Direct Evidence for the Intermediacy of Adsorbed Alkyl Species in the Isomerization of Neopentane on Platinum

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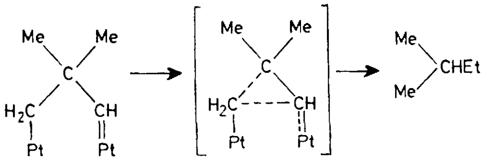
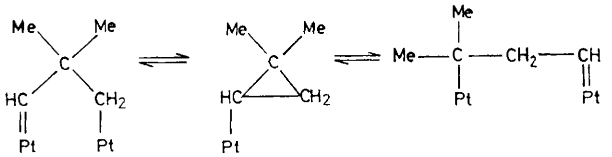
Summary The reaction of deuterium and neopentane catalysed by a sintered platinum film has been shown to yield appreciable amounts of monodeuteriated isopentane; this result strongly supports a mechanism involving an adsorbed alkyl species as the intermediate in the isomerization of small hydrocarbons.

Three mechanisms have been suggested for the Pt-catalysed isomerization of small alkanes: (i) the Anderson–Avery[1] mechanism involving the formation of a bridged intermediate from an $\alpha\alpha\gamma$-triadsorbed species (reaction 1); (ii) the Gault[2] mechanism which favours an adsorbed cyclopropane species (reaction 2); (iii) the Rooney[3] mechanism which is similar to the bond-shift mechanism in carbonium ions; it proceeds *via* an adsorbed alkyl species (reaction 3).

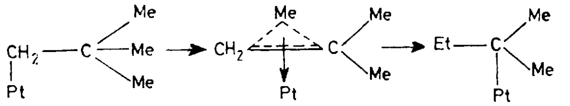
It must be emphasized that in the first two mechanisms triadsorption involving loss of three H atoms from the alkane molecule is the minimum requirement for isomerization, whereas in the third case loss of only one H atom generating a surface alkyl may be sufficient to enable the bond-shift to occur. Although recent experimental facts seem to stress the importance of the third mechanism [4] we



(1)



(2)



(3)

have performed a simple experiment in order to obtain direct evidence for this mechanism. Therefore we have used deuterium as an isotopic tracer in the isomerization of neopentane. A heavily sintered Pt film was chosen as the most convenient catalyst form;† at 523 K there is a measurable amount of isomerization of neopentane on such a film[5] and at the same temperature it is inactive in CH_4–D_2 exchange and only slightly active in C_2H_6–D_2 exchange.[6] The latter finding is important, because no conclusions on the mechanism of the isomerisation could be drawn if the D_2–hydrocarbon exchange was fast.[7] In our case, the production of a significant amount of monodeuterioisopentane would be strong direct evidence for a mechanism involving an adsorbed alkyl species.

The platinum film was evaporated in a high vacuum glass system and annealed in D_2 for 3 h at 800 K. The reaction mixture consisting of neopentane and deuterium [1:10 ratio, p (neopentane) = 266 N m^{-2}; volume of system *ca.* 700 cm^3] was then introduced on to the film maintained at 573 K. After 20 min a hydrocarbon sample was withdrawn and analysed with a Dupont 21–490 B gas chromatograph–mass spectrometer system.

Comparing the spectra of the initial and final hydrocarbon mixture we found that the total conversion leading to isomerization was *ca.* 0·2%, and the mass spectral analysis showed only the presence of comparable amounts of the mono- and di-deuterioisomers of isopentane; more accurate analysis was not possible because of the low conversion. This latter point is relevant to the current debate on the mechanism of isomerization of small alkane molecules in that it strongly supports the idea that adsorbed alkyl species are important intermediates in the isomerisation.

(*Received, 1st April* 1977; *Com.* 312.)

† The absolute reaction rate was 4·21 × 10^{11} molecules cm^{-2} s^{-1} and the selectivity for isomerization *vs.* hydrogenolysis, S_i/S_h, was 3·7, where S_i and S_h are the selectivities for isomerization and hydrogenolysis expressed as % neopentane consumed in each process divided by the total consumption.

[1] J. R. Anderson and N. R. Avery, *J. Catalysis*, 1966, **5**, 446.
[2] F. G. Gault, 'Proceedings Fifth International Congress on Catalysis,' 1972, Vol. 1, North-Holland, Amsterdam, 1973, p. 755.
[3] M. A. McKervey, J. J. Rooney, and N. G. Samman, *J. Catalysis*, 1973, **30**, 330.
[4] J. K. A. Clarke and J. J. Rooney, *Adv. Catalysis*, 1976, **25**, 125.
[5] Z. Karpiński and T. Kościelski, unpublished work.
[6] L. Guczi and Z. Karpiński, unpublished work.
[7] R. S. Dowie, D. A. Whan, and C. Kemball, *J.C.S. Faraday I*, 1972, **68**, 2150.