liquid- and gas-phase reactions.

In this Laboratory we have for some time been investigating, by a combination of several of the above techniques, the mechanisms of solid-state reactions of organic crystals. We have studied the photochemical dimerisation of substituted acrylic acids and vinyl ketones to cyclobutane derivatives, the rearrangement of *o*-nitrobenzaldehydes to *o*-nitrosobenzoic acids (and related reactions), and the phenomenon of photochromy, *i.e.*, the reversible light-induced coloration of certain classes of organic compounds such as the anils of salicyaldehydes.

Before proceeding to our own results, however, we present some examples from the published literature which provide *prima facie* evidence for the operation of topochemical factors. Three arguments may be cited:

(1) *Chemically Closely-related Compounds show Significant Differences in Chemical Behaviour in the Solid State.*—While cinnamylidenemalonic acid (I) dimerises in the solid state to the cyclobutane (II) [9] cinnamylideneacetic acid (III) dimerises to the cyclobutane (IV); [10] thus, in the malonic acid the two $\gamma\delta$ double bonds interact while the acetic acid dimerises unsymmetrically. Methyl α-cyanocinnamylideneacetate (V) forms a dimer (VI) which on ozonolysis gives α-truxillic acid; the ethyl ester (VII), on the other hand, dimerises to an open-chain compound of probable formula (VIII).[11] Dimethyl 3-oxopentadien-1,5-dicarboxylate (IX) reacts in the solid state to give a crystalline dimer to which the formula (X) has been assigned; [12,13] the diethyl ester under similar conditions forms ill-defined polymeric material.[12,14] Crystalline 2,4-dinitrostilbene undergoes light-induced dimerisation whereas the 4′-chloro-derivative is light-stable.[15] 4-Bromo-*N*-salicylideneaniline is photochromic and not thermochromic; the corresponding chloro-compound is thermochromic and not photochromic.[16] Whereas 4-(2,4-dinitrobenzyl)pyridine is photochromic in solution but not in the crystal, the corresponding 2-substituted pyridine is



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[9] Riiber, *Ber.*, 1902, **35**, 2411.
[10] Riiber, Hensel, and Simon, *Ber.*, 1913, **46**, 335.
[11] Reimer and Keller, *Amer. Chem. J.*, 1913, **50**, 157.
[12] Stobbe and Färber, *Ber.*, 1925, **58**, 1548.
[13] Corse, Finkle, and Lundin, *Tetrahedron Letters*, 1961, 1.
[14] Straus, *Ber.*, 1904, **37**, 3293.
[15] Schmidt and Sonntag, unpublished observations.
[16] Senier and Shepheard, *J.*, 1909, **95**, 1943.

photochromic in both states.[17] Similarly, the photochromic activity of crystalline sydnones varies markedly with only minor changes in the substituents of the benzene ring.[18,19] Of the two isomeric carbinols (XI) one produces highly-coloured polymeric material while the second is light-stable.[20]

(2) *A Given Compound reacts Differently in the Solid and Dispersed Phases.—trans*-Cinnamic acid dimerises in the solid state only; irradiation of its melt or solutions does not produce dimer.[21] Pure dibenzylideneacetone is light-stable in the solid state, but forms one or more photo-dimers in solution.[22] We have mentioned the difference in photochromic activity between crystals and solutions of 4-(2,4-dinitrobenzyl)pyridine. Light-induced polymerisation of polyacetylenes takes place in the solid state only.[23] Chapiro [24] quotes examples of compounds capable of undergoing γ-ray induced polymerisation on one side or other of phase-transition points (solid–solid or solid–liquid); in the majority of these examples the rate of reactions shows a maximum at the transition point itself (Hedvall effect [25]).

(3) *Polymorphic Modifications of a Given Compound show Significant Differences in Chemical Behaviour.*—Of the two crystal modifications of *trans*-cinnamic acid (XII), the stable form gives rise to α-truxillic acid (XIII) whereas the metastable form produces mainly β-truxinic acid (XIV).[26] Of the two forms of *p*-nitrophenol, the metastable form is light-insensitive while the stable modification turns red on irradiation.[27] In the field of photochromy, several examples of differences in behaviour of polymorphic modifications are known: thus, the *o*-methylanil of salicylaldehyde exists in two crystal forms of which only one is photochromic. Again, the tetrachloro-oxonaphthalene (XV) is dimorphic with only one form colourable by irradiation.[28] Perhaps the most striking example in this category is the photochemical rearrangement of tetrabenzoylethylene (XVI), analysed in detail by von Halban: [29] of the two crystalline modifications of (XVI) one is light-stable while the second is rearranged by light to the furanone (XVII). This migration of a phenyl group undoubtedly presupposes a specific geometrical configuration of the reactant molecule.

