

## Low Temperature Hydrogenolysis and Hydrogenation of Alkylbenzenes on Platinum Catalysts

G. LIETZ AND J. VÖLTER

*Zentralinstitut für Physikalische Chemie, Akademie der Wissenschaften der DDR,  
1199 Berlin, Germany (DDR)*

Received June 16, 1975

The reaction of hydrogen with mesitylene, *p*-xylene, toluene, and benzene has been studied on Pt/carrier catalysts in the gas phase between 30 and 110°C. The hydrogenation is associated with a low temperature hydrogenolysis of the methyl substituents. This new low temperature hydrogenolysis of alkylbenzenes significantly differs from the hydrogenolysis of paraffins and from high temperature hydrocracking. Hydrogenation and hydrogenolysis are parallel reactions. A mechanism of hydrogenolysis is proposed.

### INTRODUCTION

The reactions of alkylbenzenes with hydrogen may result in a hydrogenation (1) as well as in a hydrogenolysis (2, 3). The hydrogenation proceeds only at lower temperatures; at higher temperatures of about 250°C, the thermodynamic equilibrium of these reactions is more or less completely shifted towards the dehydrogenation. Only in the higher temperature range is the onset of hydrocracking reactions known. So hydrogenation and hydrogenolysis seemed to be separated by a distinct temperature gap.

This was in accordance with our previous work on the hydrogenation of alkylbenzenes on Ni, Co, and Rh, resulting in the proposal of a new mechanism of hydrogenation (4); the absence of hydrogenolytic reactions had been checked by gas-chromatographic analysis. Extending these investigations to platinum catalysts, a severe self-poisoning was observed during the hydrogenation. The reason could be a dealkylation and a poisoning by adsorbed dehydrogenated CH<sub>3</sub> groups or/and an oligomerization of reacting materials. In the case of a dealkyla-

tion, the platinum should be active in hydrogenolysis at unusually low temperatures. Therefore the aim of this paper is directed to problems of the occurrence of the hydrogenolysis and its interdependence with the hydrogenation of the alkylbenzenes toluene, *p*-xylene, and mesitylene. What are the products of the hydrogenolysis, what are the factors influencing the selectivity, and what may be the mechanism of the reaction?

### EXPERIMENTAL

The catalysts used were Pt on Coriglass or aerosil and Pt powder. The carrier catalysts were prepared by impregnation with H<sub>2</sub>PtCl<sub>6</sub> and calcination in air at 400°C. The metal content was 10 wt%. The Pt powder was prepared by reduction of (NH<sub>4</sub>)<sub>2</sub> PtCl<sub>6</sub> at 400°C in hydrogen. All the catalysts were activated by repeated oxidation-reduction cycles. The platinum surface area of Pt on Coriglass was 250 m<sup>2</sup>/g, of Pt on aerosil 200 m<sup>2</sup>/g, and of Pt powder 3 m<sup>2</sup>/g. Special care was taken in the purification of the methylbenzenes.

Toluene and *p*-xylene were shaken with concd  $\text{H}_2\text{SO}_4$ , dried, and distilled over sodium. Mesitylene was purified by preparing the sulfonic acid (4).

The benzenes were successively hydrogenated on the same catalyst in the gas phase in a dynamic apparatus described previously (5). The flow rates of hydrogen and hydrocarbon were  $2.25 \text{ l}\cdot\text{h}^{-1}$  at STP and  $8.15 \times 10^{-3} \text{ mole}\cdot\text{h}^{-1}$ , respectively. The catalyst weight was 100 mg. The partial pressure of the hydrocarbon was 60 Torr. The products trapped in liquid nitrogen were analyzed by a gas chromatograph.

## RESULTS

### Hydrogenolysis and Hydrogenation

The reaction of hydrogen with benzene and methylbenzenes has been studied on a Pt/Coriglass catalyst. The temperature ranges of the reaction were  $30\text{--}70^\circ\text{C}$  with benzene,  $50\text{--}85^\circ\text{C}$  with toluene,  $65\text{--}100^\circ\text{C}$  with *p*-xylene, and  $75\text{--}110^\circ\text{C}$  with mesitylene.

