

The Mechanisms of Cyclisation and 1,2-Bond-shift Rearrangements of 2,2,4,4-Tetramethylpentane on Transition Metal Films

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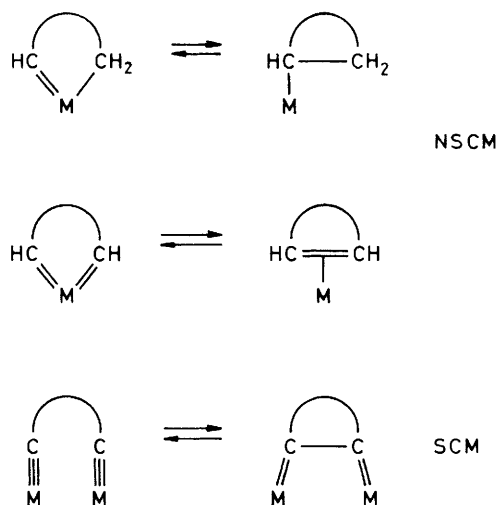
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The cyclisation/rearrangement products of 2,2,4,4-tetramethylpentane in deuterium on sintered films of Ir, Rh, Pd, and Pt, analysed by combined gas-liquid chromatography/mass spectrometry, show that chemisorbed carbene and carbyne species are not responsible.

The mechanisms of 1,5-cyclisation of alkanes and of the reverse reaction, hydrogenolysis of cycloalkanes, on transition metal catalysts have been extensively studied.¹ Two pathways have been distinguished, as exemplified in the interconversion of methylcyclopentane, n-hexane, 2-methyl-, and 3-methylpentane, a non-selective mechanism involving formation/rupture of all endocyclic bonds with equal facility (NSCM) and a selective mechanism (SCM) where only di-secondary C-C bonds are formed/ruptured. While NSCM is dominant on highly dispersed Pt catalysts,¹ SCM is virtually exclusive on Ir in an excess of hydrogen irrespective of metal dispersion and reaction temperatures.²

Gault¹ has argued that metallacarbene and metallacarbyne complexes are important intermediates in cyclisation and has suggested the mechanisms shown in Scheme 1. The dicarbyne postulate is based on the obvious fact that, for SCM, ring closure is confined to terminal C atoms, *i.e.* methyl groups in the 1 and 5 positions in a paraffin chain. However, a serious flaw in Gault's argument has been overlooked. The SCM tends to be more important at lower temperatures and higher hydrogen pressures whereas NSCM becomes



Scheme 1

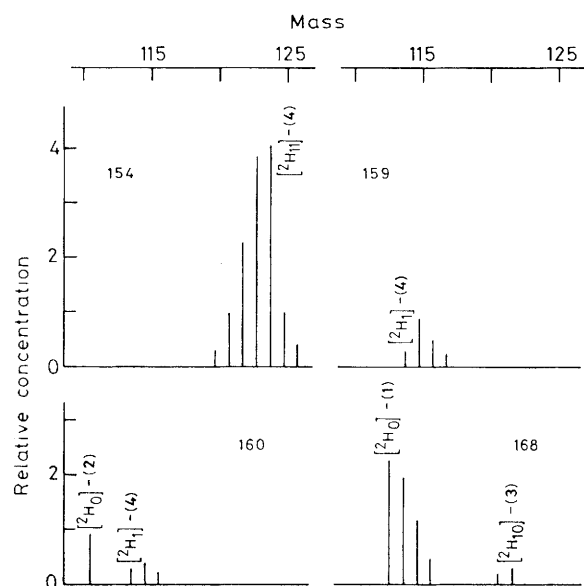
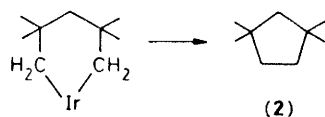


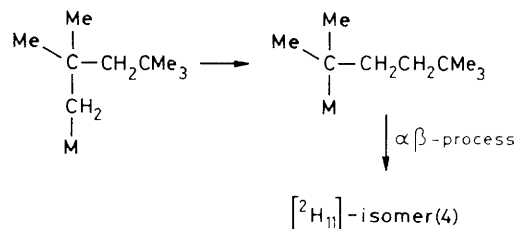
Figure 1. Reaction of (1) on Ir at 400 K. Representative mass spectrometry scans (No. 154–168) through a g.l.c. chromatogram. The notation $[^2\text{H}_1]\text{-(4)}$ signifies monodeuterio-isomer (4). Each m.s. scan is for a section of duration 1 second through a g.l.c. peak. Deuterio-isomers of the same compound have different retention times, the heaviest isomer being eluted first, and this complicates analyses (ref. 5). Thus, even in scans 159 and 160 the deuterium content of (4) is not the same and is very different to that of (4) in scan 154.



increasingly dominant at higher temperatures and lower hydrogen pressures on the same Pt catalyst.³ This indicates that the intermediates involved in NSCM are more extensively dissociated than those responsible for SCM, yet Gault invoked carbynes for the latter and carbenes for the former, although carbenes are obvious intermediates in further dissociation to carbynes. This example illustrates a key general problem in the field of metal catalysis, *i.e.* to determine the degree of dissociation required for ring closure. Another important example in this area is the mechanism of 1,2-bond shift rearrangements, *e.g.* of neopentane to isopentane where mechanisms involving dissociation of 1, 2, and 3 hydrogens (α , $\alpha\gamma$, and $\alpha\alpha\gamma$ species, respectively) have been suggested.^{1,4}

