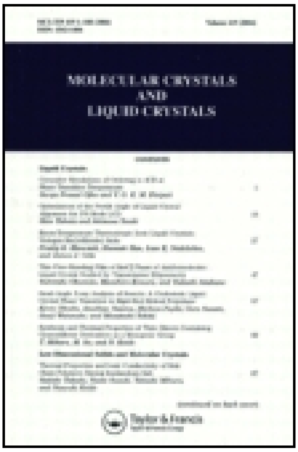

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Deuterium as Gas in Organic Solid Reactions

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Abstract Deuterium reacts with solid phenols, similar to hydrogen under mild conditions. We show that there is an addition of six deuterium atoms to the phenolic ring. The hydrogen bond of the hydroxyl group is not really affected by deuteration, no transfer or exchange with deuterium is observed. A higher rate of deuteration compared to hydrogenation is obtained. Deuterium diffuses from the metal catalyst to its support and then reacts with the organic solid.

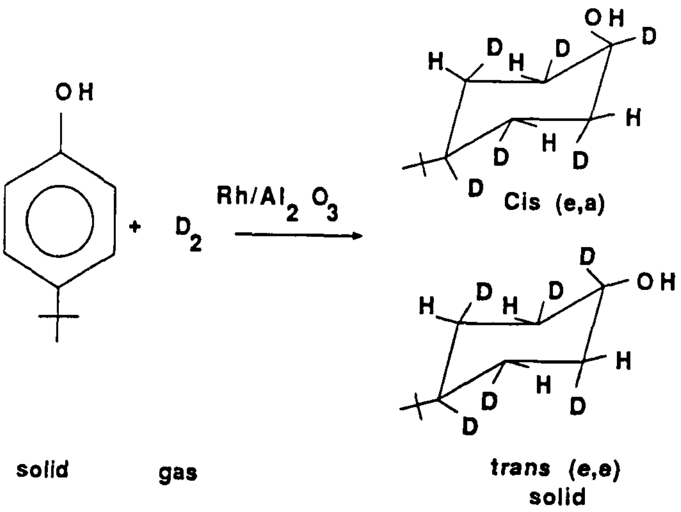
INTRODUCTION

In previous works[1,2,3], we reported that hydrogen reacts with organic solids in the presence of various catalysts under mild conditions. Double spillover effects were suggested for such reactions[4]. Activated hydrogen diffuses from metal to catalyst support (first spillover effect). By means of contacts between catalyst and organic solid, activated hydrogen moves across the organic solid reagent and reacts (second spillover effect). Deuterium was used in gas phase reactions to observe the first spillover effect[5,6]. It has been shown that deuterium spilt over from a metal catalyst can be exchanged with surface hydroxyl groups of various oxides. The use of deuterium as gas in solid state catalytic reactions can provide information on the second spillover effect and make clear the mechanism of the solid state reactions. In this study we compare deuteration and hydrogenation reactions. Deuterium reacts with solid phenols by an addition mechanism. Activated or spillover deuterium is the reactive entity.

EXPERIMENTAL

The reaction is carried out with 4-tert-butylphenol powder. Rh/Al_2O_3 is used as catalyst and mixed with the 4-tert-butylphenol powder in the proportion of 10% by weight. The reaction temperature is 20°C and the deuterium pressure is kept at 1 bar during the whole reaction time. The purity of deuterium is greater than 99,4 %. Products are isolated on silica gel column chromatography with ethylacetate - hexane (66-33) as eluent. Deuterated products are analysed by I.R. spectrography and vapor phase chromatography and are characterised by ^1H NMR, ^{13}C NMR and Mass spectrography.

Reaction



RESULTS AND DISCUSSION

Deuteration of 4-tert-butylphenol with rhodium on alumina as catalyst gives a solid mixture of cis and trans deuterocyclohexanol. The products are solid at the reaction temperature. Compared to hydrogenation, cis/trans ratio is not notably modified and is around 1.5. The exchange of hydrogen by deuterium does not modify the selectivity of this gas-solid reaction.

Deuterium reacts with solid 4-tert-butylphenol at appreciable rates. With rhodium on alumina as catalyst the conversion ratio reached 96% for a reaction time of 24 hours. As shown in figure 1, adsorption rate of deuterium is faster than adsorption rate of hydrogen. The two curves are similar, a short induction time is observed. The kinetic laws for hydrogenation and deuteration are apparently the same. Contrary to what we would expect, deuterium reacts more rapidly than hydrogen.

