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NOTES

Isomerization of Hydrocarbons in the Presence of Platinum Black

Recently it has been reported that the metal component of supported platinum (as well as platinum film) can catalyze the skeletal isomerization of saturated hydrocarbons (*1, 2*). It has been stated that this reaction can involve two mechanisms: one *via* bond shift and the other *via* C_5 ring closure and subsequent hydrogenolysis of the ring. Muller and Gault suggested that the C_5 ring closure takes place on a single metal atom (*3*); Anderson and Avery (*2, 4*), on the other hand, developed a model for a bond shift mechanism which involved α,γ-diadsorbed (or α,α,γ-triadsorbed) intermediate species on adjacent metal sites.

It was found that the main factor deciding which of these mechanisms will predominate was the degree of dispersion of the platinum on the support: in the presence of highly dispersed platinum only the five-ring mechanism will operate, whereas both mechanisms will occur on catalysts with less dispersed metal (*5*). The effect of dispersion was questioned by Dautzenberg and Platteeuw (*6*) who suggested the effect of pretreatment instead.

We have reported recently that platinum black shows entirely different catalytic activities in the presence of helium and hydrogen: the main product from *n*-hexane in helium carrier gas was benzene, whereas in hydrogen, isohexanes and methyl cyclopentane could be observed among the reaction products and their amounts were larger than that of the benzene (*7*). No methyl cyclopentane was formed in helium. When small amounts of hydrogen were admixed with helium the benzene yield from *n*-hexane increased and showed a maximum at about 20% H_2. The isomerization and C_5-dehydrocyclization exhibited their maximum yield at higher hydrogen pressures (*8*).

Since the isomeric hexanes consisted of almost exclusively methylpentanes, and their isomeric ratio was exactly identical to that obtained by the hydrogenolysis of methyl cyclopentane, their formation was attributed to the C_5-cyclic type of isomerization mechanism involving two steps: C_5-cyclization and ring opening (*7*). This was supported by the fact that the same type of isomerization of 2-methyl pentane could be observed with its analogous dependence on the hydrogen pressure (*8*).

The 2-methyl pentane also underwent aromatization to some extent which must have involved some sort of skeletal rearrangement. However, the effect of hydrogen on the aromatization of 2-methyl pentane was the opposite of that on its isomerization: the maximum amount of benzene was observed in helium (*8*); the admixture of hydrogen caused the benzene yield to decrease. This must have been caused by the involvement of another type of isomerization mechanism in this case.

In view of all these observations we decided to investigate the reactions of all five hexane isomers (and methyl cyclopentane) in the presence of helium and hydrogen. The experiments were carried out in a pulse-type microcatalytic reactor at a total pressure (of the carrier gas) of slightly above 1 atm. Typical results obtained in the presence of the same platinum black sample [described in (*7*)] have

TABLE 1

TRANSFORMATION OF HYDROCARBONS OF DIFFERENT STRUCTURE IN THE PRESENCE OF HELIUM AND HYDROGEN[a]

Starting material (hydrocarbons)	Carrier gas	Product composition (mass %)					
		$<C_6$	Unchanged hexane	Isomer hexane	Methyl cyclopentane	Benzene	Others[b]
n-Hexane	H_2	44.7	39.0	3.1	2.2	11.0	—
	He	15.2	71.2	—	—	13.1	0.5 nHex
2-Methyl pentane	H_2	25.7	63.2	5.1	4.3	1.6	—
	He	15.5	76.1	—	0.4	8.0	—
3-Methyl pentane	H_2	28.1	61.2	4.1	5.1	1.5	—
	He	17.3	74.4	—	0.2	7.8	0.3
2,2-Dimethyl butane	H_2	18.2	80.9	0.7	0.1	0.1	—
	He	25.3	72.7	—	—	2.0	—
2,3-Dimethyl butane	H_2	40.0	56.6	1.05	0.75	0.85	0.75
	He	17.4	79.3	—	—	2.2	1.1
Methyl cyclopentane	H_2	30.0	26.4		40.4	2.9	0.35 MCPe
	He	5.7	—	—	84.2	9.4	0.75 MCPe

[a] Catalyst, 0.51 g Pt; $T = 420°C$; 2 μl of hydrocarbons; carrier gas, 60 ml/min.