Since exchange of hydrocarbons with deuterium has been used to great advantage at lower temperatures to elucidate the mechanisms of hydrogenation and dehydrogenation,⁴ its potential use in like fashion for the higher-temperature reactions involving C-skeletal changes seems very attractive. This approach requires a combined g.l.c./m.s. analytical technique and was thoroughly explored by Kemball and co-workers⁵ for reactions of small paraffins on unsintered metal films. However they found that, at the temperatures required for C–C bond fission, the isotopic content of the hydrocarbons was essentially statistical as C–H(D) bond formation and fission were so rapid.

We now report that with a suitable model substrate, *e.g.* 2,2,4,4-tetramethylpentane (1), and with heavily sintered films⁶ we have succeeded in overcoming this problem of over-rapid exchange and have obtained definitive evidence concerning



Scheme 2

the mechanisms of both cyclisation and 1,2-bond shift. The sintered films have very few active sites so the exchange reactions are slow enough to be followed up to *ca.* 473 K; however, at these temperatures, the reactions involving C-skeletal changes, which have a higher temperature coefficient, achieve sufficient rates, relative to the rates of the exchange reactions, for the deuterium content and distribution patterns in the reactant and products to be mechanistically very revealing.



- (1) R = CMe₃
- (3) R = CHMeCH₂Me
- (4) R = CH₂CHMe₂

Both cyclisation to 1,1,3,3-tetramethylcyclopentane (2) and rearrangement to 2,2,4-(3) and 2,2,5-trimethylhexanes (4) of (1) were noted at 400 K on Ir films (Figure 1), together with fragmentation to lower products. While the latter reaction assumes the existence of some carbene and carbyne intermediates the following facts prove that these species are not involved in the skeletal reorganisation steps. At this temperature the exchange of (1) with deuterium was still easily followed and is stepwise in nature, showing that only adsorbed alkyls are involved. The most significant cyclic product at time of analysis[†] is the $[^2\text{H}_0]$ -isomer of (2) which shows beyond doubt that only an $\alpha\epsilon$ diadsorbed species participates in ring closure and that this reaction is a heterogeneous example of reductive elimination of a dialkyl species. The SCM is therefore confined to terminal C-atoms because of steric factors and not because of the need to dissociate 6 H-atoms. The isomeric products (3), (4) were multiply exchanged up to the $[^2\text{H}_{11}]$ -isomer (maxima at $[^2\text{H}_{11}]$ noted) but the distributions started with $[^2\text{H}_1]$ -isomer and not at the $[^2\text{H}_2]$ - or $[^2\text{H}_3]$ -isomers showing that formation of an alkyl group is sufficient to allow 1,2-bond shift and that dissociation to $\alpha\gamma$ or $\alpha\alpha\gamma$ adsorbed species¹ is not a prerequisite. The multiple exchange of the isomerised alkyl group up to the $[^2\text{H}_{11}]$ -isomer by an $\alpha\beta$ process⁴ is then expected (Scheme 2). Similar results are obtained using Rh (513 K).

At 458 K on Pd and at 433 K on Pt, while no cyclisation is observed in either case, bond shift occurs. On the latter metal, however, the exchange reactions still tend to be too fast to give a mechanistically informative deuterium distribution. The commencement of the deuterio-isomer distribution on Pd at $[^2\text{H}_1]$ confirms a mono-adsorbed intermediate for bond shift, as above.

[†] Evaporated metal films were sintered (773 K, 2 h, 3 Torr H₂/D₂) and reactions were in a static vessel. Analysis (g.l.c./m.s.) used a capillary OVI01 fused silica column temperature programmed from 293 K at 4°/min; m.s. analysis at 20 eV was made in terms of pseudo-parent ion resulting from loss of one methyl group, *i.e.* *m/e* 113 for paraffin (1), (3), (4) and *m/e* 111 for cyclic (2). Fragmentation of light (1) and (2) was *M*–1H, 2.5%, *M*–2H, 1.3%.

The exchange patterns of the isomeric products on all the sintered films still showed the characteristic features generally observed in exchange of paraffins on each of the unsintered metals⁴ at temperatures 150 K or more below those used here. This gives confidence that the active sites on the sintered films have still the same nature as those on the unsintered films.

This work clearly proves that metallocarbenes and metallocarbynes *etc.* are not required for 1,2-bond shift rearrangements and cyclisations of paraffins (for Ir and Rh at least), so that widely popular mechanisms^{1,7,8} which postulate these species for these reactions must now be modified. Such species seem to be confined to cracking, homologation,⁹ and some hydrogenolysis reactions. We will also show elsewhere that the NSCM mechanism is probably due to a more highly dehydrogenated adsorbed species of the type $\alpha\beta\epsilon$, $\alpha\beta\gamma\epsilon$, or $\alpha\beta\gamma\delta\epsilon$, and thus the SCM mechanism based on $\alpha\epsilon$ diadsorbed species is generically of the same type and indeed is the lowest limit because two is the minimum number of dissociated hydrogens required before ring closure is possible.

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