Evidence for Carbanionic Intermediates During Exchange Between Butanes and Deuterium on Alumina

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Summary Examination of the exchange reactions between isobutane and deuterium, and n-butane and deuterium on alumina has revealed that the reactive hydrocarbon intermediates possess carbanionic character.

Studies of hydrogen–deuterium exchange reactions involving saturated hydrocarbons on alumina have been confined to propane,[1] methane,[2] and ethane.[3] In the case of propane[1] and methane[2] it appears that the exchange process takes place *via* adsorbed alkyl groups which are attached to electron-deficient centres. We report here the results obtained for the exchange of isobutane and n-butane on alumina because they provide direct evidence for the participation of carbanionic intermediates in these reactions.

The experimental technique was essentially that described previously.[4] The γ-alumina was prepared by heating a high purity boehmite (Laporte Industries Ltd.) at 900 K in air for 16 h (surface area by N_2 adsorption at 77 K = 120 $m^2 g^{-1}$). The catalyst (1·0 g) was treated with oxygen at 723 K prior to evacuation at this temperature (pressure $< 2 \times 10^{-4}$ N m^{-2}) for at least 15 h. The mixture usually consisted of hydrocarbon and deuterium at initial pressures of 0·95 and 9·6 kN m^{-2} respectively in a silica vessel (3×10^{-4} m^3).

The initial rate of reaction of n-butane ($1{\cdot}4 \times 10^{15}$ molecules $s^{-1} m^{-2}$) at 273 K was 2·3 times faster than the rate for isobutane, both compounds exhibiting stepwise exchange. After extensive exchange of isobutane at 425 K, the amounts of the [$^2H_8$]-, [$^2H_9$]-, and [$^2H_{10}$]-isomers were 40, 34, and <0·5% respectively showing that 9 of the hydrogen atoms were exchanging at least 100 times more rapidly than the tenth. Analysis of results for n-butane at 316 K by standard methods[5] showed that 6 hydrogen atoms were replaced 55 times more rapidly than the remaining 4.

These results indicate that the alkyl intermediates in the exchange reactions possess carbanionic character and that neither carbonium ions nor radical species are involved. If exchange occurred *via* alkyl radicals, the methine hydrogen would have been expected to react more rapidly than those in the methyl groups in isobutane on the basis of relative dissociation energies for the two types of carbon–hydrogen bonds[6] and, similarly, the methylene hydrogens would have reacted at least as rapidly as the methyl hydrogens in n-butane. Participation of carbonium ion intermediates, although compatible with the observation that 9 hydrogen atoms of isobutane exchange readily,[7] is not consistent with the similar rates found for isobutane and n-butane. Formation of carbonium ions would occur much more easily for isobutane.

Additional evidence for the involvement of alkyl carbanionic species is provided by the fact that the methyl hydrogens in n-butane exchange at a much higher rate than those in the methylene groups. This result is expected on the basis of the relative acidities for these two types of hydrogen atoms.[8]

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