Carbocation chemistry at room temperature on solid acids

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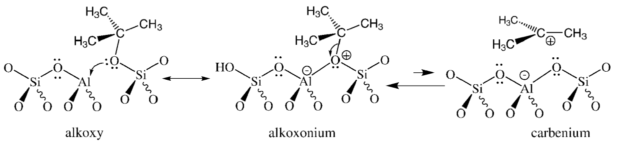
The existence of carbocationic intermediates in a zeolite environment even at room temperature is supported by hydride (and deuteride) transfers between isoalkanes as monitored *ex situ* by ^{13}C NMR.

Acid-catalysed transformations of hydrocarbons are of prime importance to the petrochemical industry.[1,2] The chemical inertness of alkanes, the main components of oil, and the low acidity of the catalysts (silicoaluminates or zeolites) are overcome by operating at high temperature and pressure. Only liquid superacids[3] are known to activate saturated hydrocarbons at room temperature and well below in relation with the σ-basicity of C–H and C–C bonds.[4] If carbocations are generally accepted as reaction intermediates in acid-catalysed hydrocarbon reactions, their mode of formation as well as their true nature is still a matter of controversy.[5,6] Whereas the number of Brønsted acid sites of a catalyst can be measured with a good precision by various techniques,[7,8] the heterogeneity of their environment and strength have been demonstrated by experiment and theory.[9] After the alkane activation step,[10] carbocation intermediates are generally present at very low concentration[11] and thus difficult to detect and observe. Moreover, with the exception of the gas phase, carbocations are never present as free ions but solvated by interaction with the lone pairs of the solvent. In the case of silicoaluminates or zeolites this solvation generates a more stable form: the alkoxy species which is in fact a mesomeric (or resonance) form of an alkoxonium ion (Scheme 1).

Oxonium ions or salts[12] are widely used as reagents in organic synthesis due to their ability to generate carbenium ions. In this paper we describe our results which, we believe, for the first time strongly support the existence of carbenium ion intermediates on zeolites even at a temperature as low as room temperature.

In a first experiment, in order to generate the alkoxy species on the catalyst, we recirculated, during 24 h at room temperature, 2-methylpentane (2MP; 220 µl), 5% in nitrogen at a rate of 20 ml min^{-1} over 200 mg of HUSY (titrated as 4×10^{-3} acid sites g^{-1})†. The recirculation loop (an all glass grease-free batch recirculation reactor) was evacuated at 10^{-2} Torr and purged with N_2 in order to evacuate the adsorbed residual 2MP. Monodeuterated isobutane (2-methylpropane-*2d*; 22.4 ml; 1×10^{-3} mol) was then introduced in the recirculation loop and the gas phase was trapped at the outlet of the reactor in a precooled U tube (ethanol–liquid N_2), then transferred to the NMR tube using $CF_2Cl–CCl_2F$ as solvent and $CDCl_3$ as reference. The ^1H, ^2H and ^{13}C NMR spectra of the resulting solution showed, next to an excess of monodeuterated isobutane and residual 2MP, a very small amount of non deuterated isobutane and an equivalent amount of 2-methylpentane-*2d* deuterated in the tertiary position. The logical explanation of this result is the deuteride transfer to the 2-methyl-2-pentylium ion generating 2-methylpentane-*2d* and the adsorbed *t*-butyl cation or *t*-butoxy species (Scheme 2).

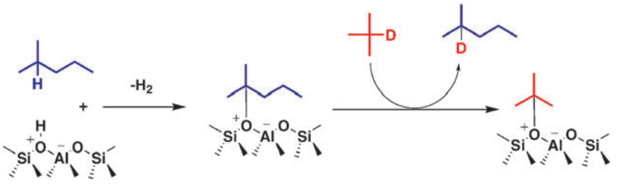


Scheme 1 Equilibrium between alkoxy species and carbenium ions.