The analysis of the products has revealed that only one part consists of the corresponding hydrogenated benzenes (Fig. 1). A second large part consists of partly or totally demethylized benzene rings including benzene and cyclohexane.

The identified products of toluene are methylcyclohexane, benzene, and cyclohexane; those of *p*-xylene are benzene, cyclohexane, toluene, methylcyclohexane, and *cis*- and *trans*-dimethylcyclohexane, and those of mesitylene are benzene, cyclohexane, toluene, methylcyclohexane, and 1,3,5-trimethylcyclohexane.

No  $\text{CH}_4$  could be detected in the gas phase. The  $\text{CH}_3$  groups are obviously adsorbed very strongly. This is in accordance with observations that no  $\text{CH}_4$  desorbs during the partial transformation of *n*-heptane to benzene under the conditions of thermal desorption (5).

According to the formation of these products we propose the reaction scheme

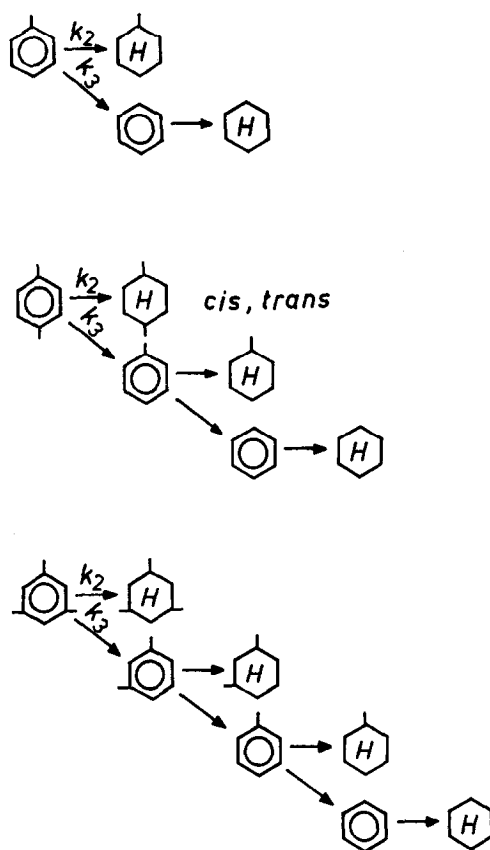


FIG. 1. Scheme of the hydrogenation ( $k_2$ ) and hydrogenolysis ( $k_3$ ) reaction steps in the reaction of hydrogen with alkylbenzenes.

given in Fig. 1.  $k_2$  denotes the direct hydrogenation, and  $k_3$  all the side reactions. They are characterized by the splitting of the C-C bond and by the following hydrogenations. The common feature of  $k_3$  is the hydrogenolysis of the methyl groups at low temperature.

The kinetic data of the reactions are summarized in Table 1. The reaction rate  $k$  is calculated according to the equation (6)

$$k = \frac{\alpha \cdot v_B}{g_{\text{Pt}}} [\text{mol g}^{-1} \text{h}^{-1}].$$

$\alpha$  is the conversion of benzene,  $v_B$  is the flow rate of benzene ( $\text{mol h}^{-1}$ ), and  $g_{\text{Pt}}$  is the weight of the platinum (g). Experimentally several values of  $k$  have been

TABLE 1  
Hydrogenation and Hydrogenolysis of Benzenes on Pt/Coriglass<sup>a</sup>

Compound	T	Total conversion		Hydrogenation			Hydrogenolysis			
		wt%	$k_1 \cdot 10^3$	wt%	$k_2 \cdot 10^3$	$E$	wt%	$k_3 \cdot 10^3$	$E$	%s
Benzene	63.0	92.6	7.41	92.6	7.41	17.9	—	—	—	—
Toluene	63.0	33.5	2.67	28.0	2.24	17.5	5.5	0.43	8.2	16.4
Toluene	76.0	82.7	6.6	74.1	5.9	17.5	8.6	0.70	8.2	10.4
<i>p</i> -Xylene	76.0	12.4	1.0	7.7	0.62	27.7	4.7	0.38	17.4	37.9
Mesitylene	76.0	1.87	0.15	1.05	0.084	30.5	0.82	0.066	27.7	43.8

