MECHANISM OF THE DEHYDROGENATION OF FORMIC ACID BY IRIDIUM AND RHODIUM COMPLEXES

E. N. YURTCHENKO and N. P. ANIKEENKO

Institute of Catalysis, Novosibirsk 90, USSR

Received March 1, 1974

The homogeneous catalytic process HCOOH $\rightarrow$ H$_2$ + CO$_2$ has been studied in the presence of carbonyl-free phosphine complexes of iridium (I) and (III), and rhodium (I). The rupture of the C - H bond has been found to be the rate-determining step. The halide ion and phosphine are first substituted by formate ion in the coordination sphere of the metal. The reaction mechanism and its peculiarities are discussed.

Recently /1, 2/ the regularities of the homogeneous catalytic dehydrogenation of HCOOH in the presence of IrClCO(PPh$_3$)$_2$ and IrCl$_3$(PPh$_3$)$_2$ were described. In this report we shall discuss the mechanism of this reaction and its features in the presence of a series of iridium and rhodium complexes.

EXPERIMENTAL

IrCl$_3$COL$_2$ type compounds were prepared according to Ref. /3/. Ir$_3$COL$_2$ was obtained by treating IrClCOL$_2$ in tetrahydrofuran with a tenfold excess of KI in air. IrCl$_3$L$_3$, IrXCOL$_2$, RhClCOL$_2$ and RhClL$_3$ were prepared as in Refs.
The reaction was followed in a solvent mixture containing 10 v/v% formamide and 90 v/v% dioxan. The concentration of the complexes was $(4-6) \times 10^{-1}$ M and that of the acid $2.2 \times 10^{-2}$ M. The evolution of reaction products was measured volumetrically. The technique of the investigation and the reaction conditions have been described in detail in Ref. /2/.

RESULTS AND DISCUSSION

Under the above conditions the reaction is first order with respect to both the acid and the metal complex. Addition of excess halogen slows down the reaction. Addition of excess phosphine produces a more complex effect; in some cases an increase in the reaction rate was observed. Table 1 shows the reaction order as a function of the halogen and phosphine, together with the pseudo-first order rate constants. For IrClCO(PPh$_3$)$_2$ and IrCl$_3$(PPh$_3$)$_2$ the rate constants at 50 °C are 9.8 and $48.8 \times 10^{-4}$ sec$^{-1}$, respectively /1/. An increase in the acidity up to $3 \times 10^{-3}$ M HClO$_4$ does not considerably change the reaction rate. * Comparison of the reaction rates in the presence of HCOOH, HCOOD and DCOOD shows that only in the last case does the reaction rate slow down 1.8–2.4 times. In Table 2 the values of the activation energy are presented for some of the complexes examined.

A comparison of the results reported in Refs. /1, 2/ and those listed in Table 1 shows that the slow-down due to the excess halide ion and phosphine

*HCOOH is an acid of medium strength ($K_a = 1.8 \times 10^{-4}$) and at the concentration of $2.2 \times 10^{-2}$ M in water the proton concentration would be $2 \times 10^{-3}$ g-ion/L. As the dielectric constant of the solution is 14 /2/, the proton concentration must be much lower.