We believe that these examples can be interpreted in terms of the topochemical principle stated earlier in this Paper; indeed, the evidence listed under (3) can hardly be explained otherwise than that the major factor responsible for the course of the chemical reaction is the molecular packing arrangement in the crystal. Similar ideas were expressed by de Jong [30] who drew attention to the fact that, in the photo-dimerisation of *trans*-cinnamic acid and its salts, mainly those truxillic and truxinic acids are formed which possess an element of symmetry; he believed that the molecular symmetry of the dimer was derived from the crystallographic symmetry relating the monomer molecules in their crystal lattice. Bohlmann [31] invoked a similar explanation to account for the photo-polymerisation of polyacetylenes in the solid state which alone provides the geometrical alignment of the rigid rod-like molecules necessary for intermolecular reaction. Evidently the crystal lattice controls not only the molecular structure of the reaction product, but

[17] Mosher, Souers, and Hardwick, *J. Chem. Phys.*, 1960, **32**, 1888.

[18] Tien and Hunsberger, *Chem. and Ind.*, 1955, 119.

[19] Metz, Servoss, and Welsh, Proc. Durham Symposium on Reversible Photochemical Processes, *J. Phys. Chem.*, 1962, **66**, 2446.

[20] Armitage, Cook, Entwistle, Jones, and Whiting, *J.*, 1952, 1998.

[21] Ciamician and Silber, *Ber.*, 1902, **35**, 4128; 1903, **36**, 4266.

[22] Praetorius and Korn, *Ber.*, 1910, **43**, 2744.

[23] Bohlmann and Inhoffen, *Ber.*, 1956, **89**, 1276.

[24] Chapiro, *Nucleonics*, 1961, **19**, No. 10, p. 65.

[25] Hedvall, " Einführung in die Festkörperchemie," Vieweg und Sohn, Braunschweig, 1952.

[26] Bachér, in " Handbuch der biologischen Arbeitsmethoden", ed. Abderhalden, Urban und Schwarzenberg, Berlin–Vienna, 1929, Abt. I, Teil 2, II, p. 1339.

[27] Fritzsche, *J. prakt. Chem.*, 1858, [1], **75**, 261.

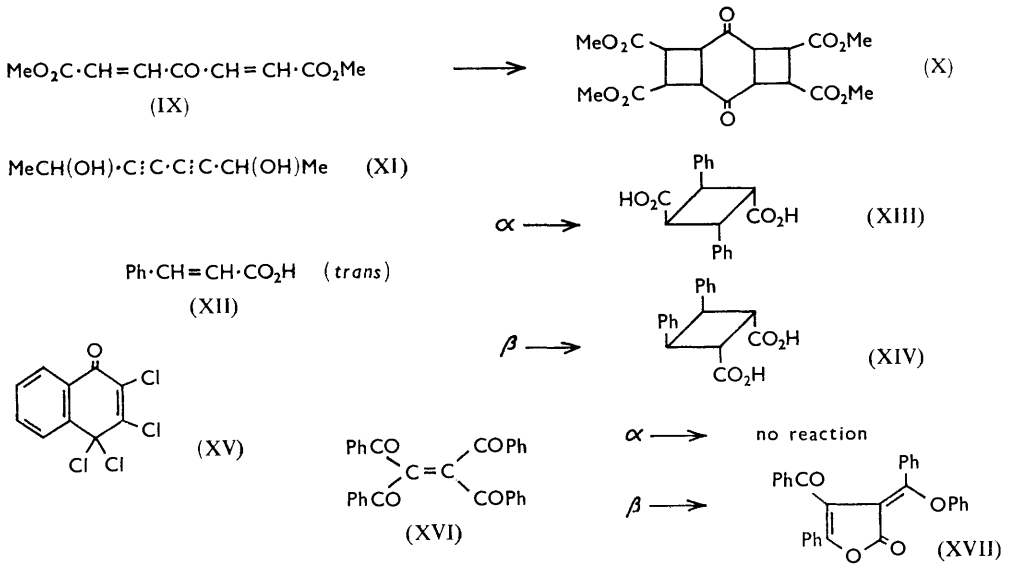
[28] Marckwald, *Z. physik. Chem.*, 1899, **30**, 140.

