

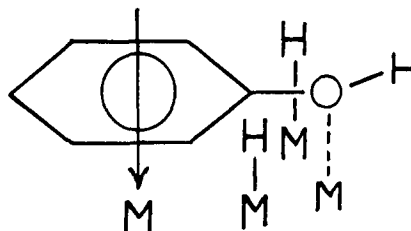
On the Mechanisms of Cyclohexanol Transformations over Pt Catalysts

In a recent paper by Richardson and Lu (1), the mechanisms of dehydrogenation and hydrocarbon formation from cyclohexanol are discussed. Both the results and the ideas in this elegant work are new and inspiring; at the same time we feel that reporting some of our results on the subjects may throw light on different aspects of the problem and may help to a better understanding of these very sophisticated processes.

The high concentration of cyclohexane in the product was interpreted in terms of direct hydrogenolytic splitting of the OH group from the cyclohexanol molecule. This reaction has not been observed so far and our results obtained on Pt black catalyst [prepared and pretreated as shown in (2)], do not support its occurrence. Very low amounts of cyclohexane were produced from cyclohexanol; the possible way of its formation was checked by reacting a mixture of radioactive cyclohexanol and inactive cyclohexane. The very low specific radioactivity of cyclohexane in the product indicated that only a negligible transition of this type could have taken place (Table 1). Even in the case of catalysts with higher activity towards C-C hydrogenolysis (e.g., Ni, Rh, Re), the direct splitting of the CO bond in cyclohexanol was not observed.

On the other hand, benzene formation was marked from cyclohexanol [and also from phenol (3)]; thus, hydrogenolytic splitting of the OH group from the aromatic ring is suggested as a main pathway of

hydrocarbon production:



This pathway is supported by the radio-tracer data shown in Table 1. The phenol intermediate would not necessarily desorb from the surface, as indicated by the higher radioactivity of benzene as compared with that of the phenol in the product.

There is a third possibility of hydrocarbon formation, namely dehydration of cyclohexanol into cyclohexene. Although this process has been shown to take place over unsupported metals [e.g., copper or nickel (4)], data obtained with the mixture of radioactive cyclohexanol and inactive cyclohexene (Table 1) indicate that this pathway is not significant in the presence of unsupported platinum.

The situation is completely different with charcoal-supported platinum catalyst [prepared after Zelinsky and Turowa-Polyak (5)]. Considerable amounts of hydrocarbons were formed including cyclohexene even in hydrogen atmosphere. In the presence of the charcoal support only (without adding platinum), cyclohexene was the only major hydrocarbon product (Table 2). This is a clear evidence that dehydration of cyclohexanol occurred; we suggest, therefore, that the formation of hydrocarbons in

TABLE 1
 Radiotracer Studies with Different Mixtures^a

Pulse	Composition (mole%)						Specific radioactivity (<i>r</i> %/mole%) ^b					
	C ₆ H ₁₂	C ₆ H ₁₀	C ₆ H ₆	C ₆ H ₁₀ O	C ₆ H ₁₁ OH	C ₆ H ₅ OH	C ₆ H ₁₂	C ₆ H ₁₀	C ₆ H ₆	C ₆ H ₁₀ O	C ₆ H ₁₁ OH	C ₆ H ₅ OH
A ^c												
Reagent	27.8	—	—	0.07	72.1	—	Background	—	0.12	1.38	—	—
Product	21.3	—	54.1	2.0	7.0	15.2	Background	1.11	0.54	0.94	1.15	—
B ^c												
Reagent	—	—	—	0.8	65.3	33.9	—	—	—	8.97	1.42	—
Product	—	—	11.3	6.6	42.6	39.2	—	—	0.56	1.41	1.44	0.44
C ^c												
Reagent	0.03	72.3	—	0.3	27.4	—	Background	—	11.4	3.7	—	—
Product	3.0	20.05	46.25	2.0	25.1	3.3	Background	0.25	4.8	2.5	2.7	—
D ^c												
Reagent	—	—	—	46.7	53.3	—	—	—	—	0.17	1.74	—
Product	—	—	11.5	42.3	40.4	5.5	—	—	0.63	0.28	1.77	0.83

^a *t* = 270°C; catalyst: 0.1 g Pt black; pretreatment: 360°C; carrier gas: 30 ml/min N₂, 1 μl pulses of reagent;

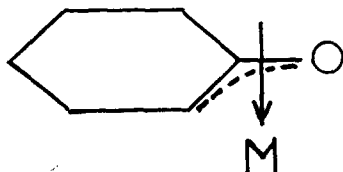
^b *r*%: percentage of counts if the total count number is 100%.

