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Reaction of Methylcyclopentane and *n*-Hexane over Evaporated Platinum Film Catalysts

J. R. Anderson* and Kin'ya Shimomura**
School of Physical Sciences, Flinders University, Adelaide, Australia

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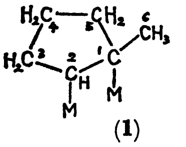
Synopsis. In the reaction of *n*-hexane and methylcyclopentane over polycrystalline platinum films evaporated in a ultrahigh vacuum condition, the initial distribution of reaction products varied with the reaction temperature and the hydrogen/hydrocarbon ratio. The effect of the reaction conditions was interpreted as depending on the possible reaction mechanisms cited.

Since hydrogenolysis of saturated hydrocarbons accompanied by skeletal isomerization over evaporated platinum films was first reported by Anderson and his collaborators, extensive studies have shown the reaction to involve a simple C–C bond shift or the use of an adsorbed carbocyclic intermediate.[1]

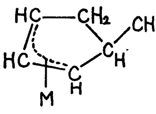
We have carried out the reaction of methylcyclopentane and *n*-hexane over unoriented platinum films evaporated in a ultrahigh vacuum in order to study the effect of the reaction conditions on the initial distribution of C_6 reaction products.

From methylcyclopentane, two classes of C_6 reaction products were obtained: (1) 2- and 3-methylpentane and *n*-hexane, (2) C_6 cyclic products (cyclohexane and benzene). The proportion of C_6 cyclic products decreased with increasing hydrogen/methylcyclopentane ratio, while this also caused the proportion of the methylpentanes to increase. Changing the reaction temperature from 240 to 310 °C caused a decrease in the proportion of the methylpentanes and an increase in that of *n*-hexane.

The possible existence of a diadsorbed σ-complex and an adsorbed π-complex (allyl type) in the reaction of saturated hydrocarbons has been suggested mechanistically.[2]



(1)

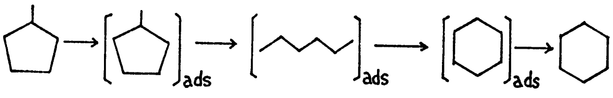


(2)

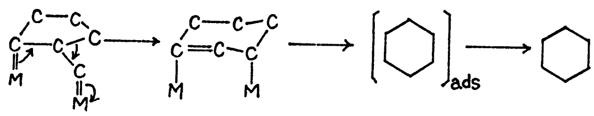
These intermediates in the hydrogenolysis of methylcyclopentane were also shown to occur over Al_2O_3-supported platinum catalysts.[3] In the present case, at a higher hydrogen ratio the probability of formation of (2) could be favoured since (2) requires only one free metal site, whereas (1) requires two sites and their geometrical distributions suitable for the structure and orientation of the methylcyclopentane molecule to be adsorbed in the positions C_1–C_2 and C_5–C_1 for *n*-hexane formation, on the surface covered predominantly with hydrogen.

The hydrogenolytic ring opening modes including diadsorbed species in the positions C_2–C_3, C_4–C_5, and C_3–C_4 for the formation of 2-methylpentane and 3-methylpentane, which might be compatible with the occurrence of (2), could also be taken into consideration in conjunction with the hydrogen/methylcyclopentane ratio. It has been proposed that the direction of hydrogenolysis of methylcyclopentane is determined by the correlation between the electron density distribution in the hydrocarbon molecule and the electron affinity of the metal atom or ion.[4] Hydrogen, chemisorbed over platinum, could exist in two forms—M^+–H^- and M^-–H_2^+ on the surface and an increased hydrogen coverage favours the proportion of hydrogen chemisorbed in the form of H_2^+.[5] This tendency could cause a decrease in the electron acceptability of platinum to increase the proportion of adsorption occurring at the positions C_2–C_3, C_4–C_5, and C_3–C_4 in conformity with the higher negative charge distribution in the methylcyclopentane molecule. However, this reaction mode does not appear dominant because the abovementioned correlation between the electron distribution among these carbon atoms and the electronegativity of platinum is not reflected in the experimental result where the ratio of 2-methylpentane/3-methylpentane produced remains almost constant with changing ratio of hydrogen.

A possible mode of aromatization of methylcyclopentane which might alternatively occur has been presented.[6]



(3)



(4)

These mechanisms could probably take place in parallel with the formation of (1) and (2) for ring opening. The fact that at a higher hydrogen ratio the proportion of *n*-hexane and C_6 cyclic products showed a concurrent decrease suggests less preferential occurrence of (3) than (4), in which the formation of 1,3-diadsorbed intermediate would be suppressed at a higher hydrogen coverage on the surface to decrease ring enlargement by a bond-shift process *via* this intermediate.

Higher reaction temperatures apparently favour the formation of a diadsorbed σ-complex to produce *n*-hexane probably by reducing the covering effect of adsorbed hydrogen.

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* Present address: CSIRO., Division of Tribophysics, University of Melbourne, Parkville, Victoria, Australia 3052.