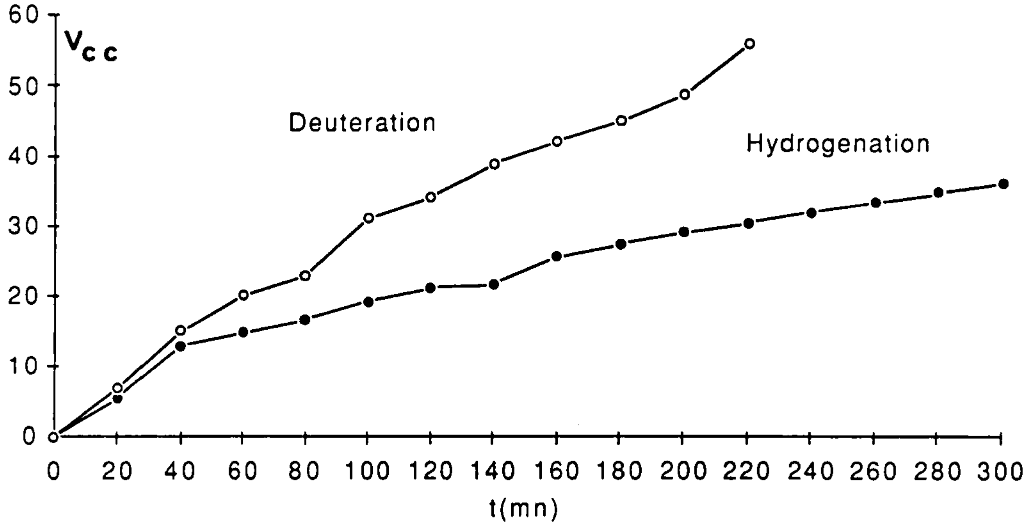


FIGURE 1 Adsorption rate of deuterium and hydrogen on solid 4-tert-butylphenol

Compared to hydrogen, higher rates of deuteration in the solid state could be explained by a reverse isotopic effect or a secondary isotopic effect. Several studies in solution dealing with isotopic effects have been published [7,8,9,10]. It would appear that the substitution of an hydrogen by a deuterium in an organic molecule has no effect on the qualitative reactivity but often has a measurable effect on the rate of reaction.

As Allinger and coworkers[11] point out,the primary isotopic effect K_H/K_D is always greater than 1. The secondary isotopic effects of deuterium can be classified as: hybridization effect, steric effect, inductive effect and hyperconjugation effect. It is possible to observe a normal secondary isotopic effect $K_H/K_D > 1$ and also a reverse secondary isotopic effect $K_H/K_D < 1$. It is difficult to distinguish these effects which often take place simultaneously.

In this solid state reaction the replacement of hydrogen by deuterium does not bring modification of cis/trans selectivity but alters the reactivity. Deuterium reacts on the aromatic ring and the formed bonds C-D are shorter than the C-H bonds.

To have more information on the reactivity of deuterium gas with organic solids and to better understand mechanisms of catalytic hydrogenation reactions in the solid state we analysed the reaction mixture and isolated the trans deuterated product.

The I R spectroscopy study of the solid reaction mixture has been achieved in anhydrous CCl_4. The I R spectrum (figure 2) shows clearly that cis and trans deuterated t-butylcyclohexanol are formed. The C-D band is observed at 2200 cm^{-1}, the O-H band at 3100-3400cm^{-1}, the C-H aliphatic is observed at 2950cm^{-1}. The large O-D band does not appear at 2500 cm^{-1}. In these conditions,there is no isotopic exchange with H bonds of the hydroxyl groups but an addition reaction occurs on the phenolic ring with formation of C-D bonds.

