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Preliminary communication

CATALYTIC FIXATION OF CARBON DIOXIDE UNDER MILD CONDITIONS IN THE SYSTEM: $TiCl_4$ + Mg + H_2 IN TETRAHYDROFURAN

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Summary

Catalytic fixation of H_2 and CO_2 was carried out in the system $TiCl_4 \cdot 2THF$ + Mg + THF and as the result magnesium formate was obtained.

We have previously [1] reported the formation of the complex $[THFMg_2Cl_2Ti]_2$ (I) in the system $TiCl_4 \cdot 2THF$ + Mg + THF under an argon atmosphere. The complex in this system combines with two moles of carbon dioxide, yielding the complex $[THFTi(OOCH)_2MgCl_{1.5}]$ (II) which reacts with C_2H_5I to give the ester $HCOOC_2H_5$, and on hydrolysis HCOOH.

Now we have succeeded for the first time to catalytically synthesise magnesium formate directly from hydrogen, carbon dioxide and metallic magnesium under mild conditions. Catalytic fixation of H_2 and CO_2 was carried out in the system $TiCl_4 \cdot 2THF$ + Mg + THF (A); $TiCl_4 \cdot 2THF$ in a solution of tetrahydrofuran (THF) when treated with excess metallic magnesium. The solution changes colour from yellow via green to black. 20 h after the reaction was started argon was replaced by hydrogen. The fixation of H_2 is catalytically possible only when free metallic magnesium is present in the system. In 24 h at a molar ratio $TiCl_4$/Mg 1/20, 3 moles H_2 per mole titatium are fixed. If the system $TiCl_4 \cdot 2THF$ + Mg + THF + H_2 (B) with fixed hydrogen was used and carbon dioxide was introduced, the CO_2 fixation was achieved catalytically. The amount of fixed carbon dioxide depends on the amount of fixed hydrogen before introduction of CO_2 to the system, fixed $H_2/CO_2 \approx 0.5$. At repeated introduction of hydrogen and carbon dioxide to the system with fixed carbon dioxide, the reaction continued. By alternate introduction of CO_2 and H_2 to the system we succeeded in fixation of some 15 moles of carbon dioxide per mole titanium at 50fold magnesium excess. If the catalytic products of H_2 and CO_2 fixation after evaporation of tetrahydrofuran under vacuum were treated with C_2H_5I, all the fixed CO_2 converted into ethyl formate, and the reaction with dilute sulphuric acid yielded formic acid.

If, after reduction of the system $TiCl_4 \cdot 2THF$ + Mg + THF under argon atmosphere the H_2 and CO_2 mixture was introduced, only CO_2 was fixed, the compound $[THFTi(OOCH)_2MgCl_{1.5}]$ was formed, and the reaction was not catalytic. This fact indicates the hydrogen transfer to magnesium only occurs when titanium in the active complex I has an empty coordination site. Hence it could be expected that the catalytic fixation process of H_2 and CO_2 should be as follows: complex I formed under argon atmosphere reacts with H_2 giving rise to the intermediate compound III, which in reaction with metallic magnesium yields magnesium hydride.

$$n[THFCl_2Mg_2Ti]_2 + n\,H_2 \rightarrow n[THFCl_2Mg_2H_2Ti]_2 \xrightarrow{n\ Mg} n[THFCl_2Mg_2Ti]_2 + n\,MgH_2 \qquad (1)$$

It is most likely that catalytic fixation of carbon dioxide follows via the intermediate compound III and via MgH_2.

$$[THFMg_2Cl_2H_2Ti]_2 + 4CO_2 + 2Mg \rightarrow [THFCl_2Mg_2Ti]_2 + 2(HCOO)_2Mg \qquad (2)$$

$$MgH_2 + 2CO_2 \rightarrow (HCOO)_2Mg \qquad (3)$$

This reaction is possible as long as MgH_2 is present in that system. The repeated introduction of H_2 and CO_2 to the system with magnesium excess alters the course of reactions 1, 2 and 3.

The reaction in the system $TiCl_4 \cdot 2THF$ + Mg + THF does not occur at all, at attempts to carry out the reaction under CO_2, or H_2 and CO_2 atmosphere failed. The most likely cause is deactivation of the metallic magnesium by carbon dioxide. In such conditions Ti^{IV} cannot be reduced and complex I can not be formed.

Reference

1 B. Jeżowska-Trzebiatowska and P. Sobota, J. Organometal. Chem., 76 (1974) 43.