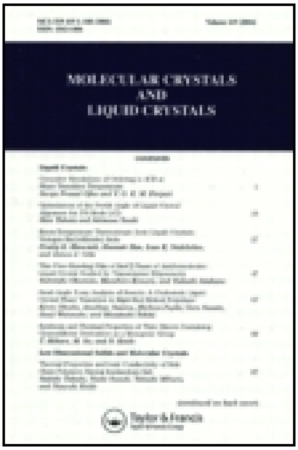

Molecular Crystals and Liquid Crystals

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Catalytic Hydrogenation of Organic Solids-Basic Problems

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CATALYTIC HYDROGENATION OF ORGANIC SOLIDS-BASIC PROBLEMS

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Abstract The hydrogenation of organic solid substances like phenols and phenoxides under mild conditions has been studied. It is shown that those reactions take place in the solid state. Because of the lack of fluid phase the classical catalysis processes cannot explain the high conversion ratios obtained;the spillover effect and the existence of mobile hydrogenating species are discussed.

INTRODUCTION

A number of organic solid-gas reactions have been carried out without any catalyst. The different gases used are carbon dioxide[1], oxygen[2], ozone[3], nitric oxide[4], sulfur dioxide[4], isobutene[5], bromine[6], chlorine[7], ammonia and different amines[8].

If we attempt to perform an organic solid-gas reaction with hydrogen, it is necessary to use a catalyst. Even with a catalyst it is difficult to believe that such reaction can occur because it is necessary to work at low temperature in order to keep the organic substance in the solid state. Under these conditions, the reaction would not occur since usually it is considered that such reaction involves adsorbed hydrogen (see figure 1). It seems clear that the organic substance, which is solid cannot migrate to this adsorbed phase.

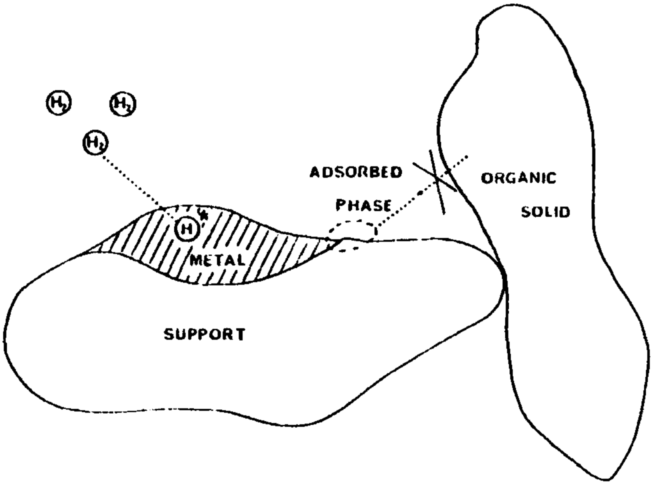


FIGURE 1. Representation of a catalytic hydrogenation.

RESULTS AND DISCUSSION

We have studied at room temperature and at 760 torr hydrogen pressure with rhodium on carbon or on alumina as catalyst, the solid state hydrogenation of phenol, 3-methyl 6-isopropylphenol, 4-alkylphenols and sodium, potassium and magnesium phenoxides. The different conversion ratios obtained in these conditions are listed in table I. Note the high conversion ratios obtained. So, experimentally we have evidence that it is possible to hydrogenate different organic solid substances like phenols and phenoxides under mild conditions.

Although all the organic phases studied are in the solid state at the reaction temperature, it is conceivable that this reaction is not a true solid state reaction but that it takes place in the liquid state or in the gaseous phase. If we accept the idea that a fluid phase is formed as a result of the dissolution of reagents by the products, for instance, we should be able to observe a very slow reaction at the beginning and a gradual increase in rate as the fluid phase is being created.

TABLE I. Hydrogenation of phenols and phenoxides : conversion ratios and hydrogenation products with Rh/Al_2O_3 as catalyst.

