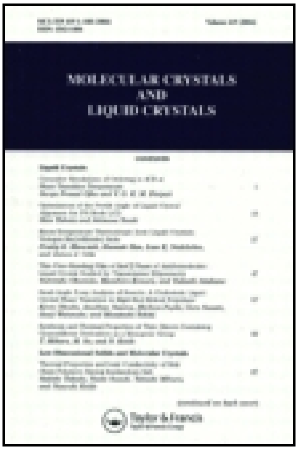

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Reactivity Dependence on the Crystalline State. Reaction of Gaseous Chlorine on Solid Phenols

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To cite this article: Jacques Vicens , Robert Perrin & Claude Bavoux (1983): Reactivity Dependence on the Crystalline State. Reaction of Gaseous Chlorine on Solid Phenols, Molecular Crystals and Liquid Crystals, 96:1, 71-73

To link to this article: http://dx.doi.org/10.1080/00268948308074693

Mol. Cryst. Liq. Cryst., 1983, Vol. 96, pp. 71–73
0026-8941/83/9604-0071/$18.50/0

Printed in the United States of America

REACTIVITY DEPENDENCE ON THE CRYSTALLINE STATE. REACTION OF GASEOUS CHLORINE ON SOLID PHENOLS

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Abstract Reaction of gaseous chlorine on powders of 3,5-dichlorophenol (A), 2,6-dimethylolphenol (B), 1 : 1 molecular compound between A and B (C) and the mixture of equimolar amounts of powders of A and B (D) is studied under different experimental conditions. When the molecules are engaged in the compound C, the reactivity of the least reactive molecules (A) decreases while the reactivity of the most reactive molecules (B) increases. An attempt is made to interpret the results from the crystalline structures of A, B and C.

INTRODUCTION

Solid-gas reactions are highly sensitive to the arrangement of the molecules in the crystalline state[1-3]. This communication deals with the idea that, because of molecular interactions due to the molecular packing, two organic molecules may react differently if they are engaged in different crystalline systems.

EXPERIMENTAL

Advantage was taken of the fact that 3,5-dichlorophenol, (A), and 2,6-dimethylphenol, (B), form a 1 : 1 molecular compound, (C)[4]. Powders of A, B, C and a mixture prepared from equimolar amounts of powdered A and B, (D), have been placed in a vessel and chlorinated simultaneously with a known amount of gaseous chlorine under different conditions (temperature from 2 to 10°C, pressure from 0.5 to 0.9 atm., time from 2 to 40 mn.). The samples were weighed before and after reaction and analysed by gas chromatography.

RESULTS

The reaction derivatives are 2,3,5-trichlorophenol and 3,4,5-trichlorophenol for A and 2,6-dimethyl-4-chlorophenol for B. From the area under each peack of CPV we calculated the ratio, ρ, of all products to unreacted starting material. The following facts are observed from experimental results :

1. A is less reactive than B in all cases : $\rho_A < \rho_B$
2. Molecules of A have the same reactivity when they are in the pure substance or in the mixture D. The same result is obtained for B molecules.
3. When the chlorination is carried out with the compound C, molecule of A are less reactive while molecules of B are more reactive than when chlorination is carried out with the mixture D.

$$\frac{\rho_A \text{ in D}}{\rho_A \text{ in C}} = 1.1 \text{ to } 4 \qquad \frac{\rho_B \text{ in C}}{\rho_B \text{ in D}} = 1.1 \text{ to } 5.3$$

these results have been observed for transformations of from 5 to 50%.

DISCUSSION

The observed effects are due to chlorination in the solid state where phenol molecules are differently surrounded in the pure substance than in the molecular compound. The crystal structures of A, B and C have been determined[5-7]. They consist of infinite chains of molecules linked by H-bonds. In crystals A and B each chain is built with one sort of molecule while in crystal C each chain is built of alternating A and B molecules. The chains are head to tail in A and B, which crystallize in the centrosymmetric space group $P2_1/c$, while they have all the same orientation in C which crystallizes in the enantiomorphous space group $P2_1$.

In view of the crystalline structures some possible explanations of the results in reactivity can be presented :

1. Arrangement of the molecules in the chains : because of the proximity of the reacting centres of A and B molecules in C crystal, the reaction occurs more easily with the most reactive species.
2. Arrangement of the chains in the crystals : because of the existence of a centre of symmetry in A and B crystals and not in C, accessible reactive positions are different in the pure substances and in the compound.
3. Facies of the crystals : well developped faces in A, B and C crystals are different ; experiments on single crystals will indicate if the facies takes an important part in the reaction. One of the precedent assumptions will be chosen after performing chlorinations on single crystals. This will permit us to conclude whether the observed effect is due to molecule-molecule interactions and/or to different approaches of the chlorine to the reactive centres.

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