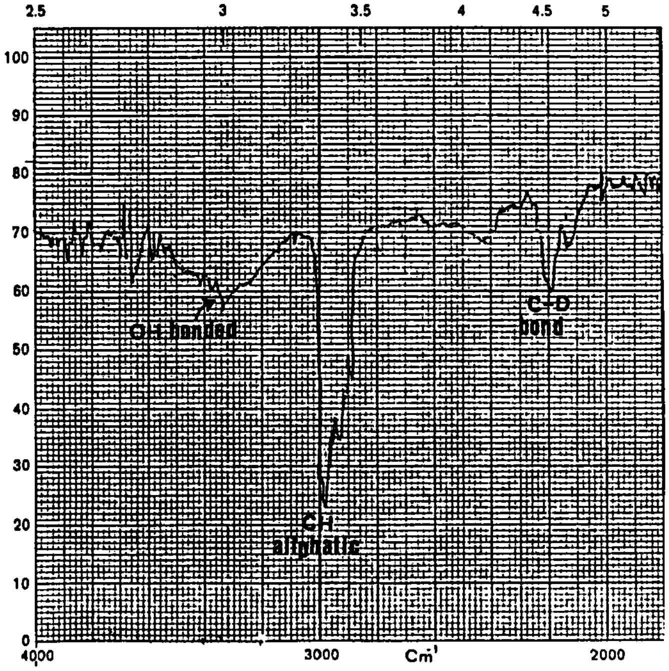


FIGURE 2 IR spectrum of solid reactionnal mixture

The number of deuterium atoms is evaluated by ^{1}H NMR spectroscopy (80 MHz) of both hydrogenated and deuterated products. Figures 3 and 4 show four hydrogen atoms are on the deuterated ring and one on the hydroxyl group. These data agree well with the mass spectroscopy results (Molecular weight = 162). We deduce that during the reaction, 6 deuterium atoms are fixed on the phenolic ring. The distribution of the deuterium atoms is studied by ^{13}C NMR and DEPT technique[12]. For the deuterated product, as figures 5 and 6 show, we observe an attenuation of the intensity of each peak for the carbon atoms bearing deuterium.