** Present address: 6th Division, National Chemical Laboratory for Industry, 2-19-19, Mita, Meguro-ku, Tokyo 153.

Table 1. Effects of reaction temperature and hydrogen/reactant ratio on the initial product distributions

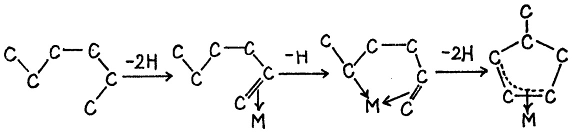
Reactant	Reaction temperature (°C)	Hydrogen/ reactant ratio	Total conversion (%)	Lower molecular products (%)[a]				C_6 products (%)[a]			
				C_1—C_4	*i*-P	*n*-P	Cp	2-&3-Mp	Mcp	*n*-H	C_6 cyclics
n-Hexane	275	7/1	2.50	1.6	trace	5.0	0.8	10.1	65.2	—	17.3
	275	3/1	0.61	1.9	trace	8.1	2.4	18.6	33.2	—	35.8
	275	1/1	0.17	17.8	trace	29.3	9.2	23.8	trace	—	19.7
	240	7/1	0.90	5.5	trace	10.4	1.1	34.3	36.2	—	12.4
	275	7/1	2.50	1.6	trace	5.0	0.8	10.1	65.2	—	17.3
	310	7/1	3.35	11.8	0.3	13.9	3.5	16.4	20.3	—	33.8
Methylcyclopentane	275	7/1	1.11[b]	1.9	0.4	1.0	2.4	74.7	—	19.5	trace
	275	3/1	0.50	trace	trace	trace	1.5	49.8	—	24.8	22.5
	275	1/1	0.31	2.0	0.6	1.0	2.7	22.4	—	33.1	38.8
	240	7/1	1.49	2.3	0.3	0.4	trace	77.6	—	19.4	trace
	275	7/1	1.11[b]	1.9	0.4	1.0	2.4	74.7	—	19.5	trace
	310	7/1	1.69	6.7	0.6	1.9	trace	54.2	—	34.2	2.5

a) *i*-P, *n*-P: isopentanes, *n*-pentane, Cp: cyclopentane, 2- and 3-Mp: 2:-methylpentane plus 3-methylpentane, Mcp: methylcyclopentane, *n*-H: *n*-hexane, C_6 cyclics: cyclohexane plus benzene.

b) Reaction time: 35 min.

From *n*-hexane, three classes of C_6 products were obtained: (1) 2- and 3-methylpentane, (2) methylcyclopentane, (3) C_6 cyclic products. The proportion of methylcyclopentane increased with an increasing ratio of hydrogen/*n*-hexane, while this also caused the proportion of the methylpentanes to decrease. Increasing reaction temperature in the range 240—310 °C caused the proportion of C_6 cyclic products to increase and the proportion of methylpentanes and methylcyclopentane to decrease.

According to the proposed mechanism for the isomerization and dehydrocyclization of hexanes,[6] the first step of *n*-hexane could be expressed as



(5)

The results could be accounted for if the effect of increasing the hydrogen concentration strongly increases the rate of desorption of the π-allyl adsorbed C_5 species (*cf.* reaction (5)), and if this effect is more important than the effect of an increased hydrogen concentration on the rate of ring opening in the π-allyl adsorbed species.

It was found that the lower the hydrogen/*n*-hexane ratio in the reactant, the greater the tendency for the formation of lower molecular weight hydrogenolysis products. This was very pronounced when the reactant ratio was 1/1. This is probably because a low hydrogen/hydrocarbon ratio favours the retention of adsorbed hydrocarbon residues on the surface, so that a greater chance for carbon-carbon bond rupture occurs.

Aromatization of *n*-hexane could be explained by a proposed mechanism[7] which proceeds *via* a direct C_6 ring formation or a C_5 ring formation followed by enlargement to a C_6 ring by two-site adsorption. The experimental facts could be explained by a retardation of the third step in reaction scheme (3) with an increasing hydrogen/*n*-hexane ratio and by promotion of both the third and fourth steps in reaction scheme (3) with increasing reaction temperature.

Experimental

The reaction system is similar to the one reported previously,[8] which consists of a bakeable reaction system and a gas handling line. A platinum filament, made of 0.1 mm diameter platinum wire wound on 0.2 mm diameter tungsten wire of a hair-pin type, was pretreated for outgassing and melting, accompanied by a slight evaporation, at a heating electric current up to 7 A in a separate bell-jar system. After the filament was spot-welded in a Pyrex glass reaction vessel, evaporation was carried out within 10^{-9} Torr at 275 °C for about an hour. The reaction mixture of hydrogen, purified by a heated palladium thimble in a separate purification system, and hydrocarbon, evaporated from a liquid nitrogen-cooled trap in the gas handling line of 10^{-6} Torr, was made in a reservoir whose pressure was measured with a capsule dial gauge. The reactant and products were collected in a trap cooled with liquid nitrogen and analysed by gas chromatography.[9] The maximum extent of reaction 45 min after the introduction of a reaction mixture was about 3%.

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