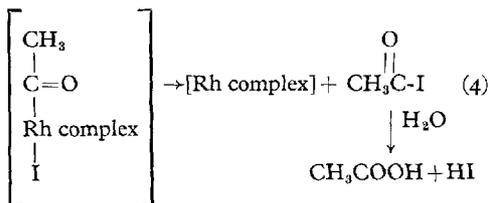


the original d⁸ rhodium(I) complex. Several different reaction modes can be proposed to describe this step. These include a direct hydrolysis of the acyl-rhodium(III) complex by water, a specific methanol-assisted solvolysis of this complex, or reductive elimination of acetyl iodide from the complex followed by immediate hydrolysis of the acetyl iodide to yield acetic acid, the starting rhodium(I) complex and HI. Of these possibilities, we favour the latter, as shown:



This overall reaction scheme is consistent with the observed reaction order dependencies and with the observed constancy of CH₃I concentration during most of the reaction, if one assumes that reaction (2) is the rate-determining step. According to this scheme, the role played by rhodium complexes is threefold, consisting of the rate-determining oxidative addition step, which

results in introduction of the methyl group into the coordination sphere and two subsequent rapid steps involving first an exceptionally facile carbon monoxide insertion reaction and then a facile reductive elimination step. This sequence leads to the establishment of a catalytic cycle. This multiple step process all occurs with a degree of selectivity that is remarkable even for a homogeneous catalytic reaction.

It has been shown (4) that a heterogeneous analogue of the homogeneous catalyst can be prepared and that the kinetics of methanol carbonylation are identical for the solid supported rhodium complex and the homogeneous liquid-phase catalyst systems. This suggests that, in spite of the obvious physical differences between these catalysts, a similar reaction mechanism is probably operative.

References

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Superconductivity in Palladium-Hydrogen Alloys

Superconducting properties have not generally been associated with the platinum group metals. However, in 1972 T. Skoskiewicz of the Polish Academy of Sciences reported that palladium enriched with hydrogen possesses superconductivity, with a transition temperature T_c of ~5 K when H:Pd=0.9.

Recent research in this field has been briefly summarised by R. Taylor (*New Scientist*, 1974, 64, (923, Nov. 14), 473), who comments on work by B. Stritzker et al. of the Nuclear Research Centre at Jülich aimed at raising T_c (*Z. Physik*, 1974, 268, (2), 261-264) and by C. A. Mackliet et al. at the Naval Research Laboratory at Washington, D.C., on the specific heat of superconducting Pd-H alloys (*Solid State Commun.*, 1974, 15, (2), 207-210).

The Jülich team, which had first raised T_c to 9.4 K by H⁺ ion bombardment to increase

the H:Pd ratio on the surface of palladium foils to more than 1, had also shown that the substitution of deuterium for hydrogen can raise T_c to 11 K. It is suggested that these additions may be modifying the lattice vibrations, or phonons, in the solids, thereby changing their coupling to the electrons, since it is the electron-phonon interaction which is believed to lead to superconductivity. Stritzker has now shown that alloying of suitable amounts of copper, silver or gold to Pd-H can raise T_c still more (to 16.6 K for 45 per cent Cu-Pd when H:Pd=0.7; the optimum silver and gold concentrations are smaller).

Mackliet and his co-workers have discovered that, whereas the peaks in the specific heat of superconductors usually drop sharply above T_c to the normal state, i.e. the superconducting state is more ordered, in Pd-H the drop is less marked.

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