Catalytic Activity of U^{III} towards Hydrogenation of Olefins

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It has been shown that UCl_3 in tetrahydrofuran can catalyse the hydrogenation of olefins by LiH or $LiAlH_4$ according to a mechanism involving two hydrogen atoms of the hydride.

Attempts to use f-block elements in homogeneous catalysis have been largely unsuccessful, even in the case of organometallic compounds. However, tri-allyluranium(IV) halide in the presence of Lewis acid has been claimed to give efficient polymerisation of olefins,[1] and more recently another class of U^{IV} organometallic compounds, the bis(pentamethylcyclopentadienyl)uranium (or thorium) dialkyls, was reported to produce CO activation and other interesting reactions.[2–4] The first example of a catalytic reaction using lanthanides was described by Evans.[5]

Among the published results, it is noteworthy that no U^{III}-catalysed reactions have been reported even though U^{III} is considered a more versatile metallic centre. As part of our interest in trivalent uranium chemistry we have investigated a simple system and found a new catalytic hydrogenation of olefins.

Trivalent uranium can be very conveniently produced by reduction of uranium tetrachloride in tetrahydrofuran (THF) by alkali metal hydrides[6,7] or $LiAlH_4$. The oxidation state of the uranium ion is easily determined by optical spectroscopy.[6] The catalytic activity of this solution can be demonstrated by bubbling ethylene into it, resulting in the appearance of ethane in the gas phase. It is well known that neither LiH nor $LiAlH_4$ in THF can reduce ethylene. In a typical run UCl_4 (10^{-4} mol) was introduced into THF (20 ml). The addition of $LiAlH_4$ (4×10^{-3} mol) produced the dark red colour characteristic of UCl_3. Ethylene (2×10^{-3} mol) was then introduced and after 30 min half of the ethylene had been transformed into ethane. The reaction may be continued until all the ethylene disappears.

With an excess of ethylene the reaction stopped when the $LiAlH_4$ was consumed and started again when more was added. This experiment was repeated with other alkenes: ethylene, propylene, but-1-ene, and *cis*- or *trans*-but-2-ene were easily reduced to ethane, propane, and butane. Isobutene was also reduced to isobutane but the reaction was slow. Butadiene undergoes a two-step hydrogenation *via cis*- and *trans*-butenes. In all cases the alkane was obtained as a gas above the solution. No hydrolysis was needed.

The mechanism of this reaction is not fully elucidated but it does exhibit some differences from the classical scheme for reduction with $LiAlH_4$. For instance, Ashby *et al.*[8] in a similar study using VCl_3 assumed that one hydrogen atom was provided by the hydride, the second coming from the hydrolysis. In order to establish unambiguously the origin of the two hydrogen atoms the reduction was carried out i, with $LiAlH_4$ in [$^2H_8$]THF and ii, with $LiAlD_4$ in undeuteriated THF, using ethylene and butadiene as substrates. The resulting hydrogenated compound was analysed by mass spectrometry. No incorporation of deuterium was found in case i, but with the deuteriated hydride (ii) two deuterium atoms were found in the resultant alkane.

Thus it is possible to infer a scheme where homolytic cleavage is involved. The appearance of an aluminium mirror on the wall of the reaction vessel can also be accounted for by this hypothesis. Lithium hydride can be used instead of lithium aluminium hydride but with some loss of efficiency. In other respects, preliminary results show that this behaviour of U^{III} is not general and, for instance, $(C_5H_5)_3U(THF)$ obtained similarly by reduction of $U(C_5H_5)_3Cl$ with $LiAlH_4$

does not exhibit any catalytic effect on the olefin hydrogenation.

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