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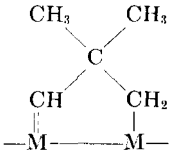
A Novel Mechanism for 1,2-Bond Shift Isomerizations of Alkanes on Noble Metals

Skeletal hydroisomerization of simple paraffins, such as neopentane to isopentane, is catalyzed at elevated temperatures by noble metals, especially Pt. This is attributed to the formation and further reaction of $\alpha\alpha\gamma$-triadsorbed intermediates, bonded to two continguous metal atoms (*1*)



This species is supposed to donate charge via the $p\pi$–$d\pi$ component of the $\alpha\alpha$-bond in order to explain behavior akin to that of carbonium ions (*1*).

We briefly report here results whch show that certain, highly strained, polycycloalkanes rearrange selectively under relatively mild conditions on Pd and Pt catalysts. Simple geometrical arguments alone show that the above type of intermediate cannot be responsible (*2*). Thus protoadamantane isomerizes with 100% selectivity to adamantane with activation energies of 24.1 kcal mole^{-1} (200–300°C) for Pd and 10.1 kcal mole^{-1} (160–300°C) for Pt.

A more striking example is the conversion of the recently reported, very strained adamantene dimer (*3*), to two new isomers which are presently not identified but are probably due to expansions of the C_4 ring at the expense of a C_6 ring (Fig. 1). Exchange and isomerization of this compound occur at comparable rates when reacted in a large excess of deuterium at 156°C on 2% Pd/pumice catalyst. The reactant undergoes only simple exchange as expected but the isomeric hydrocarbons have deuteroisomer distributions also in accord with the calculated binomial distributions (*4*) although the corresponding mean deuterium numbers are somewhat larger.

A mechanism, previously discounted on other grounds by Anderson (*1*), involving $\alpha\gamma$-diadsorbed intermediates with transient formation and hydrogenolysis of C_3 rings, is obviously ruled out, otherwise the deuteroisomer distributions should show significant deviations from binominal distributions. The results clearly reveal that loss of one hydrogen from the molecule giving a surface alkyl is sufficient for rearrangement. The surprising conclusion, therefore, is that essentially covalently bonded alkyl groups on metal surfaces can rearrange in a manner commonly found for carbonium ions. Thus neopentane and protoadamantane both undergo 1,2-carbon–carbon bond shifts, and the ease of isomerization of the polycycloalkanes parallels their facility for isomerization by acid catalysts (*2*).

The novel concept (Fig. 2) is proposed to explain carbonium ion behavior of adsorbed alkyls, using rearrangement of neopentane on Pt as an example. The transient chemisorbed species, I, has partial double bond character with the shifting methyl group symmetrically bridged [cf. mechanisms of carbonium ion rearrangements as described by Olah (*5*)].

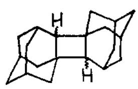


FIGURE 1.

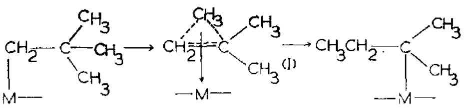


FIGURE 2.

The organic part of the complex can first be considered separately as a three-center free radical, a detailed molecular orbital treatment of which has been given by Zimmerman (*6*). The two most important of the three associated molecular orbitals have the required symmetries to combine respectively with appropriate atomic orbitals of a surface metal atom as shown in A and B (Fig. 3). In A the molecular orbital of I has the three atomic orbitals all bonding to each other, is of lowest energy, contains two electrons, and donates to an empty σ-orbital. This interaction helps to stabilize I. However, in B the atomic orbital of the shifting methyl group is both bonding and equally antibonding, and therefore nonbonding to the other two atomic orbitals which are antibonding with respect to each other. The third electron has to be in the latter molecular orbital which as a result of its net antibonding character is energetically unfavorable. Consequently free radicals have great difficulty in attaining the half-reaction state required for 1,2-alkyl shift. In the corresponding state of the equivalent carbonium ion this molecular orbital is empty and the energy barrier to bond shift is removed (*6*). However, complexing I to the metal atom drastically alters the situation. Now the net antibonding molecular orbital has appropriate symmetry to interact with a metal $d\pi$ orbital which has either one electron or is empty. The new molecular orbital B is thus sufficiently stable to be occupied so the energy barrier to formation of I is reduced. This is the main reason why the metal promotes 1,2-alkyl shift. The bonding between I and the surface is thus very similar to that in olefin–metal complexes. It is not surprising, therefore, that the 5*d* metals which seem to form the strongest olefin–metal bonds have the highest activity for 1,2-bond shift reactions.

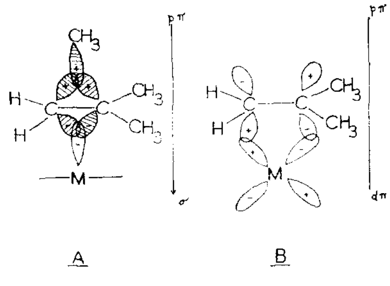


FIG. 3. Diagram of A and B.

The above results and mechanism are relevant to the current debate on "facile" and "demanding" reactions, and the effect of crystallite size on the bond shift versus cyclization–hydrogenolysis mechanisms for isomerization (*7*).

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M. A. MCKERVEY
J. J. ROONEY
N. G. SAMMAN

Department of Chemistry
The Queen's University
Belfast, Northern Ireland
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