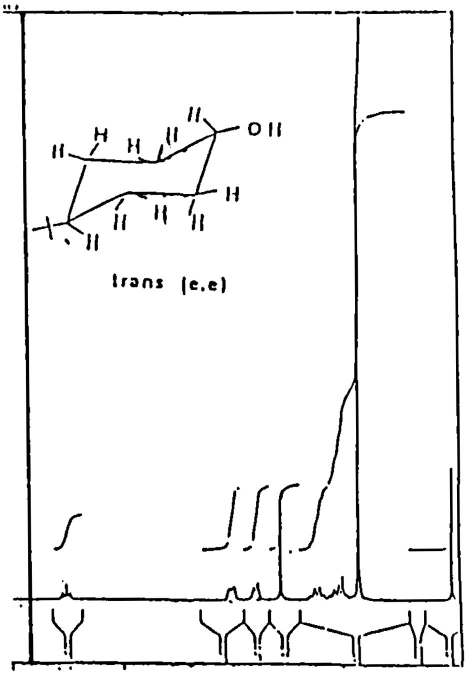


FIGURE 3 ^{1}H NMR

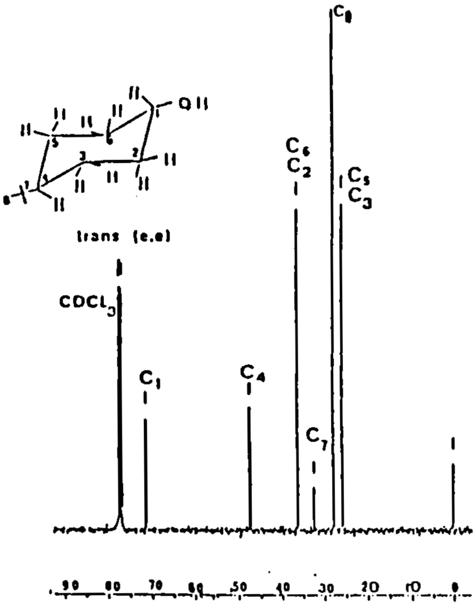


FIGURE 5 ^{13}C NMR

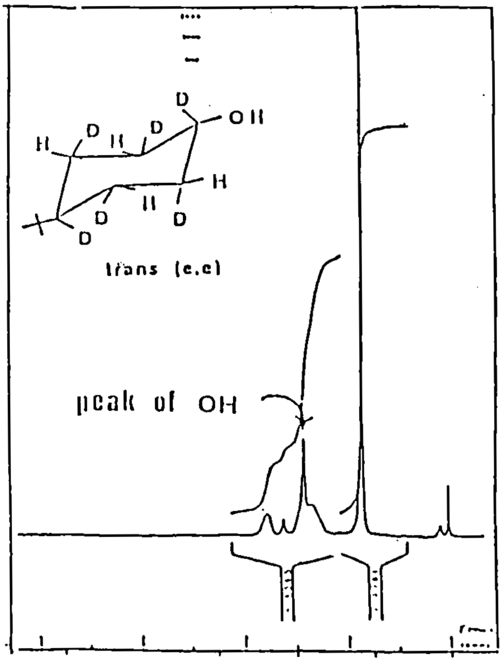


FIGURE 4 ^{1}H NMR

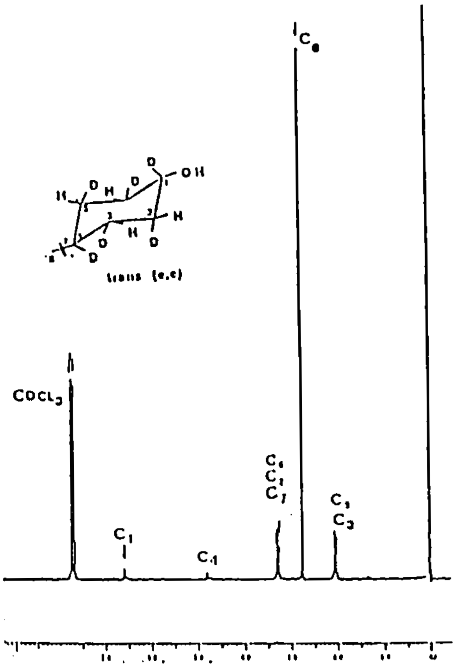


FIGURE 6 ^{13}C NMR

This result and the chemical shifts are analogous to those given in the literature[13]. It confirms there is an addition of a deuterium atom on each carbon atom of the phenolic ring. The DEPT technique well confirms that there is addition of deuterium. The peaks of carbons (C_2, C_6, C_3, C_5) bearing two hydrogens (figure 7) disappear completely for the deuterated product (figure 8) with modification of the chemical shifts. The tert-butyl group and the hydroxyl group are not affected during the solid state reation, whereas in solution or in vapor phase the exchange between hydrogen and deuterium often happens. In the solid phase, deuterium must be adsorbed on the catalyst to be reactive. After diffusion from catalyst to the organic substrate the addition reaction occurs only on the aromatic carbons.

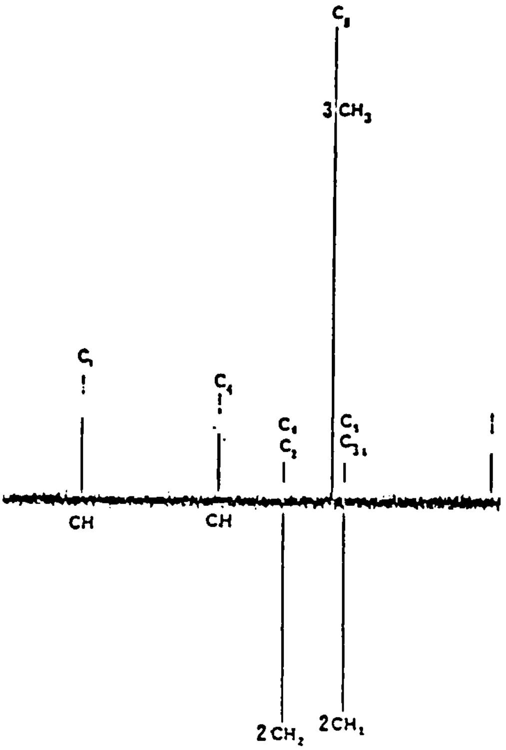


FIGURE 7 DEPT of hydrogenated product

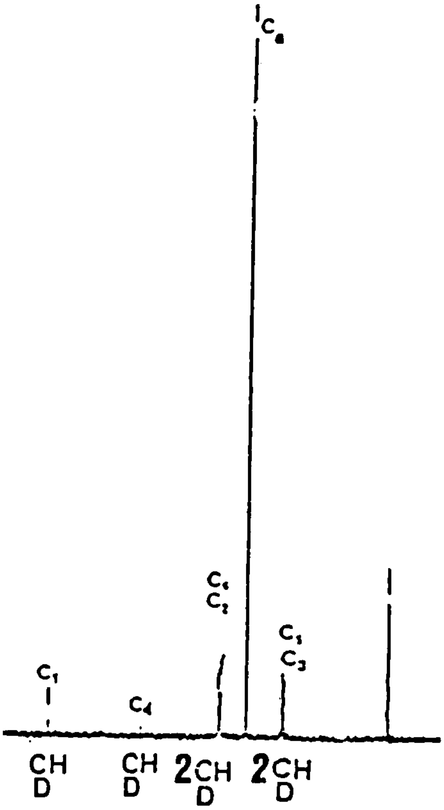


FIGURE 8 DEPT of deuterated product

CONCLUSIONS

Deuterium reacts similar to hydrogen in solid state catalytic reactions under mild conditions. Deuterium reacts more rapidly than hydrogen, the high rate of deuteration is explained by a reverse isotopic effect or a secondary isotopic effect. With deuterium there is no isotopic exchange neither with C-H bonds of the aromatic ring, neither with the O-H bond of the hydroxyl groups. There is an addition reaction on the phenolic ring. These results are in agreement with hydrogen spillover mechanisms that mean deuterium must diffuse from metal catalyst through its support, and then to the organic substrate. The diffusion model proposed by Filikov and Myasoedov[14] seems to be most likely to describe our results.

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