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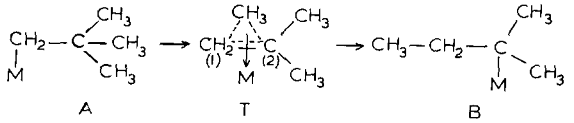
LETTER TO THE EDITORS

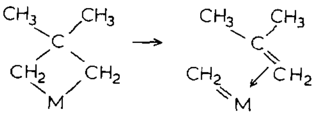
The Mechanism of Hydrogenolysis of Neopentane on Platinum Catalysts

Although it is gratifying to see that Foger and Anderson (*1*) have recently adopted the mechanism described by Reaction (1), first proposed by us (*2*), to explain at least part of the 1,2- bond shift isomerization of neopentane observed by them in excess hydrogen at elevated temperatures on dispersed platinum, we disagree with their proposal that the half-reaction state also reacts with adsorbed hydrogen to give hydrogenolysis products (Reaction 2), in essence a side reaction of (**T**).

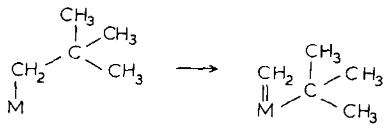


(1)

$$T + H \rightarrow CH_4 + C_4H_8 \qquad (2)$$



(3)



(4)

There are many good reasons why Reaction (2) is highly improbable. If (**T**) is truly a transition-state species in a unimolecular transformation, then as such it would have to "lurch" sideways into another transition-state species for a bimolecular reaction of (**T**) with a hydrogen atom, a theoretical impossibility. On the other hand, (**T**) may be regarded as a transient intermediate lasting for a few vibrations only, but this possibility is hardly acceptable. Thus the mechanism shown in Reaction (1) is exactly analogous to that for the corresponding but much easier rearrangement of the neopentyl carbonium ion. However, even though the appropriate half-reaction state for the latter is relatively energetically much more favorable, it is never seriously regarded as an intermediate, but is considered as a transition state (*3*). The postulate that Reaction (2) is reasonable requires a considerable probability that

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(**T**) undergo an additional substantially activated, sideways process. This cannot be true. The bonding of the migrating CH_3 group is not as weak as implied (*1*), as a consideration of the occupied molecular orbitals of (**T**) will show (*2*); so a substantial additional input of energy would be required for the synchronous fission of this CH_3 group away from $C_{(1)}$ and $C_{(2)}$. This is therefore a highly improbable process requiring that (**T**), which is already on top of a pass, go sideways over a second higher mountainous pass rather than down into the valley represented by (**B**). Furthermore, Reaction (2) is a bimolecular reaction whose probability of occurrence also demands that there should be a hydrogen atom in very close contact with the bridging CH_3 group. I find this impossible to believe on the basis of any model, since the bridging CH_3 group is anti-periplanar to the Pt atom involved, to which the hydrogen atom in question is also most likely attached. Finally, on symmetry grounds, if a hydrogen atom does react with (**T**) it will do so only in such a way as to give back either neopentane or isopentane. The effect of the concentration of adsorbed hydrogen on the relative ease of hydrogenolysis and isomerization has been attributed (*1*) to a simple kinetic effect involving (**T**), but could well be due to a direct or indirect electronic factor which determines the relative ease of formation of (**T**) and of the intermediates responsible for hydrogenolysis.

It is much more likely that if hydrogenolysis of neopentane occurs via bonding to one metal atom it does so via formation and subsequent reactions of metallocyclobutanes ($\alpha\gamma$-diadsorbed species), perhaps via Reaction (3) analogous to the well-established mechanism for olefin metathesis (*4*), or else via a retro-carbene/alkyl insertion pathway as shown in Reaction (4). A homogeneous example of this novel reaction in a nickel complex has just been described (*5*), and a recent theoretical study (*6*) of a model manganese system has also confirmed its feasibility.

In both cases the fission products would be rapidly hydrogenated off the surface under the conditions employed.

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