

# The Production of Acetic Acid

## RHODIUM CATALYSED CARBONYLATION OF METHANOL

By James F. Roth

Monsanto Co., St. Louis, Missouri

*The new Monsanto Company acetic acid process employs a rhodium-based homogeneous liquid-phase catalyst which promotes methanol carbonylation in high selectivity and at low pressures. This article describes some of the chemistry involved in this process, with particular emphasis on the role played by rhodium complexes in the catalytic cycle.*

The new acetic acid plant built by the Monsanto Company at Texas City is designed to operate at lower pressures than previous plants. The output of 300 million pounds per year of acetic acid derived from methanol is the result of the successful development of a homogeneous catalyst based on rhodium. This new catalyst was reported recently (1, 2) for the low pressure liquid-phase synthesis of acetic acid from methanol and carbon monoxide.

Previously, workers at B.A.S.F. described a commercial acetic acid process, based on methanol carbonylation and an iodine-promoted cobalt catalyst, that employs carbon monoxide pressures of about 7500 lb/in<sup>2</sup> and gives a molar selectivity to acetic acid of about 90 per cent (3). The new rhodium catalyst can be used at much lower pressures and affords reaction rates essentially independent of carbon monoxide partial pressure in the range between 200 and 1800 lb/in<sup>2</sup>. It effects methanol carbonylation in 99 per cent selectivity and displays similar selectivity even when the carbon monoxide feed contains as much as 50 per cent hydrogen.

### Catalyst Composition

The carbonylation catalyst is comprised of two components, a soluble rhodium complex and an iodide promoter. The catalytic species is believed to consist of a coordination complex of rhodium with carbon monoxide and

halogen ligands. A wide variety of rhodium compounds and iodine compounds have been found to give similar reaction rates and product distribution. This suggests that these tend to form the same active catalytic species. Solvent effects, e.g. faster rates in more polar solvents, indicate that the active species may be ionic.

### Kinetics of Methanol Carbonylation

The overall stoichiometry of the acetic acid synthesis is represented simply by



The results of kinetics studies of the rhodium-catalysed homogeneous reaction have been reported (2) and have several interesting and unusual features. The reaction was found to be zero order with respect to both reactants—methanol and carbon monoxide. An obvious consequence of the zero order dependence on carbon monoxide pressure is the ability to obtain high reaction rates at low reaction pressures. With respect to catalyst components, it was found that reaction rate was directly proportional to both the rhodium and iodide concentrations. Another key observation made relates to the fate of the methyl iodide (formed via reaction of  $\text{CH}_3\text{OH} + \text{HI}$ ) concentration during the reaction. This was determined by analysis of timed liquid samples removed during the course of the reaction. It was observed that

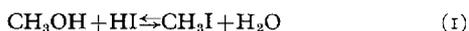
*The Monsanto Co. acetic acid plant at Texas City uses a new process based on a rhodium homogeneous liquid-phase catalyst which gives higher selectivity for the carbonylation of methanol at lower pressures than earlier processes*

methyl iodide reached a steady-state concentration very rapidly, that this concentration remained constant over most of the reaction, and that the rate of formation of acetic acid was constant during the same period.

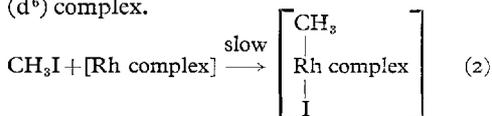
### Mechanism of the Reaction

All of the kinetics results can be rationalised by assuming that the reaction proceeds in a stepwise manner, as follows:

The initial step in the catalytic cycle consists of a rapid conversion of methanol to methyl iodide, for example, via:



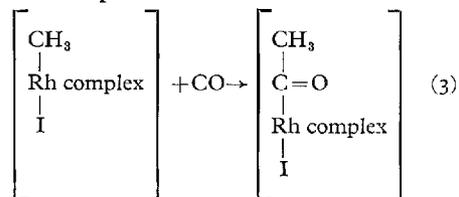
Then, an oxidative addition of methyl iodide to a Rh(I) complex ( $d^8$  square planar) occurs [Equation (2)]. This results in formation of a six-coordinate alkyl-rhodium(III) ( $d^6$ ) complex.



Rapid insertion of carbon monoxide, present as a ligand in the Rh complex, into

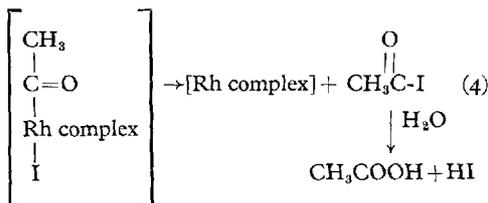


the rhodium-alkyl bond occurs to yield an acyl-rhodium(III) complex. This is accompanied by subsequent or simultaneous replacement of CO in the rhodium coordination sphere.



Finally, the  $d^6$  acyl-rhodium(III) complex reacts to produce acetic acid and to regenerate

the original d<sup>8</sup> 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 CH<sub>3</sub>I 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

- 1 F. E. Paulik and J. F. Roth, *J. Chem. Soc., Chem. Commun.*, 1968, 1578
- 2 J. F. Roth, J. H. Craddock, A. Hershman and F. E. Paulik, *Chem. Technol.*, 1971, 600-605
- 3 H. Hohenschultz, N. von Kutepow and W. Himmele, *Hydrocarbon Process.*, 1966, 45, 141
- 4 K. K. Robinson, A. Hershman, J. H. Craddock and J. F. Roth, *J. Catalysis*, 1972, 27, (3), 389

## 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<sub>c</sub> 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<sub>c</sub> (*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<sub>c</sub> to 9.4 K by H<sup>+</sup> 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<sub>c</sub> 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<sub>c</sub> 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<sub>c</sub> to the normal state, i.e. the superconducting state is more ordered, in Pd-H the drop is less marked.

F. J. S.