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LETTERS TO THE EDITORS

Mechanisms of Dehydrocyclization on Platinum and Palladium Catalysts

A study of the isomerization of hexanes on supported platinum, using hydrocarbons labeled with ^{13}C, showed that the relative importance of the two mechanisms of skeletal rearrangement, bond shift and cyclic, depends strongly upon the size of the platinum particles (*1*, *2*). Only the cyclic type of isomerization takes place on the most highly dispersed catalysts, while both mechanisms intervene consecutively on the concentrated catalysts with large crystallites (*3*). An important conclusion of this work is that the dehydrocyclization process probably involves a single metal atom (*2*).

An excellent confirmation of this proposal is given in a recent paper by Anderson *et al.* concerning the catalytic properties of polycrystalline and ultrathin films (*4*). These authors observed, in the isomerization of hexanes, very large variations in the product distributions and especially in the concentration of methylcyclopentane, according to the structure of the films: the most dispersed catalysts, "ultrathin" films with an average crystal size of 20 Å, gave rise to the highest concentration of methylcyclopentane in the reaction products. The authors interpreted their results by supposing that the cyclization process takes place on platinum atoms of a low coordination number (corner atoms) which are expected to be much more numerous in the small particles of ultrathin films than on the polycrystalline films.

In their paper Anderson *et al.* referred to unpublished work done in this labora-

TABLE 1
INITIAL PRODUCT DISTRIBUTIONS AND DEHYDROCYCLIZATION RATES OVER PLATINUM AND PALLADIUM FILMS[1]

Catalysts Reacting hydrocarbons	Platinum I	Platinum II	Platinum III	Palladium I	Palladium II	Palladium III[2]
Cyclopentanes obtained by simple dehydrocyclization	80	61.6	92	18.8	52.6	23.9
cyclization + demethylation[3]	0	21.8	0	23	19.6	1.3
Aromatics[4]	13.5	4.8	3	5.7	0.2	18.6
Acyclic hydrocarbons	3	8.8	0	52.5[5]	18.8[5]	40.6
Complete degradation to *methane* (I or II → 8 CH_4; III → 9 CH_4)	3.5	3	5	0	8.8	15.6
Dehydrocyclization rate (in molecules/min × mg × 10^{-16} at 300°C	2.0	2.6	2.2	0.18	2.6	<0.01[6]

[1] The initial product distributions are expressed as % of the reacting hydrocarbon which has disappeared.

[2] Experiment at 360°C; no noticeable reaction was observed at lower temperature.

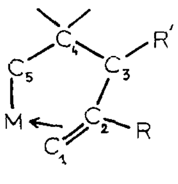
[3] And isomerization in the case of 2,2,3-trimethylpentane.

[4] Platinum: 80–90% of C_8 aromatics; palladium: mostly toluene.

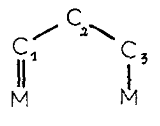
[5] 85–95% of C_7 hydrocarbons.

[6] 0.28 at 360°C.

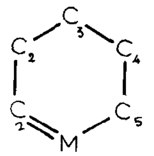
tory, concerning the mechanisms of dehydrocyclization on metal catalysts. We wish to present here the main results and conclusions of this study.



A



B

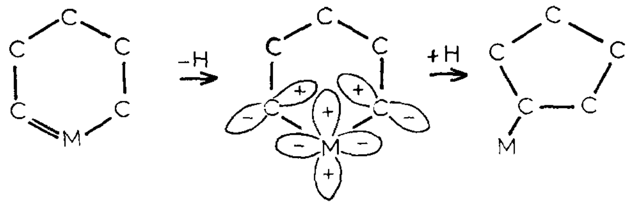


C

The reactions of three substituted pentanes: 2,2,4-trimethyl(I), 2,2,3-trimethyl (II) and 2,2,4,4-tetramethylpentanes(III) have been studied over platinum and palladium films at 300°C. The product distributions and the dehydrocyclization rates are given in Table 1 for each hydrocarbon.

On platinum, the cyclopentane obtained by a simple dehydrocyclization process is the main reaction product and its rate of formation is practically independent of the structure of the reacting molecule. An accurate determination of the relative rates of dehydrocyclization by a competitive method gave the values of 1.2, 1.2 and 1.0 for I, II and III, respectively.

On palladium the dehydrocyclization rate is much larger for II than for I and III. Moreover cyclopentanes obtained by cyclization of I and III are no longer the predominant reaction products.



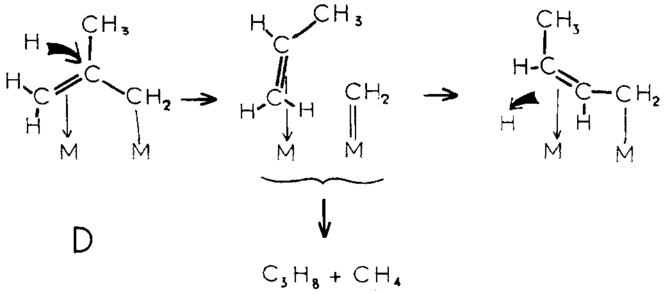
E

These results suggest that different intermediates are responsible for dehydrocyclization on platinum and palladium.

On platinum, the precursor for the dehydrocyclization process is necessarily attached to the metal by two carbon atoms only, 1 and 5, and not by three carbon atoms 1, 2 and 5, as suggested (*5, 6*) such as in species A. Molecule III indeed, which cannot form 1,2,5-triadsorbed intermediate, is dehydrocyclized with the same rate as molecules I and II.