Substances	mp (°C)	a	b	c
phenol	40,9	99	18	81
sodium phenoxide	384	20	6	14
potassium phenoxide	290	61	4	57
magnesium phenoxide	500	49	12	37
2-methylphenol	31	98	15	83
4-tert-butylphenol	99,5	72	4	68
2,6-dimethylphenol	45,6	94	20	74
3,5-dichlorophenol	68	6	--	--
3-methyl-6-isopropylphenol	49,8	86	50	36
3-methyl-4-isopropylphenol	111	20	--	--

a = conversion ratio ; hydrogenation products b = cyclohexanones, c = cyclohexanols

The reaction shown on figure 2 is 4-tertiarybutylphenol hydrogenation at 20°C with Rh/C as catalyst. The reagent is evacuated to approximately 10^{-4} torr for 15 minutes and hydrogen is then introduced.

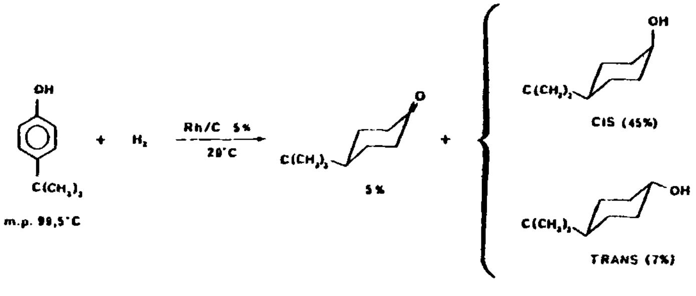


FIGURE 2. Hydrogenation of 4-tertiarybutylphenol

We have represented the hydrogen quantities absorbed and transformed into products versus time (see figure 3). A greater rate is obtained at the beginning of the process and gradually decreases thereafter. Therefore, there is no induction time and the reaction does not take place in a liquid phase.

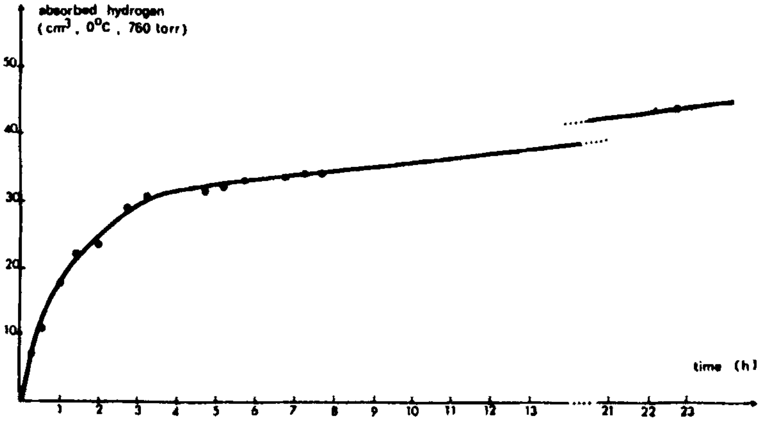


FIGURE 3. Absorbed hydrogen *vs* time for 4-tert-butylphenol with Rh/C as catalyst.

Can the reaction occur in the gaseous phase ? The hydrogenation achieved with conversion ratios varying from 20 to 70% for sodium, potassium and magnesium phenoxides with melting points of 384, 290 and 500°C are not readily explained by a reaction in the gaseous phase, as these phenoxides have very low vapour pressures at 20°C. For example, in the case of magnesium phenoxide we have verified with the apparatus described on figure 4, that no vapour phase was detectable after establishment of a dynamic vacuum for 6 hours and then a static vacuum for 4 hours. With the static vacuum, nothing is trapped by the cold finger kept at -20°C. Indeed by U.V. spectroscopic examination of the hexane used to rinse out the cold finger, we have detected no trace of aromatic products.

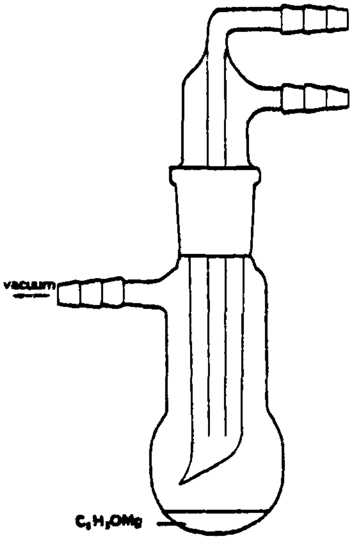


FIGURE 4. Apparatus for detection of vapor phase formation.

