Facile Activation of Dihydrogen by Long-lived Carbonium Ions on Silica–Alumina Catalysts. An Example of a Simple [2 + 2]-Type Reaction

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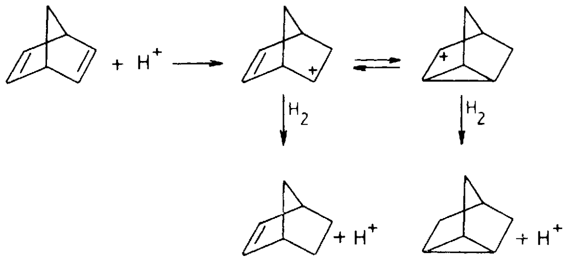
Silica–alumina catalyses the gas phase hydrogenation of norbornadiene and 1-chloroadamantane at the surprisingly moderate temperature of 90 °C showing that when the carbonium ion intermediates are long-lived the $R^+ \cdots O^-$— surface species reacts with dihydrogen in a [2 + 2]-type reaction, and does so far more readily than the corresponding $H^+ \cdots O^-$— cation–anion pair.

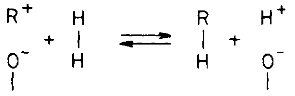
Among various attempts to establish a convenient, efficient, and highly selective vapour-phase method of rearranging the [4 + 4]-norbornadiene dimer, binor S, into its olefinic isomers, $C_{14}H_{16}$, as a step in the synthesis of triamantane,[1] the substrate was passed in flowing hydrogen at 100 °C over a silica-supported Ag_2O catalyst. To our surprise it was the $C_{14}H_{18}$ hydrogenated analogues and not the olefins which were produced in good yield; however, we were even more surprised to find that the same reaction occurred when the support was used without the Ag^+ ions, while in a dinitrogen stream the silica alone afforded the olefins as the predominant products. These results not only suggest that Brönsted acidity is responsible for the isomerizations, but also indicate that the long-lived carbonium ion intermediates involved are remarkably efficient at activating dihydrogen.

In order to test these ideas a sample of the air-dried (500 °C) granular silica (Crossfields) was cooled and added at room temperature to dry benzene solutions of triphenyl- and diphenyl-methanol indicators. Colouration of the surface (bright yellow) by the former but not by the latter was noted[2] showing that the silica possessed acid sites in the range 50—71 wt% aq. H_2SO_4. These sites are due to metal ion impurities which can be removed by washing with hot conc. HNO_3 followed by hot distilled water, as shown by a subsequent negative response of the treated air-dried silica to triphenylmethanol. A silica–alumina catalyst was then prepared from the acid-treated silica by immersing it in dry pentane, allowing it to react with Et_3Al, followed by removal of the solvent and air-activation of the solid to 500 °C for 12 h. This material was much more effective than the untreated silica in the hydroisomerization of binor S, so impurities such as iron or chromium ions cannot be responsible for the dihydrogen activation observed.

In order to provide a more simple model reaction norbornadiene was passed in dihydrogen at 90 °C over the silica–alumina catalyst and good conversions, with very high selectivity, into a mixture of nortricyclene and norbornene in *ca.* 3:1 ratio were obtained (Scheme 1). In a similar fashion 1-chloroadamantane hydrogenolysed to adamantane and HCl under the same conditions showing that the carbonium ions,

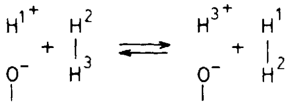


Scheme 1



$$\overset{R^+}{\underset{|}{O^-}} + \overset{H}{\underset{H}{|}} \rightleftharpoons \overset{R}{\underset{H}{|}} + \overset{H^+}{\underset{|}{O^-}}$$

(1)



$$\overset{H^{1+}}{\underset{|}{O^-}} + \overset{H^2}{\underset{H^3}{|_3}} \rightleftharpoons \overset{H^{3+}}{\underset{|}{O^-}} + \overset{H^1}{\underset{H^2}{|_2}}$$

(2)

e.g. adamantyl, and not surface polymer, are the source of dihydrogen activation.

