Solutions containing Ruthenium(I) Species and their Importance in Catalytic Reactions

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RECENT reports[1] on the homogeneous catalytic activity of nonaqueous solutions of ruthenium trichloride under hydrogen prompts us to report our findings with such solutions in dimethylacetamide. In oxygen-free conditions, thermodynamically stable solutions of ruthenium(I) chloride complexes are readily prepared. The only reported ruthenium(I) species are some rather poorly characterized carbonyls.[2]

Hydrochloric acid solutions of "$RuCl_3,3H_2O$" which is a mixture of Ru^{III} and Ru^{IV}, are reduced autocatalytically by H_2 (1 atmos) at 80° to solutions containing Ru^{III};[3] solutions of Ti^{III} are required for the production of the blue chlororuthenate(II) species.[4] Gas-uptake measurements and spectrophotometric studies show that, at room temperature, solutions of "$RuCl_3,3H_2O$" in dimethylacetamide are rapidly and autocatalytically reduced by H_2 (1 atmos.) to Ru^{III}; this is followed by a slow reduction (*ca.* 15 hr.) to Ru^{II} a process which is first order in both Ru^{III} and H_2. At higher temperature (*ca.* 60°) a further reaction occurs in which the blue Ru^{II} solutions absorb 0·5 mol. of H_2, the process again being first order in Ru^{II} and in H_2. There is no evidence for the presence of a metal–hydrogen bond in the resulting brown solutions, which can also be produced by Ti^{III} reduction of Ru^{IV}–Ru^{III} solutions in dimethylacetamide; we conclude that the brown solutions contain Ru^{I} species. The mechanism of the reduction of Ru^{III} to Ru^{II}, and of Ru^{II} to Ru^{I}, in this medium is likely to involve heterolytic splitting of the H_2 molecule:[3,5,6]

$$Ru^{n+} + H_2 \rightleftharpoons RuH^{(n-1)+} + H^+ \qquad (1)$$

$$RuH^{(n-1)+} + Ru^{n+} \xrightarrow[\text{(ligands omitted)}]{\text{fast}} 2Ru^{(n-1)+} + H^+ \qquad (2)$$

In aqueous acid solutions the reverse of reaction (1) prevents reduction of Ru^{III}.[3,5]

The brown Ru^{I} solutions are air-sensitive and a stoicheiometric oxidation with oxygen yields Ru^{III}; reaction with carbon monoxide under mild conditions (60°, 1 atmos. CO) yields $Ru^{I}(CO)$ and $Ru^{I}(CO)_2$ successively in solution and the latter is oxidized, stoicheiometrically, to $Ru^{II}(CO)_2$, which can also be formed from reaction of Ru^{II} with 2 mol. of carbon monoxide. We have isolated triphenylphosphine complexes with the Ru^{I} solutions but have not yet successfully separated and characterized these although molecular weight studies indicate that they are dimeric; again no metal–hydrogen bonds have been detected in these solids.

The ruthenium(I) chloride solution is active for homogeneous hydrogenation of olefinic substrates under mild conditions (1 atmos. H_2, 80°) and preliminary kinetic results, with maleic acid as substrate, show that the reaction is first-order in hydrogen, between zero and first order in olefin, half order in Ru^{I}, and independent of acid. There is no evidence of complexing between Ru^{I} and maleic acid under the hydrogenation conditions. The following mechanism is consistent with the data:

$$Ru^{I}_2 \overset{K}{\rightleftharpoons} 2\,Ru^{I}$$

$$Ru^{I} + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru^{I}H_2$$

$$Ru^{I}H_2 + \text{olefin} \xrightarrow{k_2} Ru^{I} + \text{saturated product.}$$

with K being small, and $k_{-1} > k_1$. There is a report[7] that solutions of ruthenium trichloride in dimethylformamide homogeneously hydrogenate dicyclopentadiene although no kinetic data or mechanism were presented.

Ruthenium(I) species may thus be readily generated in nonaqueous solvents, particularly if nonprotonic, by the hydrogen reduction of higher valency species and should be considered as possible intermediates in reactions catalyzed by ruthenium chlorides.

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