Therefore, it appears that the reaction takes place in the solid state.

For a true organic solid state reaction it was observed that the reactivity and the selectivity are correlated with the crystal structure. For instance we have considered the hydrogenation of "parathymol" or 3-methyl-4-isopropylphenol. The crystal structure has been determined by one of us[9] and the space group is $P4_1$ or $P4_3$. The molecules are linked by hydrogen bonds forming infinite chains as shown on figure 5.

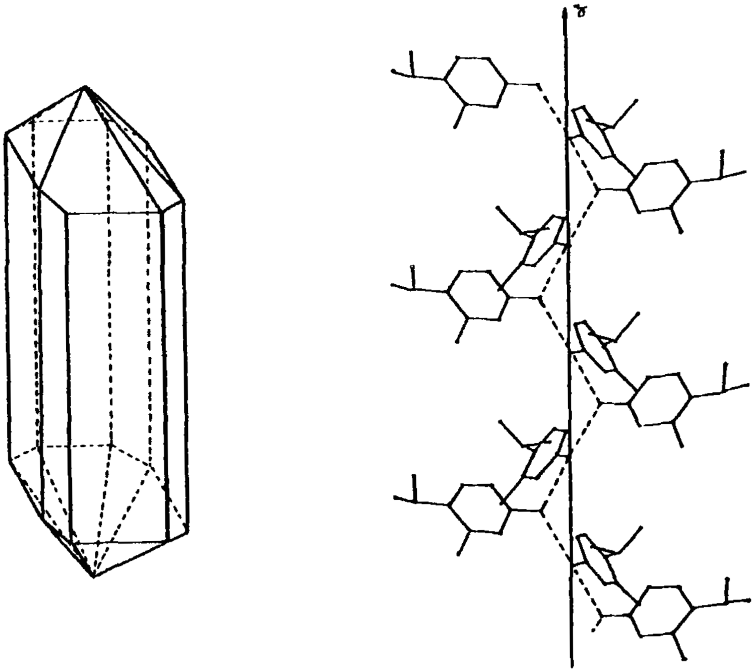


FIGURE 5. A crystal of 3-methyl-4-isopropylphenol

We have obtained right and left handed crystals. Hydrogenation of the left and right handed powders was carried out in the apparatus described on figure 6. To prevent grease contamination, we have used only teflon joints. The powder was mixed with the catalyst and placed in the reactor. The reaction mixture was collected by pumping and the products were removed from the catalyst by centrifugation. The results obtained with the left handed crystal powder are given in table II.

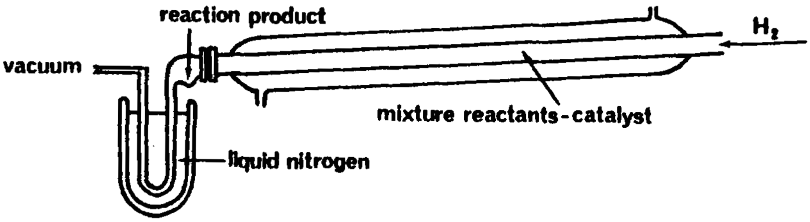


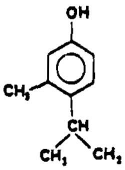
FIGURE 6. Apparatus for asymetric hydrogenation.

TABLE II Solid state hydrogenation of parathymol and natural thymol, rotatory power.

3-methyl 4-isopropylphenol

Non centrosymmetric crystalline structure.

Enantiomorphous space group $P4_3$



The powder is obtained from a 50g left single crystal.

Reaction temperature : 80°C

Reaction time : 1h 35mn

Catalyst : Pt/C 5%

Rotatory power

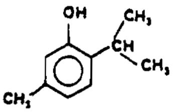
	0 h	24 h
λ = 589 nm :	+0,119	+ 0,137
λ = 578 nm :	+0.135	+ 0.128
λ = 546 nm :	+0.155	+ 0.145
λ = 436 nm :	+0.255	+ 0.236
λ 365 nm :	+0.352	+ 0.349

- -

3-methyl 6-isopropylphenol

Centrosymmetric crystalline struture.

