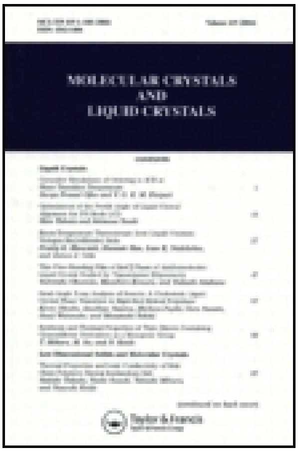

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Principle of the “Accessibility to Reactive Centers” in Gas-Organic Solid Reactions. Application to the Chlorination of Supramolecular Systems

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PRINCIPLE OF THE "ACCESSIBILITY TO REACTIVE CENTERS" IN GAS-ORGANIC SOLID REACTIONS. APPLICATION TO THE CHLORINATION OF SUPRAMOLECULAR SYSTEMS.

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Abstract : The principle of " the accessibility to reactive centers " is evoked. Its application to 4 solid organic systems brought into reaction with chlorine gas allows the interpretation of the experimental results obtained, thanks to definite knowledge of the crystal structures of these systems. In the cases studied, it can be noted that the reactivity of a phenol molecule in a supramolecular entity decreases when the crystal arrangement consists of supramolecules linked only by Van der Waals type bonds. The reactivity increases for one particular multimolecular system which consists of a three-dimensional hydrogen bond lattice.

Contrary to reactions carried out within the organic solid, gas - organic solid reactions generally occur at the surface of the organic phase. The reaction may propagate if the layer of the product is continuously removed or, due to its disorganization, allows gas to flow through it. With the exception of special cases, it does not appear that gas can migrate through the empty spaces of the crystal arrangement prior to reaction.

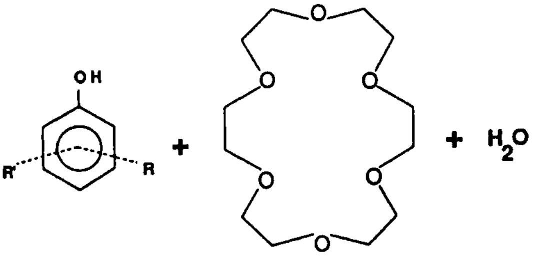
Under the above mentioned conditions, the reactivity is regulated by controlling the accessibility to the reactive centers. Therefore we propose to take into consideration the so-called principle of "accessibility to reactive centers" in order to explain various data concerning the reactivity of solid substances and the selectivity of gas - organic solid reactions. Of course it is also necessary to take into account both steric and electronic aspects.

The principle of " the accessibility to reactive centers " consists in saying that, for a given solid substance reacting at the surface with a solid, liquid or gas, the easier the access to the usual reactive centers, the greater the observed rate of reaction. In order to verify this principle, it is necessary to consider different solid systems incorporating the studied molecules. In these systems, the accessibilities of the molecules to reactive centers must differ whereas the electronic effects must be the same. In the collision theory, these different accessibilities correspond to different steric factors P, that incorporate the local properties of the reaction, the orientation required of the species and the details of how close they come in order to react.

The following systems can be considered as examples which demonstrate the principle of " accessibility to reactive centers ".

1 3,5 - dichlorophenol-18-crown-6-water (1;1;1)
2 3 - methyl - 2 - isopropylphenol -18-crown-6-water (2;1;2)
3 2,3 - dichlorophenol-18-crown-6-water (1;1;1)
4 hydroquinone -18-crown-6-water (1;1;6)

These systems are represented by the following formulae :



The studied reaction is the chlorination of phenol molecules using chlorine gas. Chlorine replaces hydrogen in the phenol ring in *ortho* and *para* positions. The results for systems 1 and 2 have already been published[1]. In the case of system 1, phenol is less reactive when associated in the molecular compound than when it is alone. The selectivity *ortho* / *para* for a same transformation rate is less for the molecular compound than for phenol alone. The data concerning the reactivity and selectivity demonstrate that it is the *ortho* substitution in particular which decreases the reactivity in the case of the molecular compound.

In system 2, the molecular compound with crown ether is practically unreactive whereas, under the same conditions, phenol alone gives a very high transformation rate.

These results can easily be interpreted when considering the molecular surroundings of the crystals containing phenol alone and that of the crystals containing the molecular compound, as well as the orientation of the molecules in relation to the principle faces of the crystals.

It can be seen that the molecular compound corresponds to a supramolecule consisting of 1 molecule of phenol, 1 of crown ether and 1 of water for system 1, and 2 molecules of phenol, 1 of crown ether and 2 of water for system 2.