These results are theoretically very interesting because it is known that silica–alumina surfaces by themselves do not activate dihydrogen below *ca.* 300 °C, as shown by the $H_2 + D_2 \rightleftharpoons 2HD$ exchange reaction,[2] and as confirmed for the present catalyst samples when subjected to this test.† Clearly reaction (1) is much more rapid than reaction (2), where R^+ is the carbonium ion, and O^-— the surface extension of an $[AlO_4]^-$ unit in the solid. This difference in ease of reaction indicates that a [2 + 2]-type activation is occurring. The cation–anion distance as well as charge separation are obviously important in lowering the energy barrier, the longer distance in $R^+ \cdots O^-$— being associated with higher reactivity, with the HOMO and LUMO orbitals of H–H becoming closer in energy as the bond stretches in order to meet the requirements of its dipolar [2 + 2]-partner. The longer distance and greater charge separation in $R^+ \cdots O^-$— are clearly a result of delocalization of charge in the carbonium ion, steric repulsion by the surface, and the fact that the empty orbital of the proton is smaller than that in the ion.

The present results and theory are also extremely important in a wider context. There are numerous systems now known, both homogeneous and heterogeneous, which readily activate dihydrogen even though oxidative addition, as for many transition metals and their complexes, is obviously not possible. They all involve cation–anion pairs, so [2 + 2]-type reactions, as in the present case, seem warranted. In the heterogeneous field two well-known examples are the $Al^{3+} \cdots O^{2-}$ and $Zn^{2+} \cdots O^{2-}$ pairs[3,4] which are the redox sites[5] in the surfaces of the activated oxides. Among many examples in the homogeneous field are the compound $Zr(\eta^5\text{-}C_5H_5)_2(\text{alkyl})H$[6] and the recently prepared $Lu(\eta^5\text{-}C_5Me_5)_2Me$, which even activates alkanes at room temperature[7] in a fashion comparable with that of the surface of $\gamma\text{-}Al_2O_3$.[3] In all of these cases the distance between cation and anion and the degree of charge separation must also be very important considerations, while the extent to which the alkyl ligand in the electron-deficient metal alkyls complexes tends to become carbenoid[8,9] is also an important question. Perhaps the most intriguing example of all is the activation of the alkane C–H bond in various substrates by the Co-alkyl complexes in vitamin B_{12} catalysis.[10] Here the critical lengthening of the Co–C bond which would be required for an easy [2 + 2]-type reaction with the substrate occurs apparently because of distortions in the corrin ring such that the alkyl ligand experiences severe steric repulsion.[11]

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References

1 F. S. Hollowood, M. A. McKervey, R. Hamilton, and J. J. Rooney, *J. Org. Chem.*, 1980, **45**, 4954.
2 B. R. T. Garrett and J. J. Rooney, *J. Chem. Soc., Perkin Trans.* 2, 1974, 960.
3 C. S. John, C. Kemball, E. A. Pearce, and A. J. Pearman, *J. Chem. Res.*, 1979, (*S*) 400; (*M*) 4830.
4 R. J. Kokes, L. A. Dent, C. C. Chang, and L. T. Dixon, *J. Am. Chem. Soc.*, 1972, **94**, 4429.
5 B. D. Flockhart, S. S. Uppal, and R. C. Pink, *Trans. Faraday Soc.*, 1971, **67**, 513.
6 K. I. Gell, B. Posin, J. Schwartz, and G. M. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 1846.
7 P. L. Watson, *J. Chem. Soc., Chem. Commun.*, 1983, 276.
8 D. T. Laverty and J. J. Rooney, *J. Chem. Soc., Faraday Trans.* 1, 1983, **79**, 869.
9 Z. Dawoodi, M. L. H. Green, V. S. B. Mtetwa, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1982, 1410.
10 R. H. Abeles and D. Dolphin, *Acc. Chem. Res.*, 1976, **9**, 114.
11 J. Halpern, *Pure Appl. Chem.*, 1983, **55**, 1059.

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