Since 1,1,3-triadsorbed precursors such as *B* seem to be responsible for the bond shift rearrangement on platinum (*7, 8, 5*) we suggest that the precursor for dehydrocyclization is a 1,1,5-triadsorbed species *C*. The symbol M is used for one metal atom. Because of the number of carbon atoms in ble, in contrast to a 1,1,3-triadsorbed species such as *B*. According to its structure, precursor *C* may lead by a simple *cis*–ligand insertion to an adsorbed cyclopentane. However an alternative route, possibly more energetically favoured, could be the transient formation of an intermediate *E*, in which the two *p* orbitals of carbon *C*, bonding to *one* metal atom seems feasi- atoms 1 and 5 are coupled together with a *d* metal orbital, resulting in a filled bonding and two empty non-bonding and antibonding molecular orbitals.

On palladium, the dehydrocyclization of II but not III can only be accounted for if the intermediate is an adsorbed olefin. Adsorbed olefins were proposed as intermediate in the 1–6 dehydrocyclization on chromium oxide (*9–11*). They were also thought to be responsible for the 1–5 ring closure on oxides and metals and were described by Shephard and Rooney in the



case of metal as species *A* 1,2-π–bonded and 5-σ–bonded to a single metal atom (*6*).

Such intermediates are very sensitive to steric factors (*11*). Indeed, in the present experiments, a careful examination of species *A* shows that in molecule I the steric hindrance resulting from an interaction between the surface and the methyl group R is considerable, while in molecule II the interaction between surface and methyl group R′ may be taken as negligible. This would explain the very large differences between the observed cyclization rates of both hydrocarbons.

The known ability of palladium to form adsorbed olefins could also explain the peculiarities of the bond shift rearrangement on this metal, when compared with platinum. Isobutane *and not* neopentane is isomerized on a palladium film (*12*). Similarly, when 1,1,3-trimethylcyclopentane is reacted on palladium, the ring enlargement takes place at the tertiary carbon atom instead of the quaternary carbon atom as on platinum (*13*).

Species *B* cannot therefore explain the bond shift isomerization on palladium, since this metal does not catalyze the reaction at quaternary centers. On the contrary an allylic precursor such as *D*, where three consecutive carbon atoms are attached to two different metal atoms by a π and a σ–bond, would account for the observed facts. An attack by hydrogen of species *D* would lead, via an intermediate also responsible for cracking, to the isomerized product.

In conclusion, most of the available results in dehydrocyclization and bond shift rearrangement are interpreted by introducing for platinum two species *B* and *C* attached to the metal at two carbon atoms only by a single and a double bond, and for palladium by introducing two species *A* and *D* simultaneously π–bonded and σ–bonded to the surface. While cyclization on both metals seems to involve a single metal atom, bond shift requires at least two metal atoms not necessarily contiguous.

The latter proposal is in good agreement with the known ability of the highly dispersed and concentrated catalysts to promote cyclization and bond shift respectively (*1*, *2*, *4*). The first one is consistent with the unique ability of platinum to form simultaneously a double bond and a single bond to the metal, as shown by the deuterolysis of gemdi-substituted cyclopropane (*15*), and with the ease of rupture of the allylic CH bonds on a palladium surface, clearly demonstrated by the results of olefin exchange (*16*, *17*).

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On the Effect of Metal Particle Size on the Isomerization of *n*-Hexane Over Supported Platinum Catalysts

In a recent publication (*1*) we reported that the relative initial formation of 2-methylpentane and 3-methylpentane, when *n*-hexane was passed over inert-alumina-supported platinum catalysts, was independent of the amount of supported platinum used, 0.5 and 1.0 wt %. Since the same result was obtained over these catalysts after they had been subjected to a reduction treatment at various severities, by which the platinum particles had sintered to various degrees, it was suggested that the isomerization behavior is independent of metal particle size. The relative formation of 2-methylpentane and 3-methylpentane from *n*-hexane was in close agreement with that observed by Barron *et al.* (*2*) and Maire *et al.* (*3*) for their 0.2 wt % Pt-on-alumina catalyst, but was in striking contrast with the value given by these authors for their 10 wt % Pt-on-alumina catalyst.

Because of our vivid interest in the possible existence of particle-size effects on platinum-catalyzed reactions and in order to remove some doubt which might still exist as to the above statement (*5*), we have extended our experiments using catalysts containing a higher loading of platinum. A UOP-type alumina (surface area, 180 m^2/g, pore volume, 0.73 ml/g) was used as the starting material. This product was steamed to remove chlorine and subsequently calcined for 3 hr at 850°C, followed by a treatment with an aqueous solution of Na_2CO_3 and a final calcination for 3 hr at 500°C (0.5 wt % Na in final catalyst). After this treatment, the carrier was essentially inert for skeletal isomerization and cyclization of hexenes, as well as for ring opening of methylcyclopentane at temperatures up to 500°C. Catalysts were prepared containing 1, 5, and 10 wt %. The metal was placed on the support via impregnation of an aqueous solution of $Pt(NH_3)_4(OH)_2$ as described previously (*1*). The final treatment prior to use comprised a calcination in air for 3 hr at 500°C, followed by a treatment *in situ* for 16 hr with atmospheric hydrogen at ca. 400°C. X-Ray diffraction analyses of the 10 wt % Pt catalyst showed that about 50% of the total platinum was present as particles larger than 30 Å. The average particle size of the visible fraction was about 80 Å.

No platinum particles could be detected