Bond-shift rearrangement during hydrogenolysis of neopentyl iodide on group VIII metal catalysts. An analogue of the mechanism of action of vitamin B$_{12}$

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Abstract

The hydrogenolysis of neopentyl iodide on reduced Co or Pt dispersed on MgO support yields increasing amounts of 2-metylbutane and 2-methylbutenes in addition to neopentane, as the temperature is raised from 50 to 150°C. These results support the idea that a π-complexed half-reaction state is simultaneously involved in activation of the R–I bond and in the evident 1,2-methyl shift. This π-complex mechanism is the same as that first suggested almost a quarter of a century ago for neopentane isomerism during hydrogenolysis at ≥ 200°C on Pt catalysts. The present results also support the contention that similar π-complexes are responsible for analogous carbon skeleton rearrangement reactions mediated by coenzyme B$_{12}$.

Keywords: Hydrogenolysis; Neopentyl halides; 1,2-bond-shift rearrangements; Vitamin B$_{12}$

The 1,2-bond shift isomerizations of alkanes and cycloalkanes [1], e.g. neopentane to isopentane, which occur in excess hydrogen at elevated temperatures on noble metal catalysts, especially Pt, is a reaction formally analogous to the methylmalonyl–CoA to succinyl–CoA carbon skeleton rearrangement mediated by coenzyme B$_{12}$ [2]. Successive hydrogen atom abstraction, 1,2-bond shift i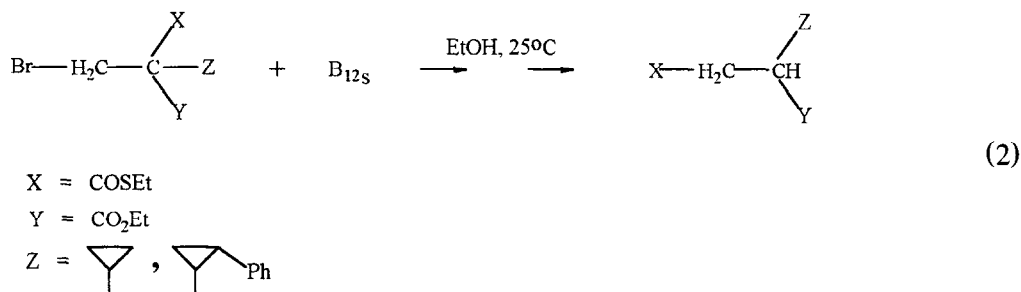somerization, and hydrogen atom addition steps are involved in both areas of catalysis, so metal–alkyls, e.g. Pt–R (surfaces) and [Co]–R′ (B$_{12}$), are common essential intermediates. However, while there is much evidence [1,3–5] since the initial suggestion in 1973 [3], that a π-complexed half-reaction state generates the 1,2-bond shift on the metal surfaces (Eq. (1)), there is no consensus even after extensive investigation of model systems about the mechanism(s) of the rearrangements in B$_{12}$ catalysis.
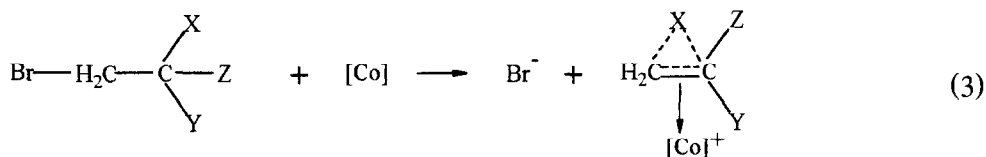

$$\tag{1}$$

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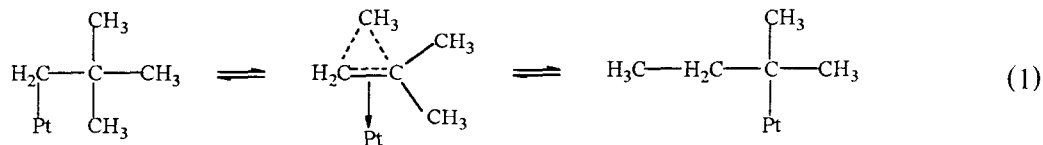
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In recent years most of the support has been for a free radical intermediate such that the central Co ion in the corrin complex of the coenzyme is merely acting as a free radical initiator, but plays no role otherwise in the H-atom abstraction and addition steps, and in the crucial bond shift step [2].

