Role of Molecular Packing and Structural Defects in Reactions of Gases with Organic Solids: Ozonolysis of *trans*-Stilbene and αβ-Diethyl-4,4′-dihydroxystilbene

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Optical microscopic examination of partially ozonolysed and wet-etched single-crystal faces of *trans*-stilbene (1a) and αβ-diethyl-4,4′-dihydroxystilbene (1b) reveal the importance of line defects (dislocations) in governing the rate of the (anisotropic) oxidative attack of the ethylenic double bond in these two solids. In the regions of enhanced reactivity at dislocations emergent on the (100) face of (1b) the rate of ozonolysis is considerably slower than at corresponding regions of the (001) face of (1a), a direct consequence of the protection afforded to the double bond in molecules of the former. As reaction product [benzaldehyde and *p*-hydroxypropiophenone for (1a and b) respectively] accumulates within each solid reactant, stresses are set up which generate more dislocations on well-defined slip planes (which are identified); these, in turn, function as new centres of preferred attack so that the reaction accelerates as ozonolysis proceeds. Very many new slip systems in crystals of (1a), and relatively few new ones in crystals of (1b), are activated by the accumulation of reaction product. This is explicable in terms of the crystallographic differences between the two solids. It is directly demonstrated that numerous new families of dislocations may be introduced during the course of a gas–solid reaction; and many of the slip systems identified here for (1a) have not hitherto been detected in other aromatic solids (such as naphthalene and anthracene) which also belong to the space group $P2_1/a$.

It is now well established[1-4] that photo-induced processes occurring within the bulk of a variety of organic molecular solids are often governed by the nature of the packing of individual molecules within the *ideal* lattice. This is strikingly demonstrated by the fact that one particular polymorph of a given photoreactive monomer yields a product the symmetry of which is related to the packing of neighbouring molecules in the monomer, whereas another polymorph of the same monomer yields a new product arising from the different packing in the parent lattice. Photochemical reactions of an appreciable number of organic solids are, however, vitally influenced by the structural *imperfections* present in the monomer crystal. Thus the photo-induced dimerization of both 1,8-dichloro-9- and 1,8-dichloro-10-methylanthracenes and other related solids,[4-7] proceed at dislocations, which, in addition to serving as exciton traps and nucleating centres for crystallization, play an even more important role in enabling neighbouring molecules to be appropriately oriented so as to facilitate the initiation of reaction in the first place.

For thermally induced heterogeneous reactions involving simple gases (such as NH_3, Cl_2, or Br_2) and a variety of rather complicated organic solids, the importance of the packing and configuration of individual molecules within the *ideal* lattice has again been established, chiefly by Paul and Curtin,[2,8-10] who have reviewed this topic. We have however previously reported[11] preliminary evidence, which shows that structural imperfections significantly modify the nature of attack of NH_3 upon acenaphthylene-1-carboxylic acid, and established that both molecular packing and dislocations affect the pattern of reactivity of this solid.

It is, therefore, of interest to enquire whether the reactions of gases with the surfaces of organic solids generally display sensitivity towards the presence of emergent dislocations (as with a number of layered[3,11] inorganic solids), or whether, on the other hand, such reactions, like those of simple gases with most metal and alloy surfaces, are less sensitive to dislocations than to other crystallographic factors associated with the ideal structure. We have, accordingly, set out to investigate more fully the relative importance of crystallographic perfection and structural imperfection in the attack, by ozone, of the relatively reactive double bond in stilbenes, a background study of which has been recently reported.[12]

This oxidation reaction is also effected in air or in oxygen when the solid is irradiated with light from a low pressure mercury lamp. Oxidation under u.v. is chemically highly selective as only one major product with inseparable traces of by products, are formed.[12] Moreover the two solids we have chosen differ significantly in their basic molecular characteristics (one has sterically prominent substituents and intermolecular hydrogen bonding, the other has neither of these attributes) yet each possesses the same type of reactive ethylenic bond.

Crystallographic Background.—We were aware from our previous (unpublished) results that both solid *trans*-stilbene (1a) and solid αβ-diethyl-4,4′-hydroxystilbene (1b) (diethylstilboestrol) are, in contrast to their direct photo-oxidation oxidation in solution, smoothly

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[1] M. D. Cohen and B. S. Green, *Chem. in Britain*, 1973, **9**, 490.

