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Preliminary communication

DIHYDROGEN ACTIVATION PROMOTED BY HOMONUCLEAR ION PAIRS INVOLVING COBALT(II) AND COBALT(—I)

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Summary

Acyltetracarbonyls have been shown to be formed from the reaction of hexene with CO/H_2 (1/1) mixtures ($P(CO) = P(H_2) = 300$ mmHg) in THF/H_2O at room temperature catalysed by homonuclear Co^{II}, Co^{-I} ion pairs.

We recently showed that the disproportionation of $Co_2(CO)_8$ in THF occurs only in the presence of water (eq. 1) [1].

$$\tfrac{3}{2}\mathrm{Co_2(CO)_8} \xrightleftharpoons{\mathrm{THF,\ H_2O}} 2\ \mathrm{Co(CO)_4^-} + \mathrm{Co^{2+}L}_n + 4\mathrm{CO} \qquad \text{(I)}$$

($L = H_2O$, THF, $Co(CO)_4^-$, bound through oxygen atom)

Under suitable conditions, $Co(CO)_4^-$ competes with water and THF for the coordination sphere of Co^{2+} and we observed ion pairing phenomena in these solutions [1]. Since the same transition metal is present in both anion and cation, we refer to interaction "homonuclear ion pairing". The reversibility of reaction 1 was interpreted in terms of such homonuclear ion pairing, which allows CO-mediated electron transfer from $Co(CO)_4^-$ to Co^{2+} to occur. The relevance of these observations to a better understanding of dihydrogen activation promoted by cobalt carbonyls is revealed by the new observation, reported here, that syngas absorption and formation of acylcobalt tetracarbonyls, C_7 aldehydes and C_{13} ketones from 1-hexene occur at room temperature and atmospheric pressure when homonuclear ion pairing equilibria between Co^{2+} and $Co(CO)_4^-$ are operating.

A 0.03 *M* solution of $Co_2(CO)_8$ in wet THF (30 ml) ($H_2O/Co_2(CO)_8$ molar ratio 2) was equilibrated with CO/H_2 1/1 at 23°C under 1 atm of total pressure

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($P(CO) = P(H_2) = 300$ mmHg).

Upon addition of 4 ml of 1-hexene (32 mmol) gas absorption began, and the reaction was monitored for 198 h gasvolumetrically and by IR spectroscopy, and the organic products were determined by GC and GC/MS.

During the first 10 h gas absorption was relatively fast and it then settled at a constant rate (0.1 mmol/h) for the remaining 186 h of the observations. At the beginning CO was preferentially consumed, but subsequently CO/H_2 reacted in 1/1 ratio. The IR spectra of the solution showed that acylcobalt tetracarbonyls [2] (2104 m, 2042 vs, 2021 vs, 2001 m and 1710 w cm^{-1}) were formed during the initial steps, and the absorptions due to other cobalt carbonyl species decreased correspondingly [1]. After 198 h, the concentration of acylcobalt tetracarbonyls slightly decreased, while the bands due to $Co(CO)_4^-$ in various environments increased, probably due to small amounts of water formed by aldehyde condensation. At 198 h, 1-hexene had reacted to give C_7 aldehydes (18% conversion, normal/branched/internal = 3.9/3.9/1), 2- and 3-hexenes (15%), C_{13} ketones (8%, 5-methyldodecan-6-one/tridecan-7-one 1.2) and minor amounts of C_7 alcohols and 2-n-pentyl-2-nonenal. Over long reaction times, amounts of CO_2 were formed, suggesting that hydrogen atoms incorporated in the products can also come from water, through a water gas shift reaction.

Solutions of $Co_2(CO)_8$ in anhydrous THF, or completely disproportionated solutions in THF containing more than 3% of H_2O, which prevents ion pairing, do not promote the hydroformylation under these mild conditions.

The products of the reaction suggest [3] the intermediacy of $HCo(CO)_4$, but this was never detected in our solutions. The reversibility of reaction 1 and the present observations prompt us to regard the Co^{2+} involved in homonuclear ion pairing as a coordinatively unsaturated and electron deficient species, probably able to activate dihydrogen.

References

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