Very recently Mu He and Dowd [6], in a series of very elegant experiments, have shown conclusively using well-designed model substrates, that free radicals do not participate in the rearrangements catalysed by B_{12}. They studied the reactions in Eq. (2) and found that the C_3 ring (group Z) remains intact after 1,2 shift of group X. Quite clearly, free radicals of the type $X-CH_2-CZY$ are not present since the C_3 ring in Z has not opened.

$$Br-H_2C-\underset{Y}{\overset{X}{C}}-Z \ + \ B_{12s} \quad \xrightarrow{\text{EtOH, 25°C}} \quad X-H_2C-\underset{Y}{\overset{Z}{CH}} \tag{2}$$

$$X = COSEt$$
$$Y = CO_2Et$$
$$Z = \triangledown, \ \triangledown\!\!\!\diagdown Ph$$

Dowd's work lends considerable support to our earlier suggestions [7–9] that π-complexes analogous to those postulated for the rearrangements on the metal surfaces also mediate the rearrangements in these B_{12} metalloenzyme catalysed reactions. Oxidative addition and bond shift may then coincide in one step in the model reactions, as shown in Eq. (3).

$$Br-H_2C-\underset{Y}{\overset{X}{C}}-Z \ + \ [Co] \quad \longrightarrow \quad Br^- \ + \ H_2\underset{\underset{[Co]^+}{|}}{C}\!\!=\!\!\underset{Y}{\overset{X \quad Z}{C}} \tag{3}$$

We therefore decided to investigate the hydrogenolysis of neopentyl iodide vapour in an excess of flowing hydrogen on catalysts consisting of reduced Pt or Co dispersed on MgO, a basic support. The prediction was that bond shift would accompany R–I bond fission (Scheme 1), and that it would be easier than the analogous rearrangement starting with neopentane. The R–I bond is longer and weaker than the corresponding R–H bond and this should favour π-complex formation during the initial fission step. The basic support rules out a carbocationic mechanism which is possible on more acidic supports, e.g. Al_2O_3, etc.

A 4 wt% Pt/MgO catalyst was prepared by impregnating the support with chloroplatinic acid from aqueous solution, followed by drying and reduction in H_2 at 300°C. A 10 wt% Co/MgO sample was also prepared by impregnating the support with $Co(NO_3)_2$ from aqueous solution, followed by drying, calcination at 500°C and reduction in H_2 at 500°C for several hours. A 10 wt% Co/SiO_2 catalyst was also made in the same way. Typical results are recorded in Table 1.

All the catalysts behaved in the same fashion with both the conversion of the substrate and the % bond shift increasing as the temperature was raised, so increasing direct formation of the π-complex intermediate (Scheme 1) is indi-

Scheme 1.
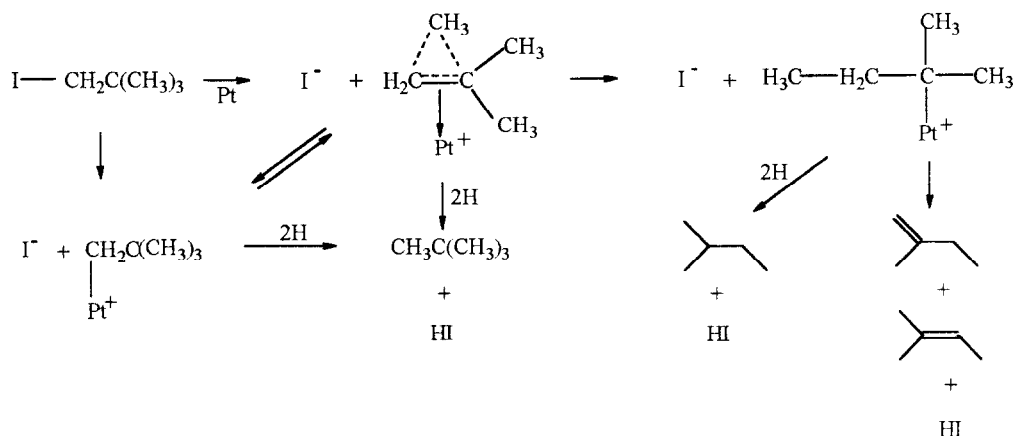
cated. There is also a concomitant increase in conversion and a more evident extensive reversible poisoning effect by I-adatoms on alkene hydrogenation. This is especially true of the cobalt catalysts. The initial 2-methylbut-1-yl species formed via the 1,2-bond shift of a methyl group is then showing an increasing tendency to eliminate a β-H atom to give the corresponding two alkenes rather than add an H atom and desorb off the surface as 2-methylbutane.

