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# A New Organic Solid State Reaction: Hydrogenation of Phenols

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# A New Organic Solid State Reaction

## Hydrogenation of Phenols

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During the past fifteen years there has been a number of detailed studies devoted to the chemistry of organic molecular solids and made by a number of groups involving chemists and crystallographers. These workers were interested in the reactions of the organic solids subjected either to a physical agent like light or heat or to a chemical one which can be a solid, a liquid or a gas.[1]

Our attention has been focused on several aspects of chemical reactions between gases and organic solids.[2] The main gas-organic solid reactions studied are listed in Table I.

As shown in this table the different gases used are: carbon dioxyde, oxygen, ozone, nitric oxide, sulfur dioxide, isobutene, bromine, chlorine, ammonia and amine. Notice that hydrogen was not used.

The purpose of this work is to evidence the fact that it is possible to hydrogenate solid state phenols at room temperature and at 760 torr hydrogen pressure, the catalyst used being rhodium on carbon or on alumina at 5% (Scheme 1).

Experimental conditions are determined as follows: the studied phenol is ground to a fine powder and mixed with the catalyst in weight ratio: 1 : 1. The resulting powder mixture is deposited as a thin layer in a cell with

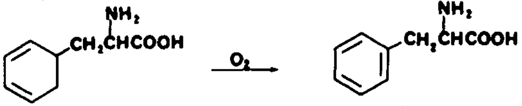
TABLE I

**CARBONATION** . Kolbe and Schmitt

Sodium phenoxide

**OXIDATION**

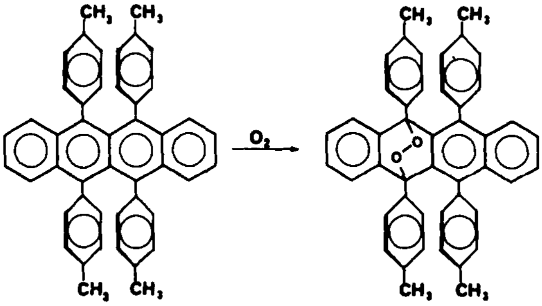
a. Ressler



S.dihydrophenyl alanine

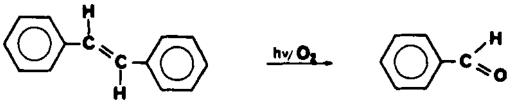
S.phenylalanine

b. Hochstrasser



Tetramethylrubrene

**OZONOLYSIS** . Desvergne and Thomas and co-workers



Trans. stilbene

Benzaldehyd

**REACTIONS OF GASES ($O_2$,NO,$SO_2$) WITH IRRADIATED ORGANIC SOLIDS** . Adler and co-workers

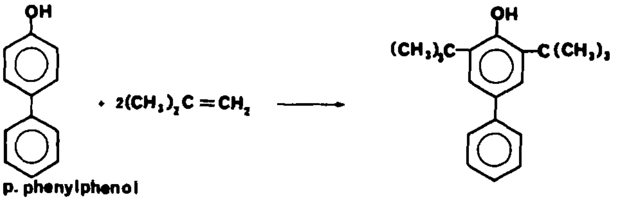
$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}$

$R^{\cdot} + NO \longrightarrow RNO$

$R^{\cdot} + SO_2 \longrightarrow RSO_2^{\cdot} \longrightarrow$ Molecular products

TABLE I (*Continued*)