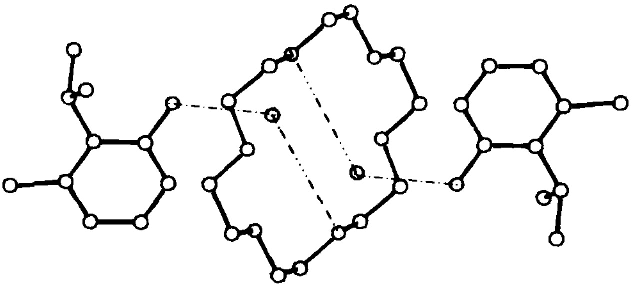


FIGURE 1 Supramolecular entity of system 2.

Hydrogen bonds ensure cohesion of these supramolecules. The crystal arrangement can be described as a pile of supramolecules which are only linked by Van der Waals bonds and therefore constitute distinct entities.

System 3 [2] and 2,3 - dichlorophenol alone were treated with chlorine under the same experimental conditions as described in the publication[1]. The crystallization of the molecular compound gives a pile of supramolecules as in the case of system 1. Within the supramolecule the water acts as a bridge, by means of hydrogen bonds, between the molecule of crown ether and the molecule of phenol[3]. A supramolecule is represented in figure 2.

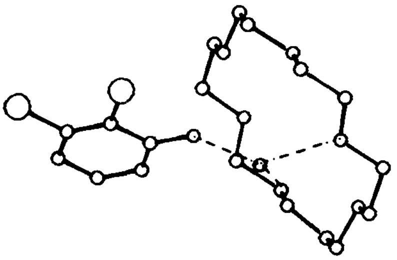


FIGURE 2 Supramolecular entity of system 3.

System 3 gives similar results to those obtained with systems 1 and 2. Figure 3 gives the degree of conversion versus time, the degree of conversion, τ, being defined as the number of molecules of chlorinated phenol versus the initial number of phenol molecules. It can be noted that the phenol molecule reacts much more rapidly alone than when associated in the supramolecule.

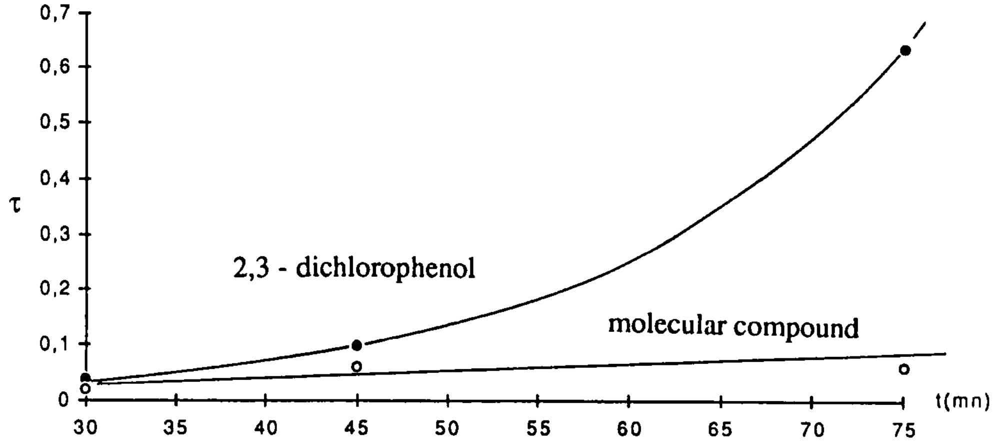


FIGURE 3 Degree of conversion versus time for system 3 and 2,3-dichlorophenol.

The curve in figure 4 represents the selectivity, ρ, defined as the ratio of the number of *ortho* chlorinated molecules to *para* chlorinated molecules produced versus the degree of conversion. It can be seen that the ratio *ortho/para* is much higher for 2,3-dichlorophenol alone than for the molecular compound whatever the degree of conversion.