Hydride transfer between alkanes *via* carbocation intermediates is a classical reaction in hydrocarbon chemistry in the large scale isomerisation reaction used to obtain high octane gasoline:

$$RH + R'^+ \leftrightarrows R^+ + R'H$$

In our experiments, the alkoxy species generated on the solid acid are tertiary substrates for which, due to steric hindrance, S_N2 reactions are not allowed.[13] We must admit for this reason that a small fraction liberates the carbenium ion intermediate in order to facilitate the hydride transfer. With the purpose of checking the reversibility of this reaction we carried out the following experiment: 2-methylpentane (100 µl, 0.75×10^{-3} mol) and 2-methylpropane-*2d* (18 ml gas, 0.75×10^{-3} mol) were recirculated over previously activated HUSY (250 mg) during 24 h under the same conditions as above, after which the hydrocarbon mixture was condensed and analysed by NMR. The ^{13}C NMR spectra show that the tertiary deuteriums and protons were equally redistributed over both isoalkanes resulting in the presence of the four compounds 2MP, 2MP-*2d*, isobutane and isobutane-*d*. Fig. 1 shows the ^{13}C spectrum of the mixture. Due to the isotope effect on ^{13}C chemical shifts and ^{13}C–D coupling the various lines are easy to assign. In comparison with the non deuterated alkanes the tertiary carbons connected to deuterium experience an upfield shift



Scheme 2 Deuteride transfer to the adsorbed 2-methyl-2-pentylium ion.

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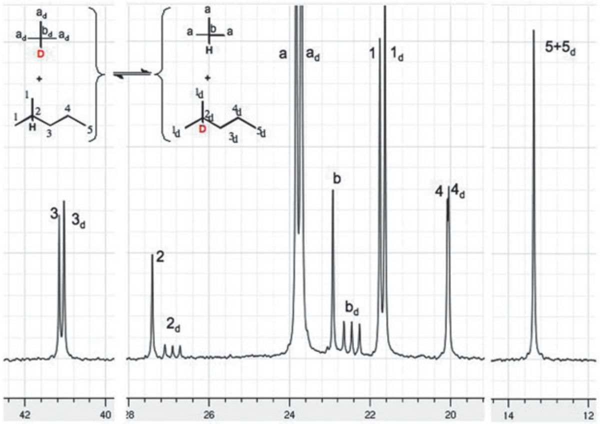
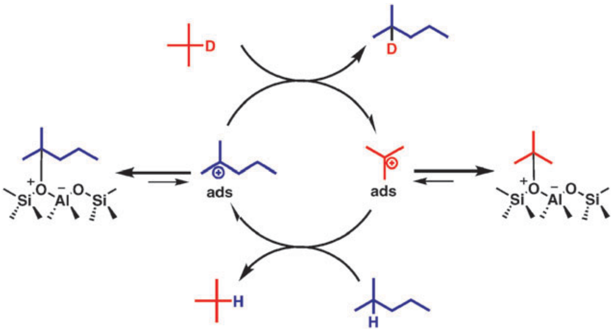


Fig. 1 ^{13}C spectrum of the mixture of monodeuterated and non deuterated 2-methylpropane (a and a_d methyl groups) and 2-methylpentane at equilibrium.



Scheme 3 Hydride and deuteride transfers between isoalkanes.

of 300 ppb and appear as a 1 : 1 : 1 triplet due to the J_{C-D} coupling of 1.9 Hz. The vicinal carbons (1 and 3 in 2MP-*2d*) and methyl carbons in 2-methylpropane-*2d* experience a smaller shift (β effect) of −80 to 100 ppb. Even a γ effect of 20 ppb can be noticed on carbon 4 in 2MP-*2d* whereas no differentiation is observable on remote carbon 5.

This redistribution of deuterium between the two isoalkanes suggests an equilibrium in which the alkoxy species and carbenium ions of both species participate as steady state reaction intermediates as illustrated in Scheme 3.

This shows that even if the most stable intermediates on solid acids are the alkoxy species, carbenium ions are necessary intermediates to rationalise hydrocarbon activation and reactivity. It further confirms the role of carbenium ions in the H/D exchange process between deuterated acidic solids and isoalkanes as described earlier.[14] In order to find out if the hydride transfers take place inside the zeolite cavities (possible confinement effect) or on the outer surface of the solid more investigations are necessary.

Notes and references

† Zeolite FAU (USY, Si/Al = 2.8; CBV500) was obtained from Zeolyst International in the NH_4^+ form and activated at 550 °C during 4 h. The number of exchangeable protons was determined using a method based on H/D exchange between D_2O and catalysts.[7]

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