^c A, C₆H₁₁OH* + C₆H₁₂; B, C₆H₁₁OH* + C₆H₅OH; C, C₆H₁₁OH* + C₆H₁₀; D, C₆H₁₁OH* + C₆H₁₀O.

Ref. (1) may have been due to dehydration effect of the support, even in the case of the relatively more inert carbon carrier, let alone alumina whose activity in alcohol dehydration is well known.

Apart from this, the carrier may also play a role in the formation of cyclohexanediol, since this compound has never been observed on unsupported platinum.

The enhanced phenol formation from cyclohexanone as compared with cyclohexanol gives additional support to our suggestion (6) that phenol formation in fact takes place also via cyclohexanone intermediate (cf. also Table 1). We propose that the dehydrogenation may involve a π-allylic type surface species being between enol and ketone:



This surface species would keep the ring nearly parallel to the surface and may either desorb as cyclohexanone or give phenol without desorption.

We agree that higher surface hydrogen

concentrations may influence also the character of primary adsorption (1): however, its effect on the two possible hydrogenation—dehydrogenation equilibria should also be pointed out. With cyclohexanol, hydrogen given off during dehydrogenation promotes hydrogenolysis in nitrogen, too, but is not sufficient for hydrogenation of ben-

 TABLE 2
 Conversion of Cyclohexanol over Charcoal and Platinum-on-Charcoal^a

Catalyst:	Pt/C		C	
	N ₂	H ₂	N ₂	H ₂
Carrier gas:	N ₂	H ₂	N ₂	H ₂
Conversion (mole%):	9.04	9.76	2.92	3.53
Product composition (mole%)				
C ₆ H ₁₂	1.11	6.45	0.09	—
C ₆ H ₁₀	1.35	0.11	6.93	3.58
C ₆ H ₆	30.96	37.31	—	—
C ₆ H ₁₀ O	18.49	20.09	87.43	82.34
C ₆ H ₅ OH	46.00	35.29	5.46	12.35
Others ^b	2.06	0.78	0.06	1.75

^a *t* = 300°C; catalyst: 3 mg Pt/C and 5 mg C, resp.; carrier gas: 30 ml/min N₂ or H₂; reagent: 1 μl cyclohexanol.

^b Various C₁–C₆ fragments.

TABLE 3
Conversion of Phenol and Cyclohexanol
over Pt Black^a

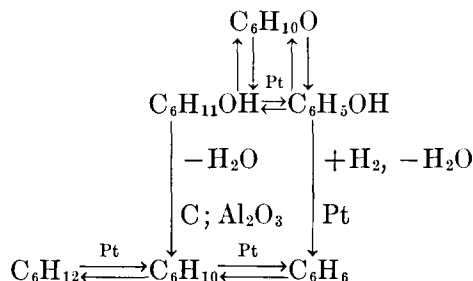
Reagent	<i>t</i> (°C)	Carrier gas	Conver- sion to C ₆ hydro- carbon (%)	Hydro- carbon composition	
				C ₆ H ₁₂	C ₆ H ₆
C ₆ H ₅ OH	210	H ₂	38.7	100	0
	270	H ₂	98.7	64.5	35.5
	270	N ₂	0.35	0	100
	330	H ₂	89.4	1.5	98.5
C ₆ H ₁₁ OH	270	N ₂	7.5	0.6	99.4
	270	H ₂	0.08	87	13

^a Catalyst: 0.4 g Pt; pretreatment: 360°C; carrier gas: 30 ml/min N₂; 80 ml/min H₂; reagent: 1 μl.

zene into cyclohexane. In hydrogen atmosphere, dehydrogenation into phenol is suppressed, and therefore less phenol and hydrocarbons are observed (3). Phenol does not react in nitrogen (since no reaction producing hydrogen takes place): in hydrogen, however, the splitting of the OH group takes place in parallel with phenol hydrogenation; at the same time, due to rapid benzene hydrogenation, an equilibrium concentration of hydrocarbons appears containing up to 100% of cyclohexane (Table 3). Hydrogenation must have been still more marked for cyclohexene wherever it is produce via dehydration.

We believe that the following general pattern can be applied for the reactions in-

involved both in our case and for the studies reported in (1) if we consider that more rapid equilibration between C₆-cyclic hydrocarbons (as compared with the processes of their formation) efficiently "masks" the actual pathway of hydrocarbon formation.



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