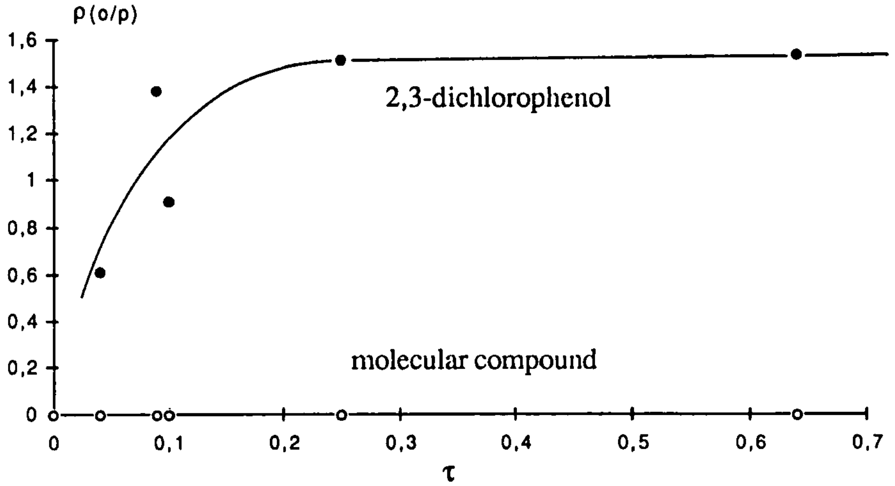


FIGURE 4 *Ortho/para* ratio versus degree of conversion for system 3 and 2,3-dichlorophenol.

It can also be noted that practically no 2,3,6-trichlorophenol is formed with the molecular compound. The crystal structure and crystal morphology of the molecular compound allow us to explain the results obtained. The monocrystals have the shape of thin plates. The large faces are lattice planes (001), the secondary faces are lattice planes ($1\bar{1}0$), (100) and (110).

Figure 5 represents the crystal structure as seen from the plane (001).

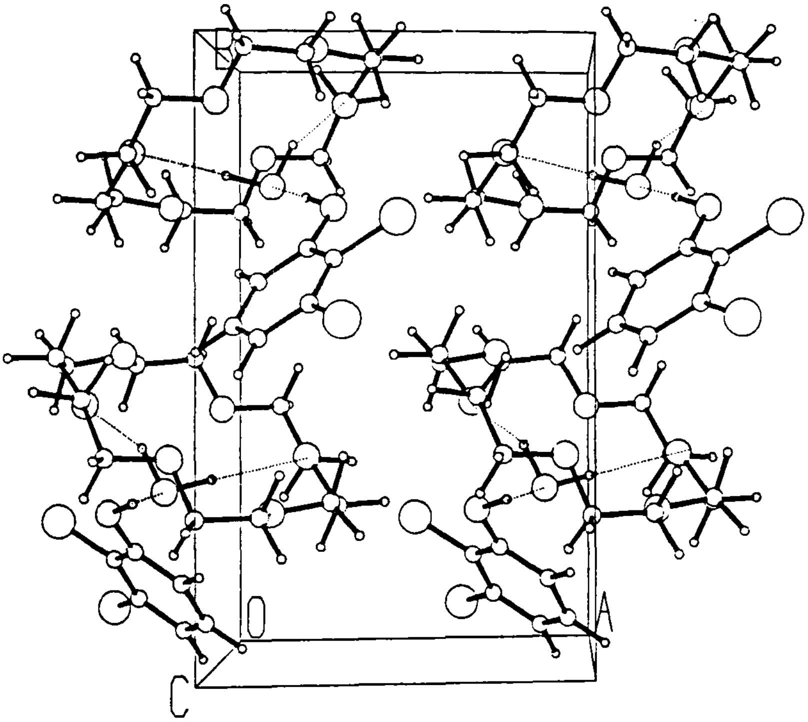


FIGURE 5 Crystal structure as seen from the plane (001) for system 3.

It can be seen that, regarding the orientation of the phenol molecule in relation to face (001), the accessibility for the chlorine molecule in *para* position is greater than its accessibility in the *ortho* position which is protected by the complexation zone.

The decrease of accessibility in the *ortho* position in the molecular compound as against 2,3-dichlorophenol alone explains the observed decrease in reactivity.

The crystal structure of 2,3 - dichlorophenol alone[4] shows that the *ortho* and *para* positions are easily accessible and in a similar way.

System 4 concerns hydroquinone. Figure 6 shows that in contrast to the other other examples, hydroquinone alone reacts to chlorine much more slowly than when it is associated in a molecular compound consisting of crown ether and water molecules.