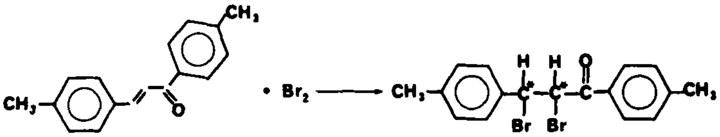
**ALKYLATION** - Lamartine and Perrin



p. phenylphenol

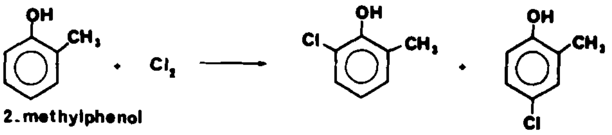
**HALOGENATION**

a. Penzien and Schmidt



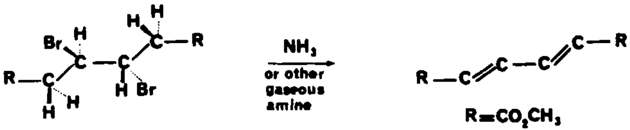
4,4'-dimethylchalcone

b. Lamartine and Perrin and co-workers



2-methylphenol

**DEHYDROHALOGENATION** - Lahav and Schmidt and co-workers

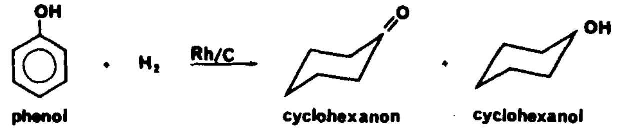


Dimethyl *meso*-β,β'-dibromoadipate

**REACTIONS WITH NH$_3$** - Miller, Curtin and Paul

$ArCOOH \xrightarrow{NH_3} (NH_3)(ArCOOH)_2$

Benzoic acid



Scheme 1

thermal control. After a vacuum of approximately $10^{-5}$ torr has been made, hydrogen is supplied. The hydrogenation time lasts from 18 to 24 h, in order to achieve conversion ratio of about 80%. A mercury buret is provided to keep a constant pressure and measure the quantity of hydrogen absorbed with time. When the reaction is finished, the reaction medium is collected in ethyl ether; it is separated from the catalyst by filtration and is then analysed by vapor phase chromatography.[3]

The results obtained with Rh/C at 5% are listed in Table II.

Over the range of temperatures of our investigation (0–45°C), we have not observed any variations of the nature and of the proportions of the cyclic ketones and alcohols that have been formed. This remark applies to pressures too in the range 1–30 bars.

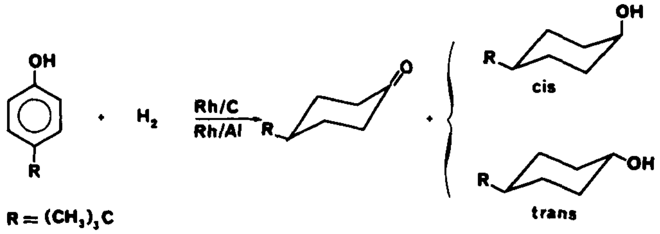
Although all phenols studied here: phenol (m.p. 40.90°C) 4-tert-butylphenol (m.p. 99.50°C) 3-methyl-4-isopropylphenol (m.p. 111°C) are in the solid state at the reaction temperature, it is possible to conceive that this reaction is not a true solid state reaction, but that it does take place in the gaseous phase or in the liquid state.

We may consider in the first place that when the reaction mixture is placed under vacuum, a certain quantity of phenol goes to the vapour phase; on the other hand, we have observed that the progress of the reaction is not substantially altered if the reaction mixture in the solid state is cooled to the temperature of liquid nitrogen during the vacuum stage. Furthermore, we

TABLE II

| Substances | *m* (°C) | Convertion ratios | Hydrogenation products | |
|---|---|---|---|---|
| | | | Cyclohexanones | Cyclohexanols |
| 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 | 93 | 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 | — | — |

have observed that the length of the period during which the reaction mixture is evacuated does not modify the course of the reaction and that it is even possible without any preliminary vacuum to hydrogenate 4-tert-butylphenol. Moreover, hydrogenations achieved with conversion ratios varying from 20 to 70% for sodium, potassium and magnesium phenoxides whose melting points are 384, 290 and 500°C respectively are not readily explained by a reaction in the gaseous phase, as these phenoxides have very low vapour pressures at 20°C (less than $10^{-2}$ torr).



Scheme 2

Another point is that the example given by the hydrogenation of 4-tert-butylphenol (Scheme 2) eliminates any possibility of the eventual progress of the reaction in a liquid phase as the products are solid at the reaction temperature, as Figure 1 shows. 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 progress of the reaction at the beginning and a gradual increase of its rate as the fluid phase is being created.