Space group R $\bar{3}$



Reaction temperature : 25°C

Reaction time : 45 mn

Catalyst : Pt/C 5%

Rotatory power

λ 589 nm : 0.000 ± 0.002
λ 578 nm : 0.000 ± ——
λ 546 nm : 0.000 ± ——
λ 436 nm : 0.000 ± ——
λ 365 nm : 0.000 ± ——

Note that the experiments were repeated by different experimenters and the rotatory power is time stable. The same experiments carried out in the same conditions with centrosymmetric crystals of natural thymol give a mixture of menthols and menthones without any rotatory power. These results which agree with the crystal structure of natural thymol shown that we are not dealing with artefacts. This reaction of an achiral compound with an achiral catalyst leading to rotatory power is an absolute asymmetric synthesis using only the chirality of the crystalline arrangement. Thus, the results obtained depend solely on the molecular arrangement in the organic solid state and rule out the possibility that the reaction proceeds via liquid or gaseous phases.

We believe that we have achieved a solid state reaction since the results are correlated with the crystalline structure.

From a catalytic point of view it is obvious that we cannot think of our reactions as normal catalytic processes. As shown on the figure 7, the reaction takes place in an adsorbed phase. In our case because of the lack of fluid phase, the organic reagent cannot be adsorbed on the catalyst.

At first we considered the spillover effect as originated by BOUDART. As shown on figure 8 the spillover effect requires hydrogen migration between metal and support. On the figure 8 we describe how we believe the solid state hydrogenation of a phenol occurs. The molecular hydrogen on contact with metal gives "activated" hydrogen. This hydrogen is transferred on the surface or in the bulk. This is the first spillover effect. By means of contacts between support and organic solid, activated hydrogen moves across the organic solid reagent and reacts. This is the second spillover effect[10]. So the support and the organic reagent make up solid phases which allow the migration of hydrogen in its activated state. The migration of hydrogen from support to organic product requires many contacts between these two phases. This is an important problem which we will now discuss.

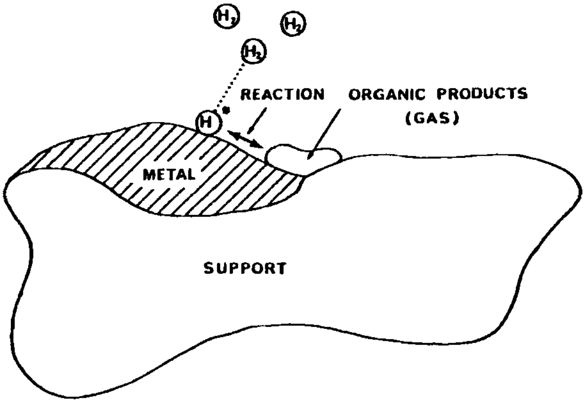


FIGURE 7. Classical catalysis. Langmuir Hinshelwood mechanism : two adsorbed species, Rideal Eley mechanism : one adsorbed species.

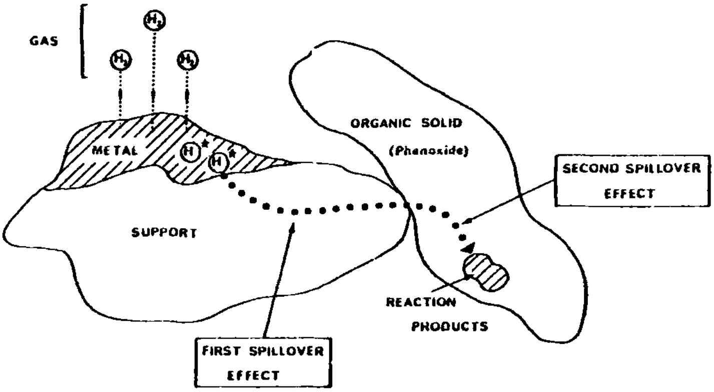


FIGURE 8. Spillover effects in a solid state hydrogenation.

For this purpose we have tried to perform the hydrogenation without contact between the support and the organic substance. The reaction was allowed to proceed as shown on the figure 9. The catalyst Pt/C or Pt/Al_2O_3 was placed in a very thin teflon cover whose pore size is 0,5μ. This membrane was placed in contact with the organic solid reagent and the hydrogenation was carried out under the same conditions as previously. Note that under these conditions the contact between catalyst and organic solid reagent is poor.