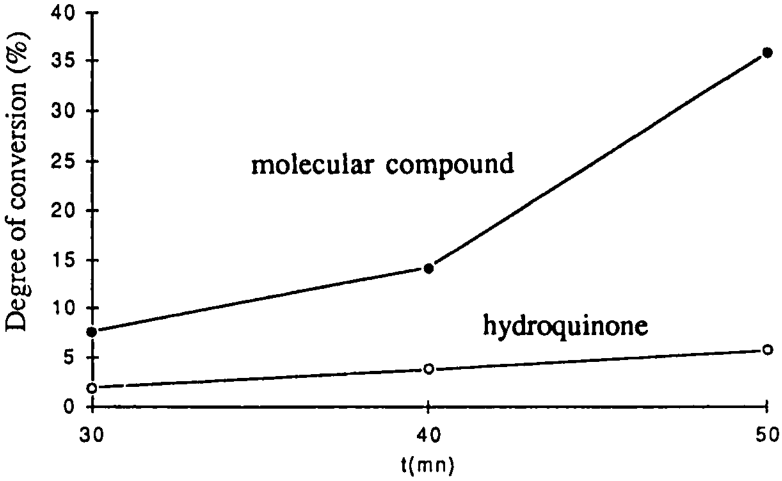


FIGURE 6 Degree of conversion versus time for system 4.

The most developped face of the crystal of the molecular compound is the (001) face. Figure 7 shows the molecule arrangement for hydroquinone on this face[5].

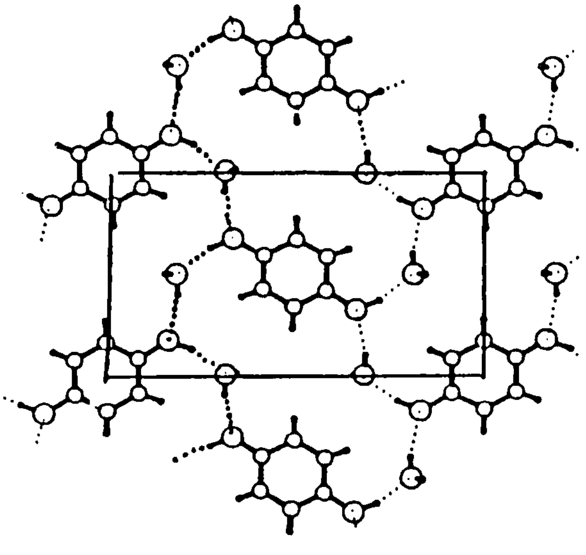


FIGURE 7 Crystal structure as seen from the (001) plane for system 4.

It can be seen that all the reactive centers are easily accessible due to the fact that the aromatic rings and the face of the crystal are parallel. This is not the case for the crystal arrangement of hydroquinone alone. In fact , in this arrangement[6] the planes of the aromatic rings form an angle of about 40° with the plane of the main face of the crystal.

It can be noted that for all the cases in which the supramolecular reactivity is lower, the crystal arrangement corresponds to supramolecules linked only by Van der Waals bonds. For the only case we have found to date in which the reactivity is greater in the multimolecular arrangement, it is to be noted that this arrangement is not simply a pile of supramolecular entities, but constitutes a three-dimensional hydrogen bond lattice, between the three sorts of molecules as seen in figure 8.

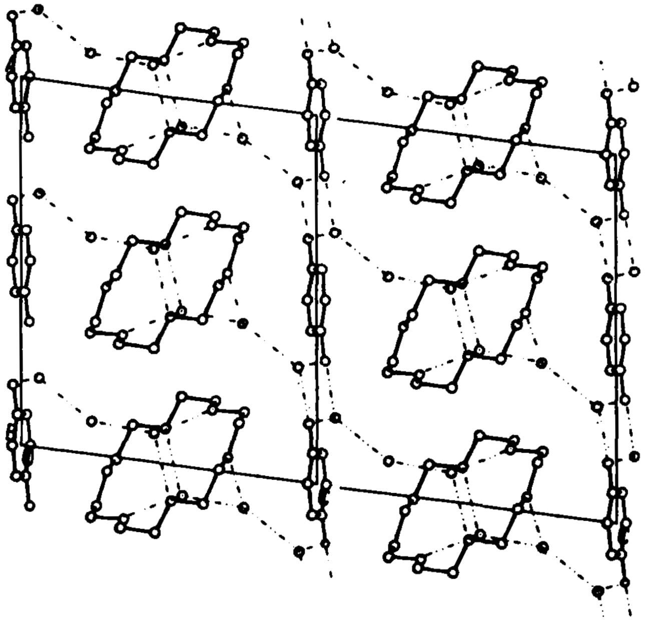


FIGURE 8 Three dimensional hydrogen bond lattice for system 4.

In conclusion, we can say that the principle of " accessibility to reactive centers " is one on which we can depend to interpret results obtained from gas-organic solid reactions. According to the arrangement obtained it is possible to increase or decrease the reactivity of the target molecule. If this molecule has several reactive sites, it is possible to modify the selectivity of the reaction.

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