[2] I. C. Paul and D. Y. Curtin, *Accounts Chem. Res.*, 1973, **6**, 217.

[3] J. M. Thomas, *Phil. Trans. Roy. Soc.*, 1974, *A*, **277**, 251.

[4] J. P. Desvergne, J. M. Thomas, J. O. Williams, and H. Bouas-Laurent, *J.C.S. Perkin II*, 1974, 363.

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[7] M. D. Cohen, Z. Ludmer, J. M. Thomas, and J. O. Williams, *Proc. Roy. Soc.*, 1971, *A*, **324**, 459.

[8] I. C. Paul and D. Y. Curtin, *Science*, in tbe Press.

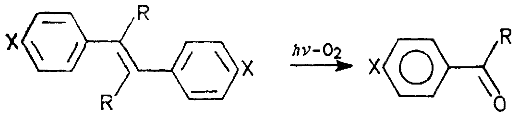
[9] C.-T. Lin, I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, 1974, **96**, 6199.

[10] R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, 1971, **93**, 2784.

[11] J. P. Desvergne and J. M. Thomas, *Chem. Phys. Letters*, 1973, **23**, 343.

[12] J. P. Desvergne, H. Bouas-Laurent, E. V. Blackburn, and R. Lapouyade, *Tetrahedron Letters*, 1974, **12**, 947.

converted[12] to the corresponding ketone derivatives (2a and b). Ideally, we would have liked to study the conversions (1a) ⟶ (2a) and (1b) ⟶ (2b) using



(1) (2)

a; R = X = H
b; R = Et, X = OH

several polymorphic forms of each compound (1a and b): this would have revealed directly the importance of packing in gas–solid reactions. Unfortunately, *trans*-stilbene exists in only one stable crystallographic form, and the same applies to diethylstilboestrol. [The latter does form at least three distinct solvates (with methanol–water, with ethanol, and with dimethyl sulphoxide) the crystal structures of which (all triclinic, $P\bar{1}$) are relatively complicated; and their reactivity would doubtless[8] be rather excessively influenced by the solvate molecules.]

