The Decomposition of Formic Acid catalysed by Soluble Metal Complexes

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MANY papers have recently described the abstraction of hydrogen and carbon monoxide from organic solvents by transition-metal complexes to give metal hydrides and carbonyls respectively (see refs. quoted in reference 1). Most of these reactions are stoicheiometric on the metal or at best give only a few catalytic cycles. Notable exceptions are the catalytic decarbonylation[2] of acyl halides by [RhCl(PPh$_3$)$_3$] and the catalytic dehydrogenation of alcohols by some rhodium salts.[3] We now report that many phosphine-stabilised complexes of transition metals, particularly iridium and ruthenium, are excellent homogeneous catalysts for the decomposition of formic acid to hydrogen

and carbon dioxide (approx. 1:1) and the system can be used to reduce functional groups. It has already been observed[4] that [PtCl$_2$(PEt$_3$)$_2$] abstracts hydrogen from aqueous formic acid to give [PtHCl(PEt$_3$)$_2$] and that ruthenium chloride abstracts carbon monoxide from aqueous formic acid to give ruthenium carbonyl chlorides,[1] but neither of these reactions were cyclic on the metal.

Most of our reactions have been carried out in acetic acid under reflux containing 3—30% formic acid and 10^{-3} to 10^{-2} M catalyst. The reactions go at lower temperature with the more active catalysts, and solvents such as esters can be employed. The results in the Table show how the

rate of decomposition (estimated from gas evolution) of formic acid (0·75 M) in acetic acid varies with the structure of the catalyst.

TABLE

Decomposition of 0·75 M-formic acid in acetic acid under reflux

Catalyst	Molar Conc. $\times 10^3$	Rate (mole.l.$^{-1}$ hr.$^{-1}$)
PtCl$_2$(PBu$_3$)$_2$	6·1	0·02
RuHBrCO(PEt$_2$Ph)$_3$ [5]	6·2	2·8
RuHCl(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$ [6]	1·7	2·0
IrCl$_3$(PEt$_2$Ph)$_3$ [7]	6·2	0·3
IrCl$_3$(PBu$_3$)$_3$ [7]	6·2	0·7
IrH$_2$Cl(PPh$_3$)$_3$ [8]	6·2	7·36

Under these conditions we find that platinum complexes of general formula [PtCl$_2$(PR$_3$)$_2$] are superior to their nickel and palladium anologues, and ruthenium complexes such as [RuHBrCO-(PR$_3$)$_3$] [5] and [RuHCl(diphos)$_2$], [6] where diphos is a chelating bisphosphine ligand, are more active than the corresponding osmium complexes. Rhodium-(III) complexes [RhCl$_3$(PR$_3$)$_3$] [9] are initially very active catalysts but during the reaction they are reduced to [RhClCO(PR$_3$)$_2$], [10] which have only slight activity. All the iridium complexes containing monodentate phosphine ligands which we have investigated, including [IrClCO(PR$_3$)$_2$], [11] are good catalysts, the most active being [IrH$_3$(PPh$_3$)$_3$]. [12] A solution of this complex (9 × 10^{-3} M) in refluxing acetic acid catalyses the decomposition of formic acid (1·25 M) at an initial rate of *ca.* 80 mole. l.$^{-1}$ hr.$^{-1}$ falling to about half this value after 11,000 cycles on the iridium, but the catalyst life can be increased by adding free triphenylphosphine.

During the reaction the catalysts are converted to complexes containing phosphine, carbonyl, hydrido, and acetate ligands but sometimes pure complexes can be isolated. Thus when [IrClCO-(PPh$_3$)$_2$] is the catalyst, high yields of [Ir$_2$HClCO-(PPh$_3$)$_2$] can be isolated[13] in the early stages of the reaction.

Although metal carbonyls are formed in the reaction no carbon monoxide could be detected in the evolved gases by mass spectra or g.l.c. Occasionally methyl formate is detected along with small amounts of butyl esters and esters of malonic acid. Radioactive tracer work shows that small amounts of carbon dioxide (depending on the catalyst and conditions) comes from the acetic acid, particularly in the early stages of the reaction.

When aldehydes are added to these systems they can be reduced efficiently to alcohols and the evolved gases contain much more carbon dioxide than hydrogen. For example at 50°, n-butyralde-hyde (1·0 M) in acetic acid can be converted to n-butanol in quantitative yield based on aldehyde and in about 70% yield based on formic acid consumed in the presence of [IrH$_3$(PPh$_3$)$_3$] (5 × 10^{-3}M).

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