<sup>a</sup> Reaction temperature  $T$  (°C), reaction rate  $k$  (mole  $\text{g}^{-1} \text{h}^{-1}$ ), activation energy  $E$  (kcal  $\text{mole}^{-1}$ , selectivity of conversion  $s$ .

determined within a temperature range of 25°C. The reported values are taken from an Arrhenius plot.

The activities of the two more active compounds are compared at 63°C, of the less active ones at 76°C.

The total conversion of the reactants  $k_1$  strongly decreases with increasing number of methyl substituents. Benzene is the most active compound, mesitylene is the least active one. The activity of the direct hydrogenation reactions  $k_2$  decreases with increasing number of methyl substituents, too. The same sequence is also to be found in the rate of hydrogenolysis  $k_3$  ( $k_3 = k_1 - k_2$ ). The activation energies  $E$  of both reactions are increasing in this sequence.

Interesting is the selectivity of the hydrogenolysis  $s$ , the portion of the total conversion which undergoes hydrogenolysis.

$$s = \frac{k_3}{k_1} \cdot 100 (\%).$$

The selectivity depends on the number of methyl substituents and on the temperature. Only 10.4% of the products of toluene, but 43.8% of those of mesitylene are partly or completely demethylized at the temperature of 76°C. So the selectivity of the hydrogenolysis is strongly increasing with increasing number of methyl substituents.

The temperature dependence of the hydrogenolysis is demonstrated by the reac-

tivity of toluene. The data are listed in Table 2. The products of hydrogenolysis are benzene and cyclohexane.

The selectivity decreases from 23.1 to 10.4%, when the temperature is rising from 53.5 to 76.0°C. So the selectivity of the hydrogenolysis is decreasing with increasing temperature.

A relative low activity of hydrogenation at low temperatures is to be seen in the ratio of the products of the hydrogenolysis, too. The ratio benzene/cyclohexane increases from about 1:½ up to about 1:2 with increasing temperature from 53.5 to 76.0°C.

The differences in the temperature dependence are also to be seen in the activation energies. With toluene the activation energy of hydrogenolysis is low (8.2 kcal/mole) compared with the high value of the hydrogenation reaction (17.5 kcal/mole). With mesitylene the differences are diminishing, the corresponding values being 27.7 and 30.5 kcal/mole, respectively.

In order to check if the hydrogenolysis is really an effect of the Pt and not the carrier, we have also studied the reactions on Pt on aerosil and on Pt powder. All these catalysts are active in hydrogenolysis.

The hydrogenation of benzene is affected by the carrier. The activation energies are 11.3 kcal/mole with Pt powder, 14.2 kcal/

mole with Pt/aerosil, and 17.9 kcal/mole with Pt/Coriglass.

### Poisoning

During the hydrogenation of the methylbenzenes a slow decrease of the activity occurred within a few hours. This effect was strongest with mesitylene and absent with benzene. The poisoned catalysts can be regenerated by weak oxidation with air at temperatures lower than 400°C followed by reduction in hydrogen. During the oxidation CO<sub>2</sub> could be detected in the products, desorbing from the catalyst.

The self-poisoning can be simply explained. The methyl groups split off and are partly dehydrogenated, forming carbon or hydrocarbon residues which poison the catalyst. These products can be removed by oxidation to CO<sub>2</sub>.