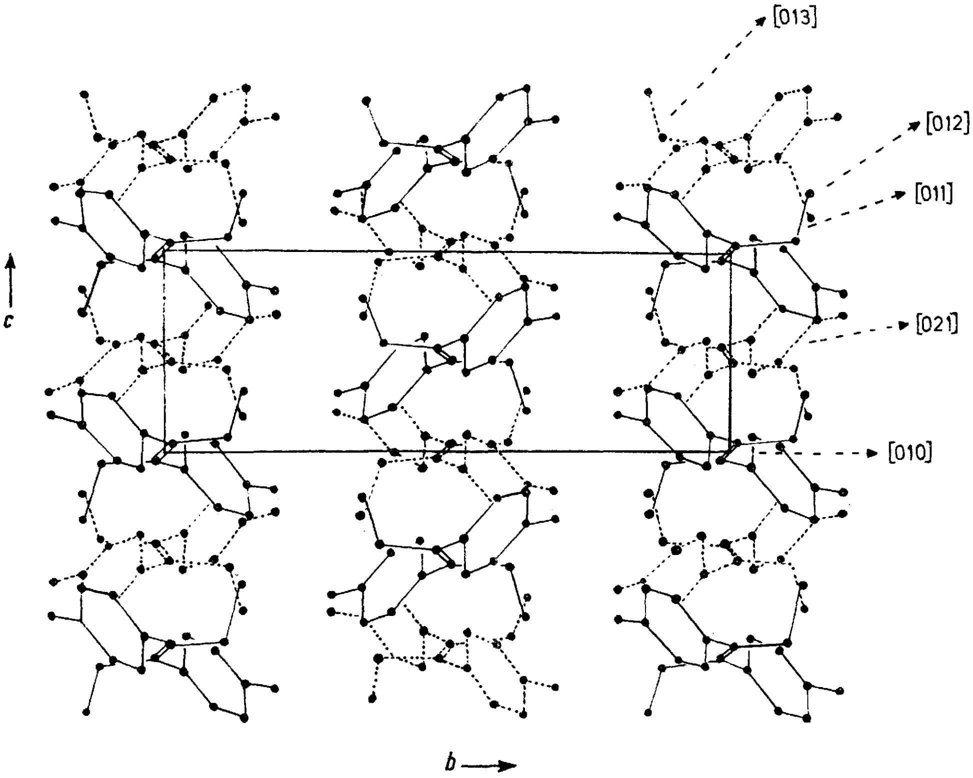


FIGURE 1 Projection on the *bc* plane of diethylstilboestrol

Diethylstilboestrol[13] belongs to the orthorhombic class and crystallizes in the space group *Pbca*, with parameters * $a = 18{\cdot}9$, $b = 14{\cdot}9$, $c = 5{\cdot}3$ Å, $Z = 4$. Microcrystals obtained by microsublimation are typically 1 × 0·25 × 0·05 mm, the most developed face being *cb* [*i.e.* (100)]. A schematic representation of the (100) projection is shown in Figure 1.

Crystals of *trans*-stilbene[14] (typical dimensions 1 × 1 × 0·25 mm) grown by evaporation from saturated solutions in benzene–ether have two main types of morphology represented by Figure 2 (*cf.* ref. 15). They belong to the space group $P2_1/a$ and were found * to have $a = 12{\cdot}3$, $b = 5{\cdot}7$, $c = 15{\cdot}9$ Å, $\beta = 112°$, $Z = 4$. The most well developed face on this solid is (001) and the relevant structural projection is schematized in Figure 3.

Microscopic Studies of Reactivity.—(a) *Diethylstilboestrol* (1b). Optical microscopic investigation of crystals of (1b) after they had been irradiated in air for *ca.* 10 h at room temperature, revealed that, in so far as we were able to judge from the microcrystals, a rather uniform attack had occurred on the (001) and (010) faces, but

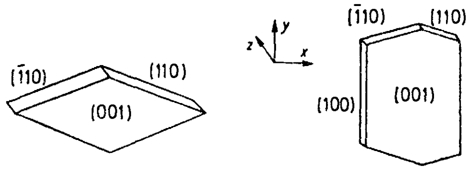


FIGURE 2 Illustration of morphology of *trans*-stilbene crystals (see text)

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* These parameters, determined from Weissenberg photographs agree very well with the previously determined values for diethylstilboestrol and *trans*-stilbene.

[13] B. Busetta and M. Hospital, *Compt. rend.*, 1969, **268C**, 2011.

[14] J. M. Robertson and I. Woodward, *Proc. Roy. Soc.*, 1973, *A*, **162**, 568.

[15] N. Y. Kolosov, *Kristallographia*, 1958, **3**, 700.

that there were strikingly non-uniform patterns on (100). Alignments of product on the (100) faces (see Figure 4 and the micrographs of Plate 1) are pronounced along [001], and there is also some tendency for alignment along [021], [012], and [013]. After prolonged attack the pencils of product which first grow along [001] thicken (in the [010] direction), and extra alignments of product phase develop along [010], on the (100) faces.