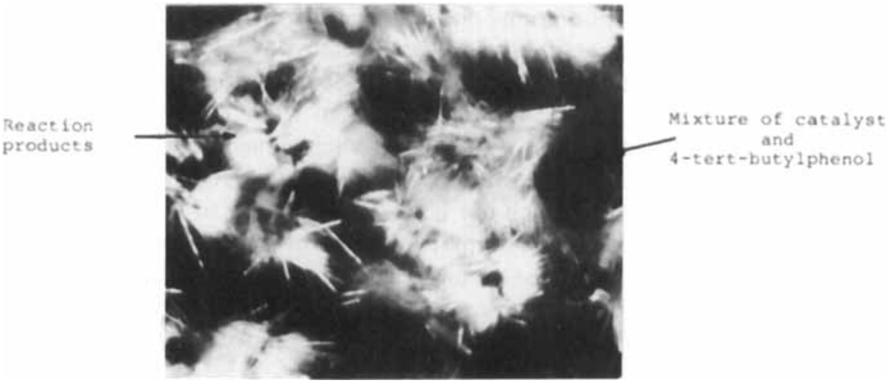


FIGURE 1 Hydrogenation of a polycristalline 4-tert-butylphenol block in the presence of traces of catalyst.

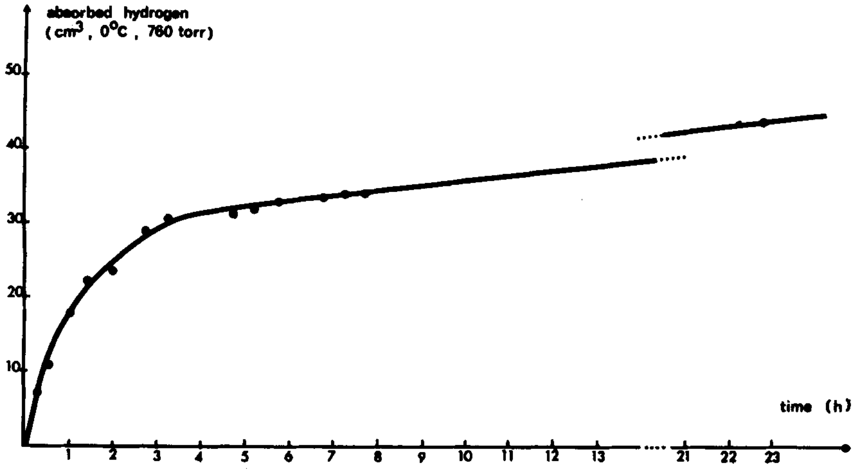


FIGURE 2 Absorbed hydrogen versus time for 100 mg of 4-tert-butylphenol with 100 mg of catalyst.

The curve of Figure 2 shows however that the greater rate is obtained at the beginning of the process. gradually decreased thereafter. Therefore, it does appear that the reaction takes place in the solid state.

As the hydrogenation reaction we are studying takes place in the solid state, it may be asked how molecular contacts between the catalyst and the reagents, phenol and hydrogen, are obtained. In the solid state, conditions are not very favourable if we assume that both hydrogen and phenol must be adsorbed on the catalyst for reaction. However, the high conversion ratios and rates observed can be explained by assuming the presence of "activated" hydrogen at some distance from the catalyst. Hydrogen must remain "activated" for some time, as needed for it to leave the catalyst, traverse the distance between solid grains and arrive in the vicinity of the reactive phenol molecule. This hypothesis is directly related to the hydrogen "spill-over" effect evidenced in other reactions of heterogeneous catalysis.[4] Therefore the migration of activated hydrogen from metal towards the nonmetallic portion of the catalyst (support) where it meets the reagent to be hydrogenated, can be compared with the migration of hydrogen from catalyst to solid phenol. The photograph of Figure 3 corresponds to the hydrogenation of a polycristalline 4-tert-butylphenol block in the presence of catalyst traces deposited on the solid substance. This shows that reaction products appear on phenol areas where no catalyst is available. It is therefore a direct proof that activated hydrogen is present at some distance from the catalytic mass.

As observed already, temperature and pressure conditions do not alter the nature and the proportion of the products obtained. But, on the other

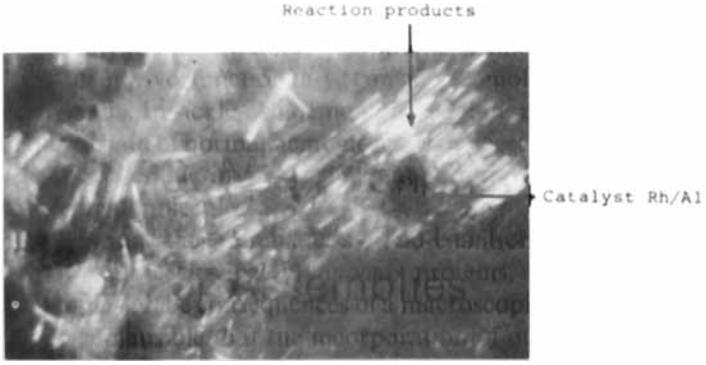


FIGURE 3 Hydrogenation of a polycristalline 4-tert-butylphenol block in the presence of traces of catalyst. Micrograph showing the distribution of products.

hand, stereoselectivity is greatly modified in the case of the variation of the catalyst support.

