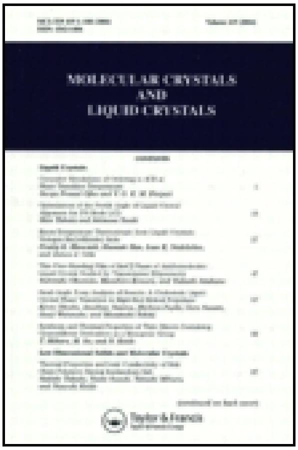

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Ozonolysis of Stilbenes: A New Example of Gas-Solid Organic State Reaction

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Ozonolysis of Stilbenes: A New Example of Gas-Solid Organic State Reaction

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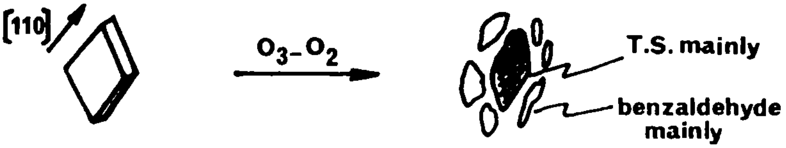
Several gas–solid organic state reactions are known,[1] and recent studies, chiefly by Curtin and Paul have rationalized the role of stacking in the lattice.[2] The role of crystal imperfections was also recently emphasized.[3]

In order to extend this type of study of gases on organic crystals, and because of the paramount importance of ozone in atmospheric pollution,[4] we have studied the ozonolysis of unsaturated compounds in the solid state.

We have investigated the attack of ozone on trans-stilbene, diethylstilboestrol, tolane and some aromatic compounds in order to elucidate the role played by molecular arrangement and defects in solid media.

Trans-stilbene (T.S.)

A single crystal of *t*-stilbene exposed to ozone on a microscope stage rapidly liquefied into a mixture of benzaldehyde and benzoic acid. The attack by gas is more rapid on the crystal edges and we have outlined below the phenomena (Figure 1).

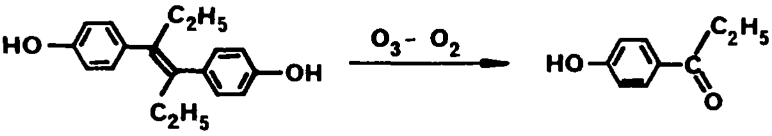


crystal of T.S. after a few minutes

FIGURE 1

Diethylstilboestrol (D.E.S.)

The attack on D.E.S. crystals is very much slower than that on T.S. Under an ozone stream the oxidation yield is about 12% after 4 hours exposure and the parahydroxypropiophenone (PHPP) is obtained pure, in contrast to the same reaction in solution.[5]



Optical microscopic investigation revealed a uniform attack on (001) and (010) faces, but that there was strikingly non uniform attack on the (100) face. The alignments of product on (100) face (see Figure 2) are pronounced along [001], and there is also some tendency for alignment along [021], [012] and [013] directions. After prolonged attack, the lines of product first grow along [001] thicken (in the [010] direction), and extra alignment of product develop along [010]. Etching by solvent (benzene) has been performed and we note that all significant directions of attack (lines of product) found in the gas-solid reaction are also found in wet-etching.

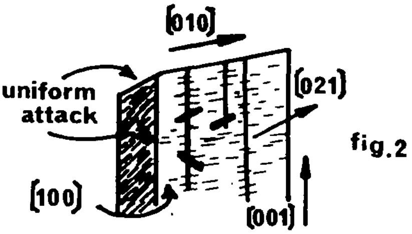


FIGURE 2

Discussion

The crystal structure of T.S.[6] is less tight than that of D.E.S.[7] in which hydrogen bonds provide strong intermolecular binding. This might well explain why benzaldehyde is formed faster than PHPP. We have substituted the hydrogens of the hydroxy groups of D.E.S. by CH_3, and have noted an enhancement of the overall reaction rate. We might also suggest that these different rates are due to the presence of the ethyl groups in the α, α' positions of the stilbene skeleton; these groups play the role of a shield for the reaction.

We must note also that ozonolysis of D.E.S. leads to a solid product (PHPP), whereas T.S. gives a liquid (benzaldehyde).

Moreover as in other gas–solid reactions involving single crystals of organic solids, we observe here the influence of crystal anisotropy upon reactivity.[2]

For T.S., oxidation is easier along the [110] direction on (110) faces, the gas may diffuse in smoothly and the product have enough room to be formed. This behaviour is reminiscent of other gas–organic solid reaction.[8]

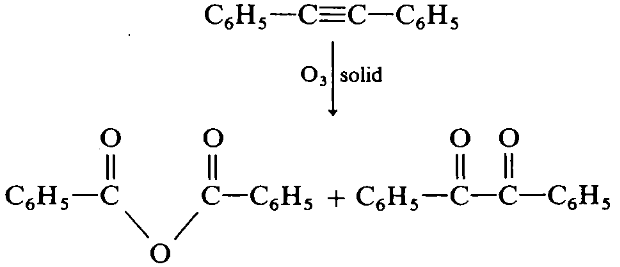
With D.E.S. access of gas to the ethylenic double bond is not easy from any one of the three major crystallographic faces, because of the extended network of hydrogen bonds, which prevent penetration of the gaseous reactant into the structure. So the three faces should be weakly reactive, however the reaction is anisotropic, the (100) face being the least reactive one, except where there are structural defects.

In conclusion, oxidation of solid ethylenic compounds is seen to be controlled by the crystal lattice. Crystal faces exhibit different reactivities because of the different relative orientation of the species. Defects also play a significant role in oxidation, perhaps simply because they provide diffusion paths for the gas.

Ozonolysis of other crystals

Tetraphenyl ethylene, like T.S. and D.E.S., leads to the corresponding benzophenone (64 % yield after 24 hours of ozone stream exposure).

Ozonolysis of diphenyl acetylene give two major products; the acid anhydride and α-diketone. In solution several extra products are formed[9]



We have obtained after 12 hours of O_3 exposure, 80 % of anhydride, 14 % benzil and 3 % of recovered tolane (VPC).

The yields at intermediate times are:	benzil	benzoic anhydride
after ½ hour exposure	1.3 %	—
1 hour	2.4 %	13 %
2 hours	3.4 %	26.5 %

At the beginning of the reaction the anhydride yield seems very small (VPC), but increases very rapidly. We note that the substrate is no longer crystalline and anhydride formation may be accelerated in non rigid media.

For condensed aromatic compounds the reaction is very slow; after several hours exposure to a stream of ozone, naphthalene, anthracene (A), acenaphthylene; 9,10 dimethyl-A; 1,8-dichloro-9 methyl A; 9,10 diphenyl A, pyrene, chrysene and tetracene[10] are recovered unchanged in our experimental conditions.† However in solution most of these compounds can be very easily ozonolyzed.[11]

From these results, we note that only ethylenic and acetylenic derivatives react easily in the solid state with O_3; in contrast to the polynuclear aromatic hydrocarbons. To rationalize the behaviour of fused-ring aromatic molecules we must probably consider the arrangement of molecules in the solid.

Conclusion

We have described the first examples of ozonolysis in organic solid state in relation with crystal structure and imperfections. Extension of this work in view of a better understanding of the mechanism is under current investigation.

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† If we expose for several days anthracene to ozone, we can observe oxidation, but the yield is low.