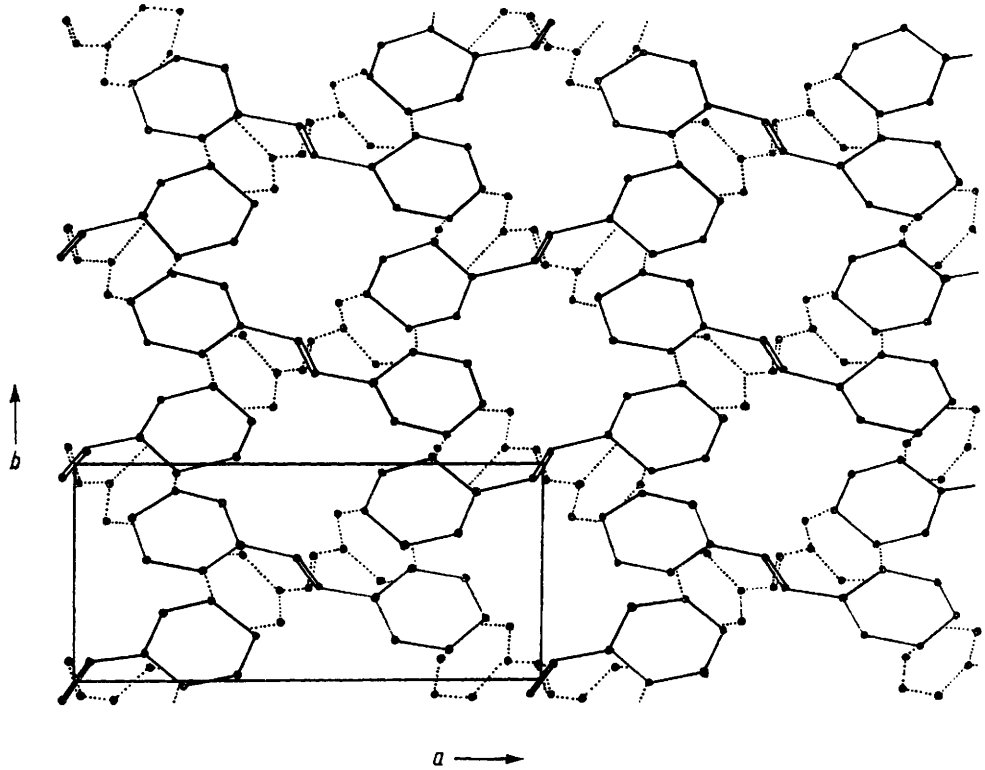

Figure 3 Projection on the *ab* plane of *trans*-stilbene

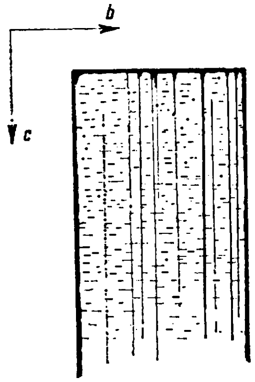

Figure 4 Schematic illustration of the nature of the patterns of attack upon ozonolysis from the gas phase

The crystals are, unfortunately, too small and too brittle to permit satisfactory cleavage and subsequent oxidation studies of matched halves (contrast situation that exists for other gas–solid systems[16,17]), and of appropriate studies of mechanical deformation. But they are amenable to etch-pit studies which serve to locate emergent dislocations and to identify, through the operative slip-systems, the planes in which the dislocations glide and the directions of their associated Burgers vectors. Typical dislocation etch-pit patterns are shown in Plate 2, and Table 1 summarizes the directions along which alignments of etch-pits and nuclei of reaction product were observed. It is to be noted that essentially all the directions found to be significant in the gas–solid reaction are also found in the wet-etching.

Table 1

Summary of alignments of etch-pits and photo-product nuclei on (100) faces of diethylstilboestrol. Particular slip systems capable of explaining these alignments are also given

Product nuclei	Dislocation etch-pits	Slip systems
[001] (mainly)	[001]	(010) [001]; (110) [001]
[010]	[010]	(101) [010]; (001) [010]
[021]	[021]	$(2\bar{1}2)$ [021]
[013] (rare)	[013]	$(3\bar{1}3)$ [013]
[012]	[012]	$(1\bar{2}1)$ [012]
	[011]	$(1\bar{1}1)$ [011]

(b) trans-*Stilbene* (1a). Ozonolysis of this crystalline

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[16] J. M. Thomas, *Adv. Catalysis*, 1969, **19**, 202.

[17] J. M. Thomas and J. O. Williams, *Progr. Solid State Chem.*, 1971, **6**, 121.