Neopentyl bromide reacts in the same way as the iodide but the Br-adatoms do not poison hydrogenation to the same extent as the I-adatoms. Thus, the only products are paraffinic consisting mainly of neopentane at low conversion at 70°C, but largely 2-methylbutane at high

conversion at 150°C using the Pt/MgO catalyst. MgO by itself is virtually inactive at 100°C but affords the two isomeric alkenes without hydrogenation at 150°C. As a final test, PtO_2 without a support and reduced at 150°C was found to give the same results as Pt/MgO for hydrogenolysis of both the iodide and bromide, i.e. only the two paraffins, which are mainly neopentane at 100°C and mainly 2-methylbutane at 150°C. This proves that the metal sites alone are responsible.

The correspondence between the solid metal and the metalloenzyme catalysis described here is powerful support for the π-complex mechanism. The same mechanism also applies to all the bond shift rearrangements noted for B_{12}, and especially to the hydroxy group shift in the 1,2-diol rearrangements [2], where a free radical mechanism per se is not immediately obvious. Indeed, the π-complex mechanism for the 1,2-diol reaction was first suggested in 1977 by Salem et al. [10], even though these authors were then unaware that the same mechanism had been advanced several years earlier to account for neopentane isomerization to 2-methylbutane on Pt [3].

Another very important consequence if the π-complex mechanism is valid for B_{12}, is that the metal bound radical, and not the free radical, may be involved in the next crucial step, namely

Table 1
Product distributions from neopentyliodide hydrogenolysis

Cat.	°C	NP	2MB	2MB-1	2MB-2	% Bond shift
Pt/MgO	75	96.4	3.6	—	—	3.6
	100	31.4	68.6	—	—	68.6
	150	10.5	43.3	4.8	41.4	89.5
Co/SiO$_2$	75	72.9	15.8	3.1	8.2	27.1
	100	5.9	22.0	7.3	64.8	94.1
Co/MgO	70	96.5	0.9	2.6	—	3.5
	100	36.7	1.2	5.9	56.2	63.3

NP = neopentane; 2MB = 2-methylbutane; 2MB-1 = 2-methylbut-1-ene; 2MB-2 = 2-methylbut-2-ene.

H atom abstraction from an incoming substrate molecule [2]. We have recently obtained good evidence [11] that a π-bonded alkene may react directly with an H_2 molecule via an Eley-Rideal type activation on certain metal hydrogenation catalysts (Eq. (4)).

$$\tag{4}$$
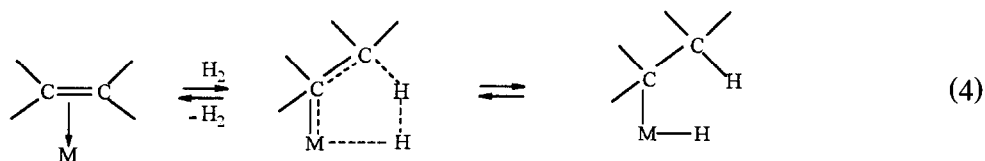
Various canonical forms including both ionic and radical may be considered for the half-reaction state here. In like fashion, it is probable that the half-reaction state π-complex in B_{12} catalytic systems also activates the R–H bond in the incoming substrate (Eq. (5)).

$$\tag{5}$$
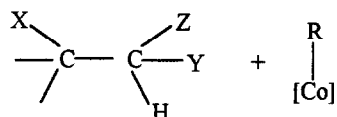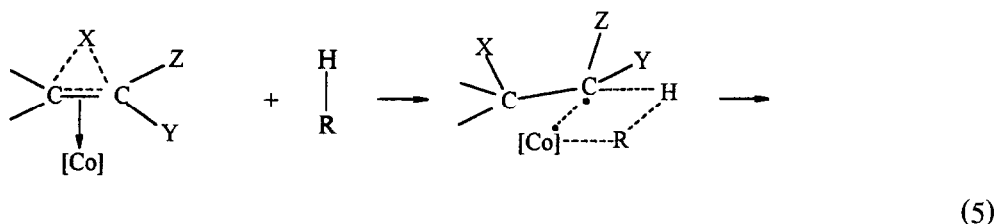
Here a di-radical canonical form of the π-complex may be most important involving a residual carbenoid $p\pi$–$d\pi$ contact with the Co ion such as that found in metallocarbenes ([M] $= C\langle$). The reaction is then that of the R·–[Co·] di-radical engaged in a [2 + 2] addition to R–H. Such [2 + 2] reactions are well known and are often very stereospecific in the area of catalysis by electron-deficient metal complexes, especially Ziegler–Natta polymerization of simple alkenes [12]. The H-atom abstraction step in the B_{12} field of catalysis is also very stereospecific [2] and this is to be expected [7] if it is the bound radical and not the free radical which is responsible, as described by Eq. (5).

In conclusion, the [Co]–alkyl chemistry involved in B_{12} catalysis may have many features in common with important aspects of metal–alkyl behaviour in the general field of catalysis, both homogeneous and heterogeneous.

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