[29] Schmid, Hochweber, and von Halban, *Helv. Chim. Acta*, 1947, **30**, 1135.

[30] de Jong, *Ber.*, 1923, **56**, 818.

[31] Bohlmann, " Vortrag über Polyine," Chemiker-Tagung Köln, 1951 (quoted in ref. 23).

also the reaction type, as in the photo-reactions of cinnamic acid derivatives to either cyclic (truxillic or truxinic) or open-chain dimers. Griffin and his co-workers[32] have


(IX) (X)

$MeCH(OH){\cdot}C\vdots C{\cdot}C\vdots C{\cdot}CH(OH)Me$ (XI)

(XII) (XIII) (XIV) (XV) (XVI) (XVII)

recently considered that in solid-state dimerisation reactions the stereochemistry of the dimer is probably influenced by monomer lattice geometry. Several groups of workers have suggested that there is a marked influence of the crystal lattice on the course of solid-state polymerisations initiated by high-energy irradiation.[33-35]

At least three experimental routes to the solution of the problems outlined here have been envisaged by us. The first approach combined kinetic and *X*-ray crystallographic techniques: given the distances between reactive centres from structure analysis and the relative rates of rearrangement in the solid one might attempt correlation between the two sets of measurements. We chose as a first reaction type the solid-state rearrangement of *o*-nitrobenzaldehyde, and its 4-iodo-, 5-bromo-, and 6-chloro-derivatives; preliminary (unpublished) work showed that this reaction proceeded in more than one step, with at least one step not under the control of the parent lattice; consequently this line of attack was abandoned.

An improvement on this first approach is the study of an " either—or " reaction, *i.e.*, the comparison of the crystal structures of systems which do or do not undergo reaction. We have used this technique in studying the oxygen transfer between two molecules of *p*-nitrophenol, which occurs on irradiation of the stable crystal form but not of the meta-stable form.[36]

The second approach seeks to correlate the molecular structure of the reaction product with the packing arrangement of the reactant species in its crystal lattice. Here, one would wish to investigate a solid-state reaction giving a product whose structure (or stereochemistry) is sufficiently complex to be critically determined by the lattice geometry of the reactant molecules. A fruitful example of such a reaction turned out to be the dimerisation of substituted acrylic acids and of αβ-unsaturated ketones to cyclobutane derivatives. In particular, cinnamic acid and some of its derivatives, because of their

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[32] Griffin, Vellturo, and Furukawa, *J. Amer. Chem. Soc.*, 1961, **83**, 2725.

[33] Schulz, Henglein, v. Steinmetz, and Bambauer, *Angew. Chem.*, 1955, **67**, 232.

[34] Restaino, Mesrobian, Morawetz, Ballantine, Dienes, and Metz, *J. Amer. Chem. Soc.*, 1956, **78**, 2939.

[35] Lawton, Grubb, and Balwit, *J. Polymer Sci.*, 1956, **9**, 455.

[36] Coppens, Ph.D. Thesis, Amsterdam University, 1960.

accessibility, the detailed chemical information on their dimers previously available, their relative crystallographic simplicity, and their abundant polymorphism—though only in a few lattice types—have been the main object of our study. The Papers that follow report both chemical and crystallographic material based on this type of approach.

The later Papers in this series deal with the problem of solid-state photochromy. This phenomenon falls within the scope of this programme since, as we have pointed out above, it is crystal-structure dependent. Here the experimental problems are qualitatively different in that the light-produced species is stable only in a rigid matrix and cannot be isolated. We have studied this species by optical methods in the crystal and, where possible, in rigid-glass solution; observations have been made on the variation of photoyield and fluorescence behaviour with change in the chemical and crystal structures of the parent material. On this basis we shall discuss the energetics, stereochemistry, and mechanism of photochromy for the anils of salicyladehydes.

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