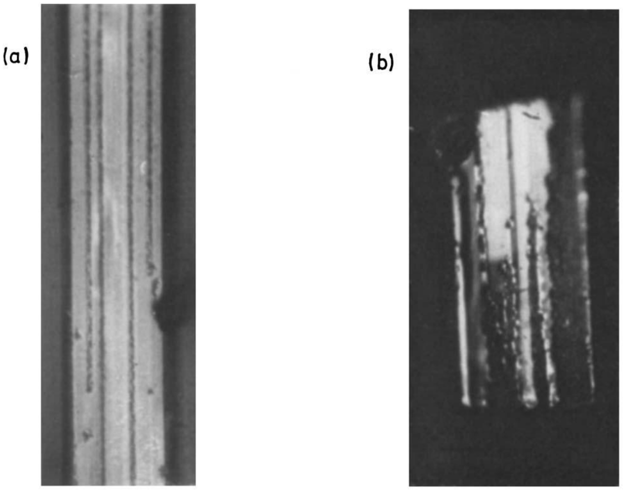

Plate 1 Typical optical micrographs showing preferential and aligned nature of the growth of product during ozonolysis of diethylstilboestrol (magnification × 300 throughout)

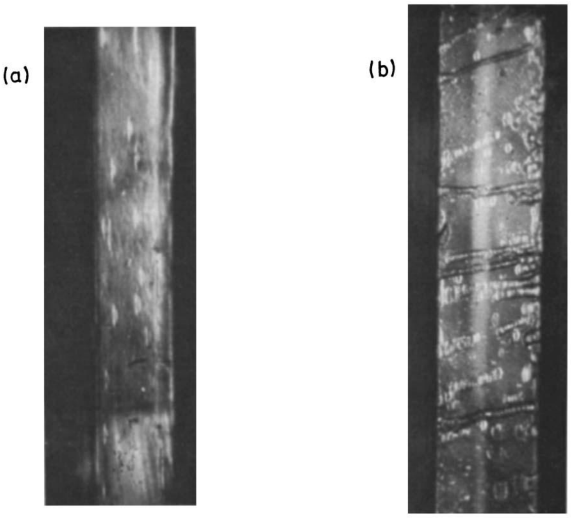

Plate 2 Micrographs showing dislocation etch-pits at the (100) faces of diethylstilboestrol (see Table 1) (magnification × 300)