[b] nHex: n-hexenes; MCPe: 1-methyl cyclopentene; products not marked were not identified.

been summarized in Table 1 and can be interpreted as follows.

A. In helium, all hexane isomers (and methyl cyclopentane) could be transformed into benzene. The apparent activation energy E of the aromatization of n-hexane was about 10 kcal/mole. On the other hand, E fell between 17 and 20 kcal/mole in the case of all other hydrocarbons used as starting material where the aromatization must have been accompanied by skeletal rearrangement. This indicates that the energy of activation was most likely to have been determined by a *common* rate determining step in the case of methyl pentanes, dimethyl butanes and methyl cyclopentane, which is in all probability the skeletal rearrangement. This, in turn, indicates a common mechanism of skeletal rearrangement in all cases. Since dimethyl butanes are included among the hydrocarbons in question, this cannot involve the C_5-cyclic mechanism; all the more so because the opening of the five-membered ring does not occur.

B. In hydrogen, the extent of the aromatization of n-hexane is about the same as in helium while isohexanes formed less benzene. The isomerization of n-hexane and methyl pentanes was about of the same extent, but that of the dimethyl butanes was considerably smaller.

On this basis we can offer the following explanation: Platinum black is able to promote the skeletal rearrangement of saturated hydrocarbons. The results indicate the occurrence of two types of mechanism as a function of the hydrogen partial pressure:

In the absence of hydrogen, *only* the bond shift mechanism occurs. Under these conditions, however, the result of this reaction is benzene formation; no isomeric hydrocarbons are formed. Thus, the bond shift leads in this case to *dehydro-isomerization.* It has not been shown whether or not this reaction involves unsaturated intermediates; the formation of methyl pentenes from methyl pentane and methyl cyclopentenes from methyl cyclopentane could be observed. Minor amounts of C_5-cyclic compounds are formed in some cases; if these are involved in benzene formation, this must occur *via* bond shift expansion since no C_5-ring opening can occur without hydrogen.

In the presence of hydrogen, *both* bond shift and C_5-cyclic isomerization takes place. The former must be responsible for the isomerization of dimethyl butanes and the formation of the minor amount of 2,3-dimethyl butane from *n*-hexane (especially at higher temperature). The relative role of these two processes can be estimated by comparing the amount of hexanes (ring cleavage) and C_6-cyclic products (bond shift) formed from methyl cyclopentane as a function of the hydrogen partial pressure (Fig. 1, Curves 1 and 2). (Curve 3 representing the amount of isomeric hexanes formed from 2-methyl pentane indicates that at higher hydrogen pressures the *formation* of a five-membered ring must be somewhat hindered as compared with its *rupture*.)

It must be emphasized that all the experiments quoted (*1–6*) were carried out in a large excess of hydrogen. Under those circumstances the conditions permitting either *both* mechanisms or the *cyclic* isomerization only have been revealed. Our experiments show the third possibility, when—in the absence of gas phase hydrogen—*only* bond shift isomerization takes place.

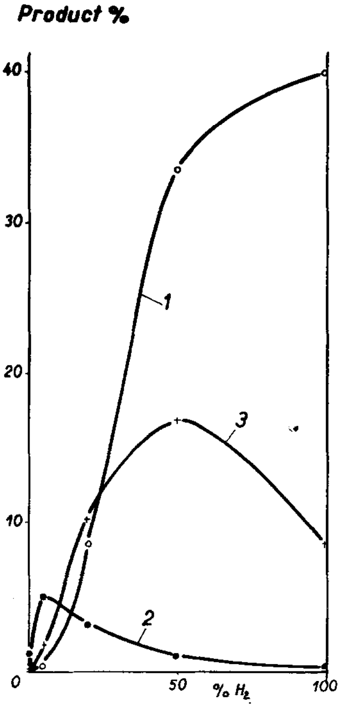

FIG. 1. The amount of products as a function of the hydrogen content of the carrier gas: (1) sum of hexanes formed from methyl cyclopentane; (2) sum of C_6-cyclic hydrocarbons (and methyl cyclopentenes) formed from methyl cyclopentane; (3) sum of isomer hexanes and methyl cyclopentane formed from 2-methyl pentane. $T = 360°C$; catalyst 0.4 g Pt; pulses, 3 μl each.