Poisoning of the Pt catalyst may also be caused by the adsorption of molecular gases. We have investigated the influence of CO and of O<sub>2</sub>. Poisoning was studied using a pulse technique. Known amounts of the gas were injected into the gas stream of the hydrogen/hydrocarbon mixture. At constant temperature the variation of the activity was measured. A pulse of 30 μl CO at STP strongly decreases the activity of the hydrogenation. This poisoning effect subsequently diminishes and after 30 min the initial unpoisoned activity is restored again. A pulse of 1 ml at STP causes a

strong poisoning effect of several hours. Small amounts of 2–5 μl of CO, which have almost no effect on the hydrogenation, completely poison the hydrogenolysis. This reaction is much more sensitive to CO than the hydrogenation. A self-regeneration as in hydrogenation could not be observed. Therefore the selective poisoning by CO is an effective new method to suppress the hydrogenolysis, and to increase selectively the hydrogenation pathway. The low temperature oxidation of CO-poisoned catalysts was ineffective in regeneration of hydrogenolysis activity.

Pulsing of oxygen into the reaction mixture causes only a very small and temporary decay of activity, which is somewhat stronger in hydrogenolysis than in hydrogenation.

### DISCUSSION

The results clearly indicate the existence of hydrogenolysis of the methyl substituents in a low temperature range under 100°C. The reaction is still observed at 30°C. Characteristic is the decrease of selectivity with increasing temperature. This low temperature hydrogenolysis is competing with the hydrogenation. At higher temperatures of about 100°C nearly only hydrogenation takes place (Table 2).

At very high temperatures of about 400°C, again an intensive C–C bond splitting on Pt takes place in the well-known

TABLE 2  
Hydrogenolysis of Toluene on Pt/Coriglass

Temperature (°C)	Conversion (%)	Composition of the product				Ratio benzene/ cyclo- hexane (approximate values)	Selectivity of hydrogenolysis (%)
		Toluene (%)	Methyl- cyclo- hexane (%)	Benzene (%)	Cyclo- hexane %		
53.5	16.9	83.1	13.0	3.0	0.9	1:½	23.1
63.0	33.5	66.5	28.0	2.9	2.6	1:1	16.4
76.0	82.7	17.3	74.1	2.8	5.8	1:2	10.4

reactions of dealkylation, hydrocracking, and isomerization. So one can distinguish between a low temperature hydrogenolysis at temperatures of about 50°C and a high temperature hydrogenolysis at about 400°C.

The low temperature hydrogenolysis obviously is restricted to the dealkylation of methyl substituents of aromatics. The hydrogenolysis of paraffins has been investigated extensively (3, 7, 8). Carter *et al.* (9) have found the following order of activity in the hydrogenolysis of *n*-heptane: Ru > Ir, Rh ≫ Pt > Pd. Ru is 10<sup>5</sup> times as active as Pt. With butane the order of activities is Rh > W > Ni > Pt > Pd (8). Ni is more active than Pt in extensive cracking of methylcyclopentane (10). The hydrogenolysis of ethane and of butane on Pt requires temperatures of 320 and 300°C, respectively (7). These data reveal the following: (i) Pt is a poor catalyst of hydrogenolysis of paraffins, and (ii) the reaction temperatures are in the range between 250 and 400°C.

The observed dealkylation of methylbenzene proceeds in the range between 30 and 100°C on platinum. In this process Pt is very active, but Ni, Co, and Rh are completely inactive (4). So we have two opposite orders of activity in hydrogenolysis, namely, Rh > Ni > Pt with paraffins, and Pt ≫ Ni, Rh with alkylbenzenes.

The conclusion is that the hydrogenolysis of C-C bonds in paraffins and the low temperature hydrogenolysis of R-CH<sub>3</sub> bonds in methylbenzenes are completely different processes. An unusually high activity of platinum catalysts in the hydrogenolysis of the C-O bond during the hydrogenation of 1-methyl-4-*t*-butyl-1-cyclohexenyl ether in the liquid phase recently has been reported (11).

The hydrogenation and especially the hydrogenolysis of methylbenzenes is very sensitive to poisons. The dealkylation is connected with a slow decrease of activity of both reactions. This self-poisoning is a

simple hint of the appearance of the hydrogenolytic splitting.

The adsorption of CO selectively or completely poisons the hydrogenolysis. Therefore CO is a powerful means of changing the selectivity of the catalyst. In this way, it is possible to avoid the dealkylation of the methyl groups and the connected self-poisoning of the catalyst.