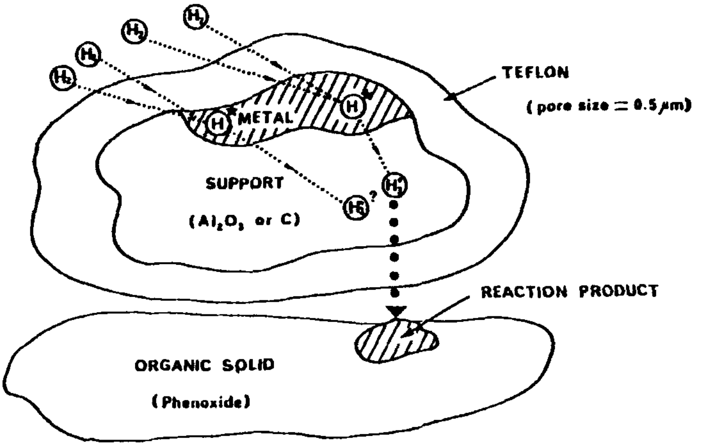


FIGURE 9. Hydrogenation without contact. The catalyst is placed in a teflon cover.

Nevertheless the reaction occured, although slowly. We observed the hydrogenation of magnesium phenoxide at 80℃ in accordance with the figure 10. The products obtained were phenol, cyclohexanol and dicyclohexylether. These products formed a liquid reaction mixture which deposited in tiny drops on the cold wall of the reaction cell and were analysed directly by gas chromatography. The formation of the products requires the rupture of the O-Mg bond and the formation of magnesium or magnesium hydride although these products are not yet well identified. The formation of dicyclohexylether also requires the breaking of a C-O bond for a number of molecules. In any case the reaction takes place in the solid state as a first stage reaction.

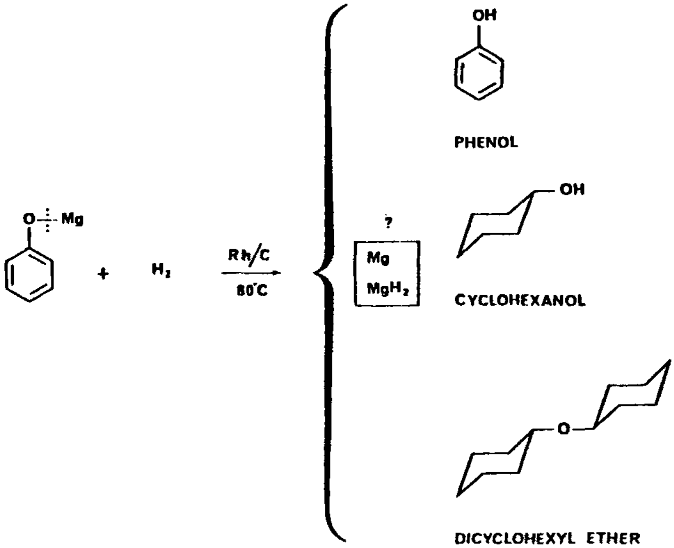


FIGURE 10. Products formed in the hydrogenation of magnesium phenoxide. The catalyst Rh/C is placed in a teflon cover.

Because the contacts between the catalyst (rhodium/carbon) and the organic solid reagent are poor, it is difficult to explain the course of the reaction solely on the basis of spillover. In accordance with the figure 9 we consider a gaseous phase such as H_3^+ or $H_3^\bullet$ which migrates through the teflon pores. These H species were recently discussed by TEICHNER and PAJONK[11]. These species can result from the interaction between molecular hydrogen and activated hydrogen and presumably would be charged by contact with the support.

CONCLUSION

So the hydrogenation of organic solid products throws a new light on processes which occur in a catalytic reaction. Solid state hydrogenation, as described here, provides additional experimental proof of the first spillover effect and shows the existence of mobile hydrogenating species.

Concerning the applications, the results obtained here might be applied to the study of the coal liquefaction and "in situ" recovery of the gaseous species, e.g. CH_4, by pumping. These results might also be useful for the study of less soluble organic substances such as steroïds.

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