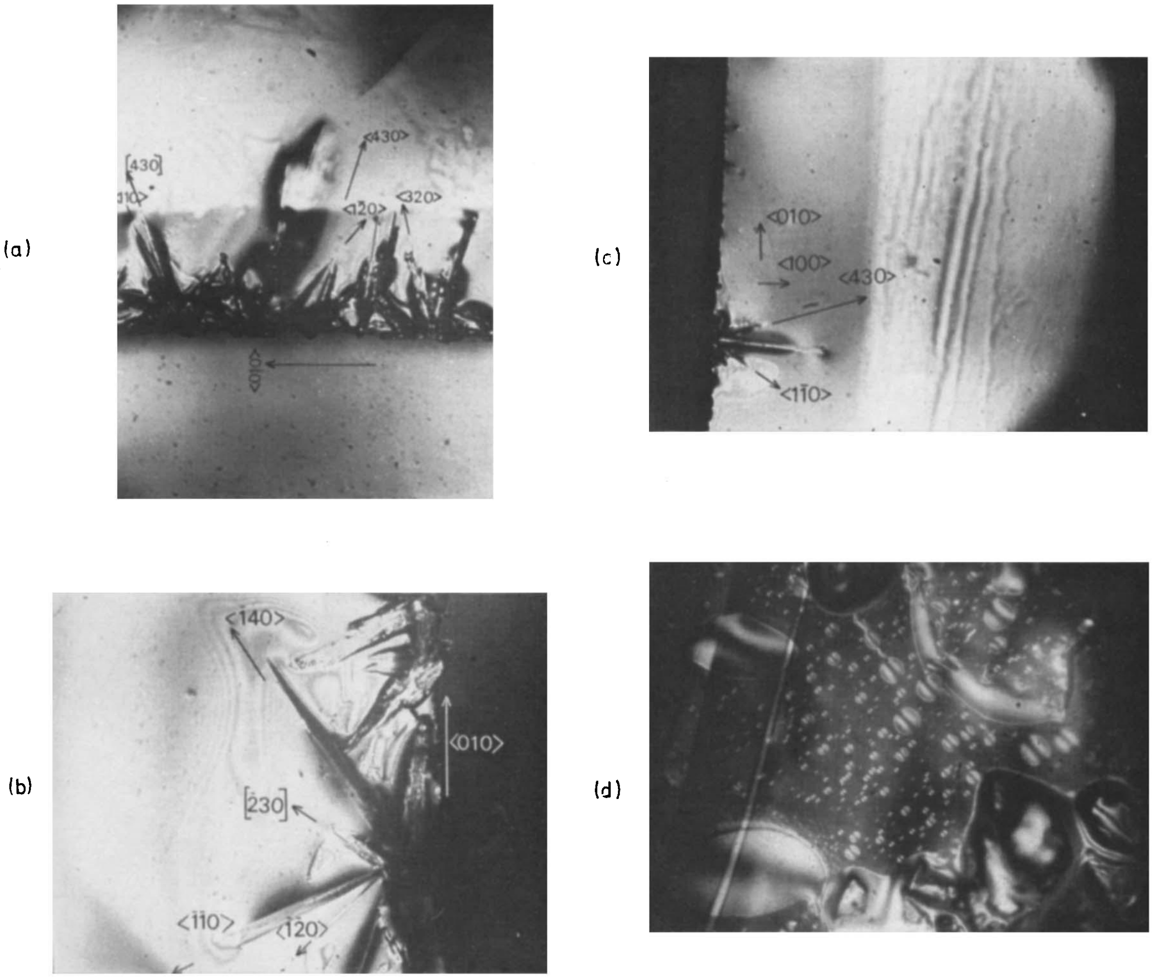

Plate 3 Product accumulation during ozonolysis of *trans*-stilbene (see text and Table 2) (magnification × 300)

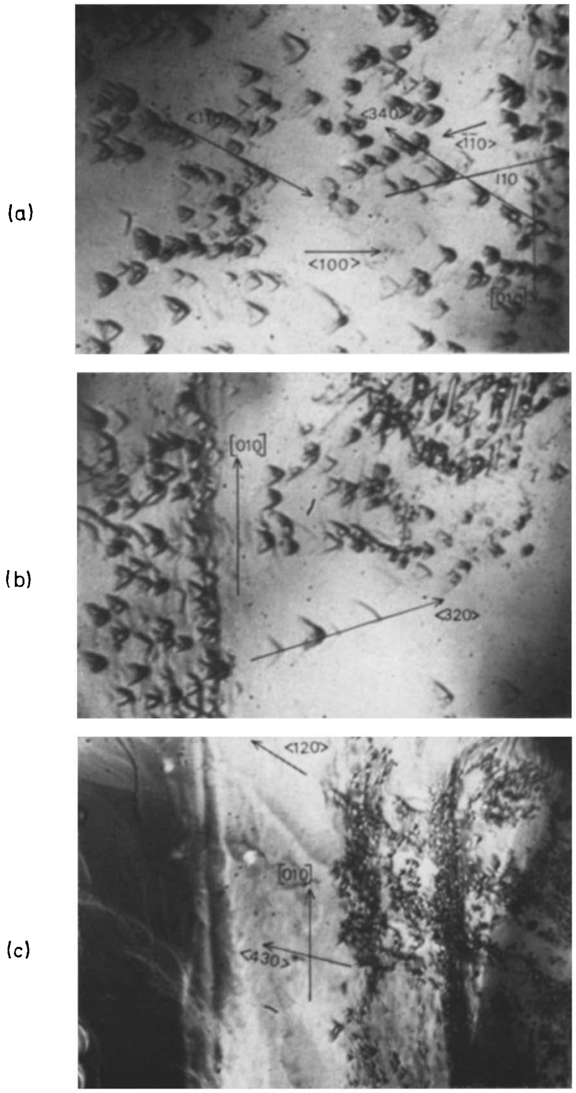

PLATE 4 Dislocation etch-pits on (001) face of *trans*-stilbene crystals (see Table **2**) [magnification ×300 for (a) and (b); ×70 for (c)]

solid, which yields small droplets of the rather volatile product (benzaldehyde [12]), is more rapid in this case than with (1b). Penetration is particularly marked along [110] directions on (110) faces. There is also considerable attack at (100) faces from which extra penetrative paths radiate in well defined crystallographic directions into the crystal as illustrated in Plates 3(a) and (b). On the (001) face, however, as with (1b), oxidation is centred only at sites which are associated with aligned or isolated dislocations [see Plates 3(c) and (d)] which were identified by etching in benzene (Plate 4). Table 2 summarizes the relevant crystallographic directions along which etch-pit alignments and/or oxidation product were detected.