The strong adsorption of small amounts of CO may be the reason why the low temperature hydrogenolysis has not been observed previously.

The hydrogenation is far less sensitive to CO poisoning, and this effect is reversible. The reversibility is explicable by the proved existence of a reversible equilibrium of adsorption and desorption of CO (12). When the partial pressure of CO in the flow system is decreased, then CO is desorbing and the poisoning effect diminishes.

The selective poisoning of the hydrogenolysis by CO may be explained by competitive adsorption of CO and the benzene ring on the strongest adsorption sites. The selectivity of hydrogenolysis increases with increasing number of methyl groups (Table 1) and in this sequence increases the stability of the adsorbed benzene  $\pi$ -complexes (4). So the strongest adsorption sites should facilitate hydrogenolysis whereas the weaker ones should facilitate hydrogenation. In this case initially adsorbed amounts of CO should poison predominantly the hydrogenolysis.

The sequence of decreasing hydrogenation activities  $k_2$  (Table 1) with increasing number of methyl substituents is the same as is observed on Ni, Co, and Rh (4). This sequence is in accordance with the proposed  $\pi$ - $\sigma$  mechanism. But the decay of the activities is stronger than observed on those metals. This may be due to the self-poisoning of the Pt by the methyl benzenes. A scheme of the different reaction steps of hydrogenation and hydrogenolysis is proposed in Fig. 1. One question is whether these two reactions are consecutive steps or

parallel reactions. Among the products from toluene there is benzene in a certain degree (Table 2). This benzene cannot be formed in a consecutive step from cyclohexane or methylcyclohexane. A necessary dehydrogenating step is thermodynamically impossible at these low temperatures. In order to reinforce this statement, we have tried to demethylate methylcyclohexane. Between 30 and 110°C neither cyclohexane nor benzene was formed. The conclusion is that the hydrogenolysis is a parallel reaction of the hydrogenation. This route is depicted in Fig. 1.

The observed low temperature hydrogenolysis is explained by a new mechanism. The various mechanisms of C-C fission by hydrogen proposed in the literature are as far as we know only concerned with paraffins (6, 13, 14). Different di- and tri-adsorbed species are proposed.

As mentioned above, paraffins and methylbenzenes behave completely differently towards Pt. Therefore, we assume this difference is caused by special adsorption properties involving the benzene ring. Moreover, this hydrogenolysis is intimately connected with the hydrogenation. Both reactions take place simultaneously. The rate of both reactions (Table 1) decreases with increasing number of methyl groups. These reasons suggest a common first adsorption step of both reactions. This should be a  $\pi$ -adsorbed benzene ring, a complex which is proposed by several authors to be the first step of the hydrogenation (1, 3, 4, 15).

In this adsorbed species a methyl group is to be substituted by hydrogen. The mechanism of substitution in organic chem-

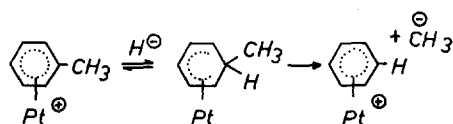


FIG. 3. Mechanism of hydrogenolysis.

istry ( $S_N2$ ,  $S_E2$ ) include as a transition state or, perhaps as an intermediate, a species in which both reaction partners are bonded to the carbon atom. So it should be necessary to add one hydrogen atom to the benzene ring. Such a reaction type is known from the manganese  $\pi$ -complex shown in Fig. 2. The  $\pi$ -bonded benzene ring easily adds a hydride ion in an  $\alpha$  (endo) position (16).

Analogous to this reaction we propose the hydrogenolysis reaction shown in Fig. 3. On the Pt surface there are  $\pi$ -adsorbed methyl benzenes and hydride ions. The existence of hydride ions on metal surfaces has been proposed by various authors (17-19). The hydrogen is added by a nucleophilic attack of a hydride ion from below the plane of the ring. This selectively hydrogenated species decomposes by splitting off a negatively charged methyl group. The latter is either hydrogenated forming desorbing methane or dehydrogenated forming carbon or hydrocarbon residues on the surface.