The α,γ-interaction suggested in this reaction requires more than one surface site, whether the end product is saturated, unsaturated or aromatic hydrocarbon. This is a common feature with the aromatization of normal-chain C_6 hydrocarbon, for which we assumed a stepwise elimination of hydrogen atoms mainly *via* α,β (or π-allylic (α,β,γ-) interactions with the catalyst surface. (In this case the normal carbon chain facilitates the process of dehydrogenation along the molecule resulting in ring closure which is thermodynamically more favorable than isomerization.) Both reactions take place on catalysts which have a relatively small coverage of hydrogen in equilibrium with only a small partial pressure of hydrogen or retaining only hydrogen from the regeneration process (*9*): they thus possess a large number of free sites.

The decreased reactivity of the hydrocarbons in higher hydrogen pressures is obviously due to the fact that the catalyst is covered with so much hydrogen that displaced the hydrocarbons from the active sites. Higher hydrogen pressures can stop any reaction at lower temperatures, whereas with increasing temperature the maximum catalytic activity can be observed at higher and higher hydrogen partial pressures (*10*). These features indicate clearly that it is the hydrogen coverage and not the partial pressure proper which is the important factor in determining the reactivity. At medium coverages such an intermediate state must occur when only single surface atoms remain uncovered by the hydrogen; thus the isomerization involving C_5-cyclic intermediates which requires such single surface atoms may become predominant.

At the same time it must be pointed out that the coverage of the surface with carbonaceous deposits will not lead to the same result: this relatively hydrogen-free metal surface is active only in taking off hydrogen atoms from the hydrocarbons even from benzene (*11*). The presence of hydrogen is necessary to maintain the metal surface in such a condition which renders the formation of the relatively hydrogen-rich products such as isomers and methyl cyclopentane possible. It cannot be excluded that hydrogen *held by the catalyst* plays an active role in the surface complex for C_5-cyclization, similar to that suggested by Liberman (*12*) for the reverse reaction, i.e., the hydrogenolysis of the C_5 ring. In this case the assumption of diadsorbed species in the bond shift mechanism may be of secondary importance. Further work is being done on this problem.

These results are consistent with the concepts of Muller and Gault (*3*) for C_5-cyclization. It has been shown, however, that the very fine dispersion of the metal is not the only way to create active centers for this reaction; partial coverage of the surface of a carrier-free metal by hydrogen may lead to the same result. This, in turn, emphasizes that the same catalyst may show different types of activities according to the experimental conditions.

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Valence State of Palladium in Y Zeolite*

All known stable square planar complexes of Pd(II) and Pt(II) are diamagnetic with low-spin d^8 configurations, but the corresponding complexes obtained by loss or gain of an electron should give d^7 or d^9 paramagnetic species possibly observable by ESR. There are only a few ESR studies about Pd ions reported in the literature. Pd(III) ions have been observed in various matrices (*1–3*) while ESR of Pd(I) has only been reported recently by γ-irradiation of single crystals of bis(acetylacetonato)palladium (II) (*4*), K_2PdCl_4 and $(NH_4)_2PdCl_4$ (*3, 5*) and also of metaphosphate glasses (*6*). On the other hand, palladium has been correspondingly little investigated [see, for instance, (*7*)].

Recently, zeolites have been used to obtain well-dispersed platinum catalysts (*8, 9*). It was shown (*9*) that tetrammine-platinum(II)-exchanged Y zeolite decomposed in oxygen prior to reduction gave well-dispersed platinum. In the present study the ESR technique has been used to follow the change of oxidation state of the cation in the case of tetrammine-palladium(II)-exchanged Y zeolite during decomposition in oxygen or *in vacuo*.

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