The Mechanism of 1,2-Bond Shift Rearrangements of Paraffins on Transition Metal Surfaces

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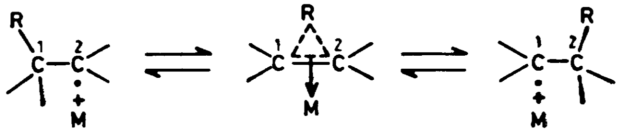
Isomerization of protoadamantane to adamantane and of bicyclo[2.2.2]octane to bicyclo[3.2.1]octane occurs on reduced molybdenum powder or on reduced molybdena/alumina catalysts in excess of hydrogen at ⩾275 °C; an olefin metathesis-type mechanism is precluded by the structures of these caged compounds, so simple bond shift in alkyl radicals on transition metal surfaces seems to be a generally valid reaction pathway in heterogeneous conversions of paraffins.

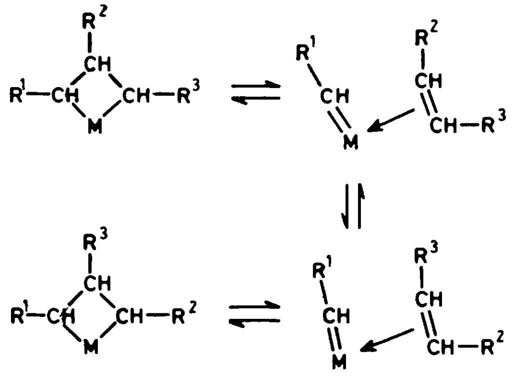
The 1,2-bond shift isomerizations of paraffins in excess of hydrogen at elevated temperatures on transition metal catalysts now constitute a classic reaction which has aroused a great deal of mechanistic interest[1] ever since the initial discovery[2] of the rearrangement of neopentane to isopentane on platinum films. The general consensus[3] now is that two pathways are possible, the first of which is closely akin to that of carbonium ion rearrangements. Here an alkyl radical is generated at the metal surface by C–H bond fission which then isomerizes *via* a π-complexed half-reaction state in which occupancy of the unstable anti-bonding Walsh molecular orbital is somewhat stabilized by pπ*–dπ bonding to a metal dπ-orbital (Scheme 1).

At one extreme the alkyl species is a physically adsorbed free radical and at the other a covalently bonded ligand, so that this mechanism may well have a counterpart in the vitamin B_{12} catalysed vicinal interchange reactions,[4] and in the rearrangement of alkyl radicals sometimes noted in Kolbé electrolysis of carboxylates.

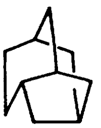
The alternative mechanism often advocated[5] for rearrangement is formation of a surface metallacyclobutane complex followed by metathesis-type cleavage to afford an alkene–metallacarbene in which the alkene then rotates and the moieties recombine to give an isomeric metallacyclobutane (Scheme 2). Rooney and coworkers[3,6,7] have argued that this mechanism will only be significant when there is simultaneous methanation and homologation of the substrate. An alkylidene larger than methylene will rearrange by itself too readily to the corresponding alkene at elevated temperatures (*e.g.* ethylidene to ethylene) to be a viable shifting entity. This constraint and the necessity for a good steady state density of surface methylenes therefore confines this mechanism to shift of methyl groups and to the region of lower hydrogen pressure. A further constraint is the nucleophilicity of the methylene moiety in the surface $M{=}CH_2$ complex which will govern the tendency to afford chain branching. All these restrictions point to the conclusion that the metathesis mechanism should have very limited application, and this is borne out in practice. *E.g.*, Pt surfaces are very good at bond shift in general but very poor at homologation and methanation,[6,7] whereas tungsten films are excellent catalysts for selective linear homologation but give very little chain branching bond shift (linear homologation is indicative of an



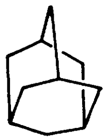
Scheme 1



Scheme 2

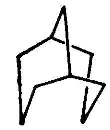


(1)

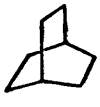


(2)

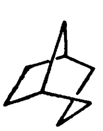
(3)



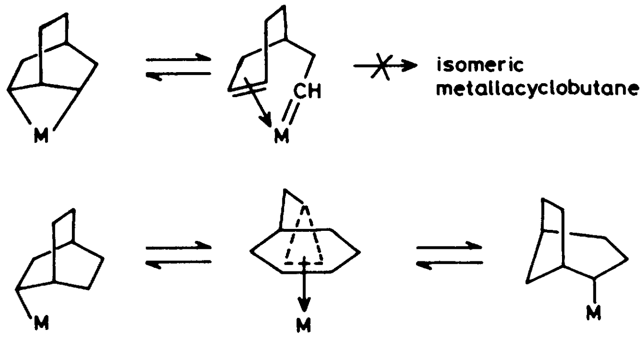
(4)



(5)



(6)



Scheme 3

electrophilic methylene species).[7] The only significant example so far reported of the operation of the metathesis mechanism in bond shift seems to be the conversion of n-butane to isobutane on Pd and Ni catalysts at higher temperatures and rather low hydrogen pressures where isomerization was accompanied by very extensive homologation and methanation processes.[8]

There is a claim[5] that reduced molybdenum powder rearranges paraffins at 623 K in excess of hydrogen by a general metathesis mechanism involving shift of alkylidenes as well as methylenes in the absence of extensive cracking. Since ^{13}C-labelling makes no distinction between the alkyl radical and metathesis mechanisms, the only evidence offered in support of the latter is that molybdenum complexes are often excellent metathesis catalysts.