So the hydrogenolysis is explained by an  $S_N2$  mechanism with the formation and decomposition of a selectively hydrogenated  $\pi$ -adsorbed methylbenzene species.

The mechanism explains (i) the observed connection between hydrogenolysis and hydrogenation by a common surface  $\pi$ -complex, (ii) the reaction pathway by an  $S_N2$  mechanism known from organometallic chemistry, and (iii) the observed sequence of reactions. In other words, the hydrogenolysis is not a consecutive but a parallel reaction of the hydrogenation; the hydrogenated products cannot form  $\pi$ -complexes, and therefore only aromatic systems are involved in this type of hydrogenolysis mechanism.

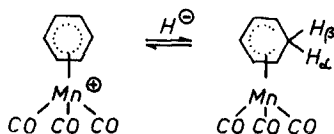


FIG. 2. Reaction of a manganese  $\pi$ -complex with hydrogen.

The main results may be summarized as follows:

1. Hydrogenation of methylbenzenes on Pt is associated with a low temperature hydrogenolysis of the methyl groups.

2. This low temperature hydrogenolysis significantly differs from the known high temperature hydrocracking and from the known hydrogenolysis of paraffins.

3. The selectivity of low temperature hydrogenolysis increases with increasing number of methyl substituents and with decreasing temperature. CO adsorption selectively poisons the hydrogenolysis.

4. Hydrogenation and low temperature hydrogenolysis are parallel reactions. A scheme of the reaction pathways is proposed.

5. A mechanism of the low temperature hydrogenolysis is proposed with a  $\pi$ -complex adsorption and an  $S_N2$  substitution mechanism.

#### REFERENCES

1. Moyes, R. B., and Wells, P. B., *Advan. Catal.* **23**, 121 (1973).
2. Setínek, K., Pecev, N., and Bazant, V., *Coll. Czech. Chem. Comm.* **33**, 1451 (1968).
3. Sinfelt, J. H., *Advan. Catal.* **23**, 91 (1973).
4. Völter, J., Hermann, M., and Heise, K., *J. Catal.* **12**, 307 (1968).
5. Walkov, W., Genkin, W. M., Sklyarov, A. W., and Völter, J., *Z. Physik. Chem. (Leipzig)*, in press.
6. Völter, J., Lange, B., and Kuhn, W., *Z. Anorg. Allgem. Chem.* **340**, 253 (1965).
7. Sinfelt, J. H., *Catal. Rev.* **3**, 175 (1970).
8. Kembal, C., *Catal. Rev.* **5**, 33 (1972).
9. Carter, J. L., Cusumano, J. A., and Sinfelt, J. H., *J. Catal.* **20**, 223 (1971).
10. Maire, G., Plouidy, G., Prudhomme, J. P., and Gault, F. G., *J. Catal.* **4**, 556 (1965).
11. Takagi, Y., and Teratani, S., *J. Catal.* **34**, 490 (1974).
12. Schay, Z., Sklyarov, A. W., Prokop, M., and Völter, J., *Kinet. Katal.* **13**, 1234 (1972).
13. Anderson, J. R., *Advan. Catal.* **23**, 1 (1973).
14. Guzzi, L., Sárkány, A., and Tétényi, P., *Proc. 5th Intern. Congr. Catalysis* (Miami Beach, 1972), p. 1111. North-Holland, Amsterdam, 1972.
15. Garnett, J. L., *Advan. Catal.* **16**, 95 (1966).
16. Cotton, F. A., and Wilkinson, G., in "Anorganische Chemie," p. 733. VEB Deutscher Verlag der Wissenschaften, Berlin, 1968.
17. Horiuti, J., and Toya, T., *Solid State Surface Sci.* **1**, 1 (1969).
18. Parravano, G., *J. Catal.* **22**, 96 (1971).
19. Kraus, M., and Bazant, V., *Proc. 5th Intern. Congr. Catalysis* (Miami Beach, 1972), p. 1073. North-Holland, Amsterdam, 1972.