Homogeneous Catalytic Decomposition of Formic Acid by Rhodium and Iridium Iodocarbonyls and Hydriodic Acid

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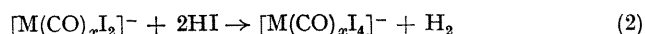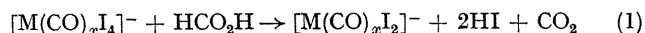(Central Research Department, Monsanto Co , St Louis, Missouri 63166)

Summary Decomposition of formic acid to hydrogen and carbon dioxide has been observed in the presence of homogeneous catalyst systems consisting of rhodium or iridium iodocarbonyls and hydriodic acid, a mechanism is suggested involving discrete steps for the production of the hydrogen and carbon dioxide

RECENTLY there have been several reports[1,2] of studies on the action of formic acid on rhodium(III) and iridium(III) halides in hydrohalic acids The investigations showed that in chloride- or bromide containing systems reduction occurred and the final products were $M^I(CO)_2X_2^-$ ions By contrast the only species obtained from iodide-containing rhodium systems were rhodium(III) iodocarbonyl derivatives[1,2] This apparent order of stability of the halide complexes toward reduction would be novel and some theoretical justification was attempted[1] We present some further experimental results on these systems which suggest an alternate explanation

We have studied (by g l c) the gaseous products of the experiments described previously and some related experiments We find that rhodium or iridium halides in the presence of hydrochloric or hydrobromic acids are reduced by formic acid to the univalent metal halogenocarbonyl anions with concomitant evolution of carbon dioxide However, in the presence of iodide, homogeneous catalytic decomposition of the formic acid to hydrogen and carbon dioxide (1 1) is observed † E g , 70% aqueous formic acid is decomposed by a catalyst system comprising NaI (2 8 M) and Rh (7 × 10⁻² M) at a rate of 0 31 mol l⁻¹ h⁻¹ at 100° § The corresponding iridium system at the same concentrations of metal and iodide catalyses the reaction at approximately one third of the above rate ¶ As already mentioned, the reduction of the metal(III) halides by formic acid is accompanied by evolution of CO_2 and we find that the maximum rate of evolution accompanying the reduction of $[Ph_4As][RhBr_4(CO)MeOH]$ by 70% aqueous formic acid containing 2 8 M HBr is almost exactly half of the rate of total gas evolution observed in the catalytic decomposition of formic acid observed in the iodide-containing rhodium

system Further, we have previously described[3] that $Rh^I(CO)_2I_2^-$ ions are rapidly oxidized by hydriodic acid giving hydrogen and rhodium(III) iodocarbonyls, whereas oxidation of $Rh(CO)_2X_2^-$ (X = Cl or Br) by aqueous hydrochloric acid or hydrobromic acids at 100° could not be detected Thus, we feel a plausible explanation for the catalytic decomposition of formic acid in the iodide containing systems is as in reactions (1) and (2)

$$[M(CO)_xI_4]^- + HCO_2H \rightarrow [M(CO)_xI_2]^- + 2HI + CO_2 \quad (1)$$

$$[M(CO)_xI_2]^- + 2HI \rightarrow [M(CO)_xI_4]^- + H_2 \quad (2)$$

(M = Rh or Ir, x = 1 or 2)

If the conditions are such that step (1) is rate limiting the predominant species present in solution is expected to be the trivalent metal complex The conditions described previously[1,2] involve high concentrations of HI relative to the metal and since we find that the rate of reaction (2) increases with increasing HI concentration, attempts to isolate complexes from systems with these high concentrations always result in isolation of rhodium(III) or iridium(III) halogenocarbonyl species It follows that if the conditions are chosen so that reaction (2) is rate determining then it should be possible to isolate univalent metal complexes from iodide-containing systems Addition of 3 mol equiv of iodide per rhodium to a solution in 70% aqueous formic acid containing Rh (7 × 10⁻² M) and HBr (0 3 M) at equilibrium [i e , all rhodium(I)] results in evolution of traces of H_2 and CO_2 but the solution remains pale and addition of a solution of Ph_4AsCl in water results in precipitation of $[Ph_4As][Rh(CO)_2I_2]$ Similarly, addition of Ph_4AsCl to 70% aqueous formic acid containing Ir (4 2 × 10⁻² M) and HI (0 27 M) after equilibrium has been established precipitates a mixture of $[Ph_4As][Ir(CO)_2I_2]$ and $[Ph_4As][Ir(CO)_2I_4]$, further evidence for the two-step reaction mechanism already proposed

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† Traces of hydrogen and carbon dioxide were observed from the iridium-hydrobromic acid system but the rates were too slow for accurate measurement

‡ The rhodium is most conveniently added as $[Rh(CO)_2Cl]_2$.

§ There is a simultaneous decomposition of the formic acid to CO and water catalysed by hydrohalic acids in the absence of the metal complexes The rate is about one tenth that of the metal catalysed reaction to $H_2 + CO_2$ described in this particular example although we have noted certain conditions where the metal complexes can also markedly increase the rate of formic acid decomposition to $CO + H_2O$

¶ Certain iridium–phosphine complexes are known to catalyse formic acid decomposition (R S Coffey Chem Comm , 1967, 923) in the absence of hydrohalic acids The rhodium and iridium systems described in this work are unstable in the absence of excess of halide being reduced to metal

[1] R Colton R H Farthing and J E Knapp Austral J Chem 1970 23 1351
[2] M J Cleare and W P Griffith J Chem Soc (A) 1970 2788
[3] D Forster Inorg Chem 1969 8 2556