TABLE 2

Summary of alignments of etch-pits and photo-product nuclei on (001) faces of *trans*-stilbene. The slip systems capable of explaining these alignments are also given

Product nuclei	Dislocation etch-pits	Slip systems [a]
[010]	[010]	(100) [001]; (100) [010]; *h*0*l* *uvw*
[100]	[100]	(010) [100]; (010) [001]; 0*kl* *uvw*
[110]	[110]	$(\bar{1}10)$ [001]; $(\bar{1}10)$ [110]; 11*l* *uvw*
[120]	[120]	$(\bar{2}10)$ [001]; $(\bar{2}10)$ [120]; $\bar{2}1l$ *uvw*
[130] (rare)		$(\bar{3}10)$ [001]; $(\bar{3}10)$ [130]; $\bar{3}1l$ *uvw*
[140] (rare)		$(\bar{4}10)$ [001]; $(\bar{4}10)$ [140]; $\bar{4}1l$ *uvw*
[210]	[210]	$(\bar{1}20)$ [001]; (120) [120]; 12*l* *uvw*
[230]	[230]	$(\bar{3}20)$ [001]; $(\bar{3}20)$ [320]; $\bar{3}2l$ *uvw*
[250] (rare)		$(\bar{5}20)$ [001]; $(\bar{5}20)$ [520]; $\bar{5}2l$ *uvw*
[320] (rare)	[320]	$(\bar{2}30)$ [001]; $(\bar{2}30)$ [230]; $\bar{2}3l$ *uvw*
[340] (rare)	[340] [rare]	$(\bar{4}30)$ [001]; $(\bar{4}30)$ [430]; $\bar{4}3l$ *uvw*
[450]	[450] [430]	$(\bar{5}40)$ [001]; $(\bar{5}40)$ [520]; $\bar{5}4l$ *uvw*

[a] Two typical, specific slip systems are quoted which could account for the alignments. Since detailed deformation and/or transmission electron microscopic experiments need to be performed before the systems are fully characterized, the generalized notation for the family, given in Miller indices, appears third for each entry in this column.

DISCUSSION

As in other gas–solid reactions involving single crystals of organic solids,[2,8,11] we observe here the influence of crystallographic anisotropy upon reactivity. With (1b) access of ozone to the ethylenic double bond is not easy from any one of the three major crystallographic faces, chiefly because of the extended network of hydrogen bonds, which prevents penetration of the gaseous reactant into the structure. Of the three main faces, so far as may be gauged from the minute crystals, the (100) is the least reactive, except where there are structural irregularities (see below). With crystals of (1a), because of the absence of strong intermolecular bonding, attack by ozone is considerably faster than for (1b) and at some faces of this solid [*e.g.* (110)] into which the gaseous species may readily diffuse (in [110] directions) because of its relatively open structure and unimpeded access to the most closely spaced (*ca.* 6·7 Å) ethylenic bonds reaction is obviously rather rapid. As with acenaphthylene-1-carboxylic acid, we again see that at one face, (001), reaction with gas occurs very slowly, except at the sites of emergent dislocations. The fact that attack is slower even at the irregularities on the (100) face of (1b) than at those on the (001) face of (1a) is not surprising since the presence of the two ethyl groups in the α and β positions of the stilbene skeleton in the former serves as an obstacle, at the molecular level, to the incoming ozone as it attaches itself to the ethylenic double bond.

Tables 1 and 2 enumerate the families of dislocations required to interpret the various kinds of alignments of etch-pits found for each of the two stilbenes. (The detailed reasoning required to arrive at the identity of the characteristic dislocations has been presented previously; see, for example refs. 16—18.) The fact that there is very good correspondence between the alignments found in both gas reaction and wet-etching demonstrates that essentially all the centres of activity in the dry oxidation process are at isolated or aligned dislocation or their consequential features, such as slip traces. (Perfect 1 : 1 correspondence is not to be expected since some dislocations are susceptible, for the same reasons that they enhance reactivity, to poisoning by various adventitious impurities; see, for example, ref. 19 for a specific manifestation of this effect.)