We think that there is a simple answer to this problem. In the rearrangements of caged compounds, *e.g.* protoadamantane to adamantane or bicyclo[3.2.2]nonane to bicyclo-[3.3.1]nonane which occur in excellent yields over platinum and palladium catalysts,[9] the metathesis mechanism is precluded since the intermediate alkene–metallacarbene complex, even if it could form, cannot rearrange since internal rotation of the transient alkene moiety about the metal–alkene bond axis is precluded (Scheme 3).

So we passed (**1**) (a few mm of Hg pressure) in an atmosphere of hydrogen over the same molybdenum powder (Goodfellow Metals) activated in the same fashion as used by the Strasbourg group,[5] *i.e.* in air and then in hydrogen gas at 823 K. It was found that (**1**) isomerizes to (**2**) at >548 K. At 648 K cracking and aromatization to naphthalene, together with the formation of two $C_{10}H_{12}$ isomers, were also noted in addition to the major process of isomerization (22% conversion). Further increases in reaction temperature made aromatization, especially to naphthalene, and cracking as important as isomerization. Similar behaviour was observed using a 5% (by wt.) MoO_3/Al_2O_3 catalyst reduced at 823 and 1173 K, respectively, although the sample reduced at the lower temperature was much more active (23% selective isomerization at 543 K) than the sample reduced at 1173 K which had an activity comparable to that of the metal powder.

Isomerization of (**5**) to (**6**) on the same catalysts under the same conditions was also tested and found to be slight, the main reaction being hydrogenolysis to yield ethylcyclohexane and 1,4-dimethylcyclohexanes at lower temperatures. As the temperature increased, aromatization of these compounds on the MoO_3/Al_2O_3 catalyst became dominant, accompanied by significant disproportionation affording products ranging from benzene to naphthalene.

A 2% (by wt.) Pt/SiO_2 catalyst, under the same conditions, was found to be much more selective and active for the conversion of (**1**) into (**2**) and of (**5**) into (**6**), especially at <573 K in accordance with previous results.[9]

It must be concluded therefore that the most general bond shift reaction for Mo as well as Pt is simply *via* formation of free radicals. Whether or not gaseous free radicals are present is a moot point[10] but their involvement in reactions of caged compounds on metal surfaces is strongly implied by the recent spectacular synthesis of dodecahedrane[11] from its $C_{20}H_{20}$ isomeric precursor, pagodane, a synthesis which is based on the work of McKervey and Rooney[12] in this area.

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References

1. J. K. A. Clarke and J. J. Rooney, *Adv. Catal.*, 1976, **25**, 125.
2. J. R. Anderson and N. R. Avery, *J. Catal.*, 1966, **5**, 446.
3. J. J. Rooney, *J. Mol. Catal.*, 1985, **31**, 147.
4. V. Amir-Ebrahimi, J. Grimshaw, E. A. McIlgorm, T. R. B. Mitchell, and J. J. Rooney, *J. Mol. Catal.*, 1984, **27**, 335.
5. Y. Hall, F. Garin, G. Maire, A. Muller, P. A. Engelhard, and J. Grosmangin, *J. Catal.*, 1987, **104**, 211.
6. O. E. Finlayson, J. K. A. Clarke, and J. J. Rooney, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 191.
7. C. O'Donohoe, J. K. A. Clarke, and J. J. Rooney, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 345.
8. A. Sárkańy, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 103; *J. Catal.*, 1986, **97**, 407.
9. H. A. Quinn, J. H. Graham, M. A. McKervey, and J. J. Rooney, *J. Catal.*, 1972, **26**, 333.
10. J. K. A. Clarke, R. Darcy, B. F. Hegarty, E. O'Donoghue, V. Amir-Ebrahimi, and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 1986, 425.
11. W. D. Fessner, B. A. R. C. Murty, J. Worth, D. Hunkler, H. Fritz, H. Prinzbach, W. D. Roth, P. von R. Schleyer, A. B. McEwen, and W. F. Maier, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 452.
12. W. Burns, M. A. McKervey, T. R. B. Mitchell, and J. J. Rooney, *J. Am. Chem. Soc.*, 1978, **100**, 906.