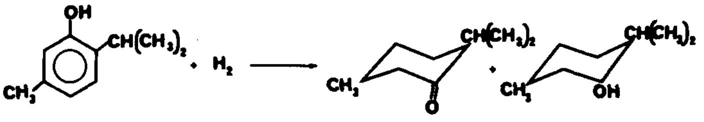
The data listed in Table III show that the hydrogenation of 4-tert-butylphenol in the presence of rhodium on carbon gives a mixture of alcohols with high *cis*-4-tert-butylcyclohexanol content, while hydrogenation under similar conditions in the presence of rhodium on alumina gives a mixture containing approximatively the same quantities of *cis*- and *trans*-alcohols.

TABLE III

| | | Products | | |
|---|---|---|---|---|
| | Hydrogenated 4-tert-butylphenol | | Cyclohexanols | |
| Catalyst | % | Cyclohexanone | *cis* | *trans* |
| Rh/C | 57 | 5 | 45 | 7 |
| Rh/Al | 67 | 5 | 28 | 34 |

Therefore the catalyst support seems to be an essential factor regarding the stereoselectivity of the reaction. A different choice of catalyst supports and more particularly the use of chiral supports might lead to new results in this field.

Hydrogenation of thymol (Scheme 3) is a very interesting reaction because, in this way, we can obtain menthols. As shown in Figure 4, the catalyst is deposited on one face and this is the only face which reacts with hydrogen; so it is possible to study the reactivity face by face. The ratio of the reaction products ketones/alcohols varies according to the particular crystallographic direction. It is likely that this change in the ketones/alcohols ratio could be



Scheme 3

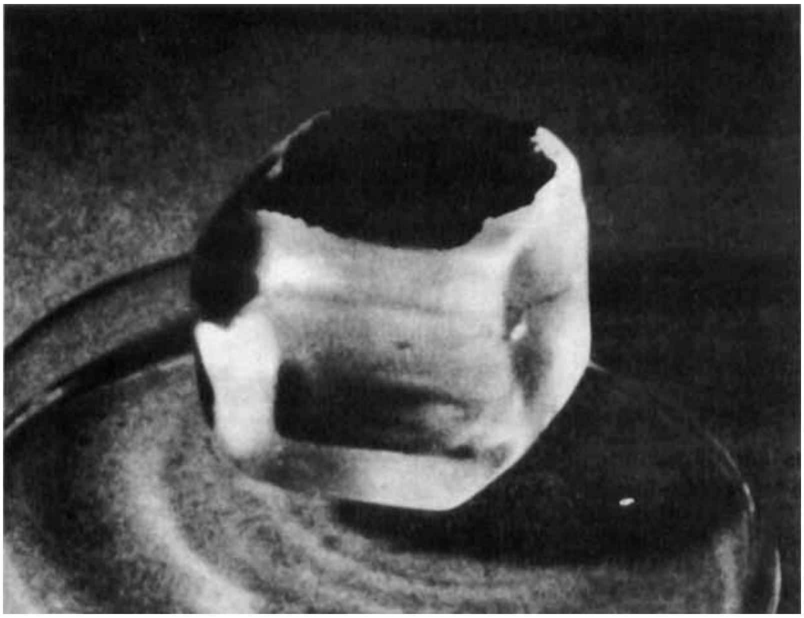


FIGURE 4 Hydrogenation of a single crystal of thymol. The catalyst is deposited on one face.

correlated with the existence of intermolecular hydrogen bonds. As was shown by the crystal structure the molecules are linked by hydrogen bonds to form hexamers. It seems necessary to consider the orientation of these hexamers relative to the crystallographic directions in order to correlated structure and reactivity. The correlation between the crystal structure of thymol and its morphology and its reactivity is currently under investigation.

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