The enhanced reactivity towards ozone of these single-crystal stilbenes is similar to the nature of the preferential attack, by ground-state molecular oxygen, of single crystals of graphite [20] and molybdenite [21] where the loci of gross attack at the least reactive faces [(0001) in each case] are invariably emergent (non-basal) dislocations.* But there are two clear differences. First, with the high symmetry solids such as graphite, which has infinite two-dimensionally extended covalent bonding, there are only a few feasible families of dislocations that are operative {*e.g.* $(10\bar{1}l)$ $[11\bar{2}0]$ and $(11\bar{2}l)$ $[10\bar{1}0]$ are the only important ones that influence the reactivity of graphite [20]}. However for organic molecular solids, which are generally of lower symmetry than the simple elemental solids, and which lack strong two- or three-dimensional extended bonding, a multiplicity of feasible dislocation families (Tables 1 and 2) are, in principle, operable and capable of facilitating heterogeneous reaction.[23-25] Secondly, the dislocations in the stilbenes

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* Using refined transmission electron microscopy [22] it has been shown that point defects, as well as dislocations are centres of enhanced attack in these solids. Point defects are less likely to be present, and were very much more difficult to detect, at the surfaces of organic molecular crystals.

[18] J. O. Williams, D. T. B. Tennakoon, J. M. Thomas, and P. W. M. Jacobs, *J.C.S. Faraday I*, 1972, 1987.

[19] J. M. Thomas and G. D. Renshaw, *J. Chem. Soc.* (*A*), 1969, 2749, 2753, 2756.

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do not seem, in themselves, to offer obvious specific preference for oxidation, but function rather more as diffusive routes for the reactant gas to attack otherwise inaccessible regions of the crystal.* This is well illustrated by Figure 4 and Plate 1, which show how a (100) face, once 'opened' by oxidation at aligned emergent dislocations of the type (010) [001] or (010) [100], is further smoothly oxidized as reaction progresses. As product species further accumulate, lattice strains are, in turn, set up and new dislocations, which act as new centres of reactivity, are activated; *e.g.* the striations along [010] arise from the generation of (001) [010] type dislocations.

It is particularly interesting to note the far greater profusion of slip planes which are activated in crystals of (1a) than in (1b) as the reaction products build up in the solid during the course of the ozonolysis. This is a direct result of the smaller degree of intermolecular attraction in *trans*-stilbene than in its hydrogen bonded, substituted analogue. But the occurrence of hitherto unrecorded slip systems (see Table 2 and compare refs. 12 and 24) in other aromatic hydrocarbons which crystallize in the space-group $P2_1/a$ is a little surprising, though not altogether unexpected since it is known that the slip planes which may be activated in a given crystalline structure depend critically upon the conditions of stress applied to the particular sample of the solid. It is obvious that the build up of benzaldehyde within *trans*-stilbene brings into operation a far greater number of slip systems than those introduced into the crystallographically similar crystals of anthracene and naphthalene by the classical procedures [26] of applied mechanical deformation.

It is also of interest to note that several of the slip systems deduced in this study (Table 1) to be activated in diethylstilboestrol as a result of the solid-state production by ozonolysis of *p*-hydroxypropiophenone have not been hitherto identified in other orthorhombic crystals. Very little is, as yet, known about dislocations in orthorhombic crystals, and such data as exist refer to inorganic oxysalts (ammonium perchlorate [27-29] and barium sulphate [18]) which belong to the space group *Pnma*, so that it is premature to compare the nature of the distortions wrought in the solid state by, for example, the thermal decomposition of ammonium perchlorate on the one hand with solid-state ozonolysis of (1b) on the other. Some similarities undoubtedly exist {(010) [001] and (101) [010]; (110) [001] and (001) [010] are but a few of the slip systems involved in those solids} but deeper comparisons await further cognate investigations.

To a first approximation, the present studies indicate that all types of dislocations increase the room temperature reactivities about equally, and convert otherwise non-reactive faces into reactive ones.

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* This is reminiscent of Adler's results on the reactivity of irradiated solid aliphatic amides with gases: in this case the reaction seems to be regulated by the facility with which gases can diffuse to reach the trapped radical sites.

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