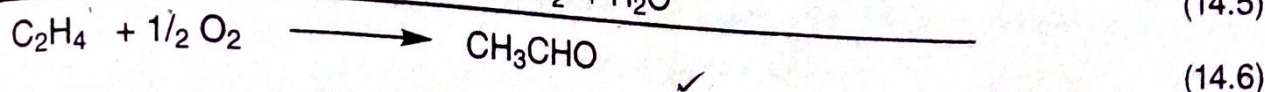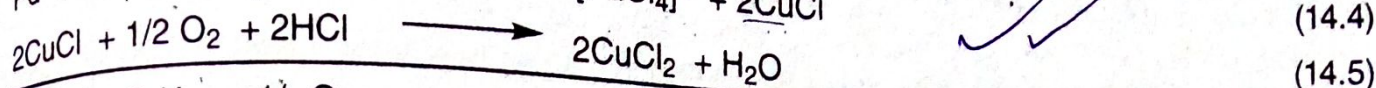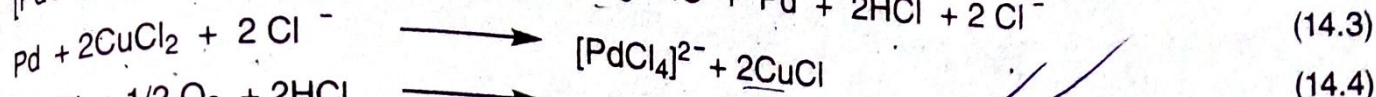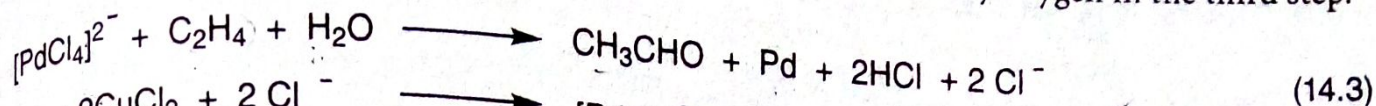## 14.6. THE WACKER PROCESS

In the 1950s, Wacker Chemie discovered that ethylene could be oxidised with high efficiency to acetaldehyde or to vinyl acetate in the presence of acetic acid.

$$CH_2=CH_2 + \tfrac{1}{2} O_2 \longrightarrow CH_3CHO \longrightarrow CH_3COOH \qquad (14.1)$$

$$CH_2=CH_2 + \tfrac{1}{2} O_2 + CH_3COOH \longrightarrow CH_2=CHOC(O)CH_3 \qquad (14.2)$$
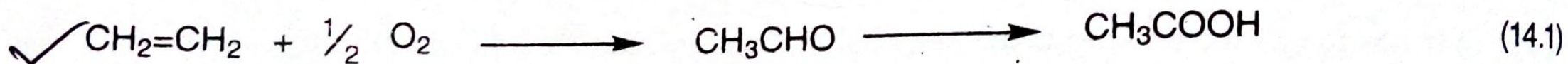
Stoichiometric oxidation of ethylene to acetaldehyde by aqueous $PdCl_4^{2-}$ along with the deposition of metallic palladium has been known even before the beginning of twentieth century. In 1959, J Smidt and W Hafner of Wacker Chemie, discovered that the reaction could be made catalytic in

Pd by using a cocatalyst CuCl$_2$, which could re-oxidise Pd(0) back to Pd(II). The reaction can be written in three steps. The first step is the oxidation of ethylene to acetaldehyde whereby Pd metal is obtained. The second step uses cupric chloride to oxidise Pd back to the soluble PdCl$_4^{2-}$ form. The cuprous chloride formed is re-oxidised back to the cupric form by oxygen in the third step.

$$[PdCl_4]^{2-} + C_2H_4 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl + 2 Cl^- \qquad (14.3)$$

$$Pd + 2CuCl_2 + 2 Cl^- \longrightarrow [PdCl_4]^{2-} + 2CuCl \qquad (14.4)$$

$$2CuCl + 1/2\, O_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O \qquad (14.5)$$

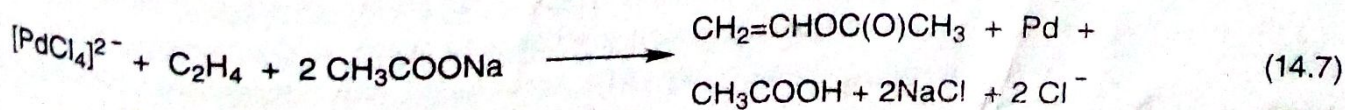$$\overline{C_2H_4 + 1/2\, O_2 \longrightarrow CH_3CHO} \qquad (14.6)$$

In reality, the commercial processes operate by two methods—one involving two stages and the other a single stage. In the two stage method, ethylene is oxidised to acetaldehyde in a dilute HCl solution containing PdCl$_2$ and CuCl$_2$ (10 bar, 100–110°C). Heat produced in the reaction is used to separate the volatile acetaldehyde by fractionation without the decomposition of the catalyst. Once the catalyst activity is lost, the solution is circulated through a second reactor where air is used to regenerate CuCl$_2$ and the CuCl$_2$ regenerates the PdCl$_4^{2-}$. After this, the solution is sent back to the first stage for reaction with ethylene.

In the single stage process, the O$_2$/C$_2$H$_4$ mixture is fed to an aqueous solution containing PdCl$_2$ and CuCl$_2$ (3 bar, 100–120°C). The catalyst is regenerated in situ. Mechanistic studies for the Wacker process gave the following rate equation.

$$\text{Rate} = k\frac{[PdCl_4^{2-}][C_2H_4]}{[Cl^-]^2[H^+]}$$

The rate equation implies that during the process, PdCl$_4^{2-}$ has to gain an ethylene unit and lose two chloride ions and a proton. The various steps thought to be involved in the mechanism are shown in the catalytic cycle (Fig. 14.5). The first step involves the coordination of the alkene as a π complex. In the next step, a solvent water molecule converts this alkene to a β-hydroxy ethyl σ complex of palladium. This can be envisaged to occur by coordination of a water molecule to the metal which loses a proton resulting in an OH group bound to the metal followed by a migratory insertion of the hydroxyl group on the alkene. This proposal was later found to disagree with the detailed mechanistic studies carried out using deuterium labelled alkenes. The presently accepted mechanism shows that the metal coordinated alkene is attacked by a free water molecule from the solvent, converting it to a β-hydroxy ethyl σ complex. In the next step, a β hydrogen transfer occurs converting the σ complex to a vinyl alcohol π complex. This coordinated vinyl alcohol, by multiple insertion elimination steps, rearranges to give the stable aldehyde. In the case of solvents other than water, the final step does not occur and the complex dissociates to give the vinyl product. For example, by using acetic acid as solvent, one can get vinyl acetate as the product.
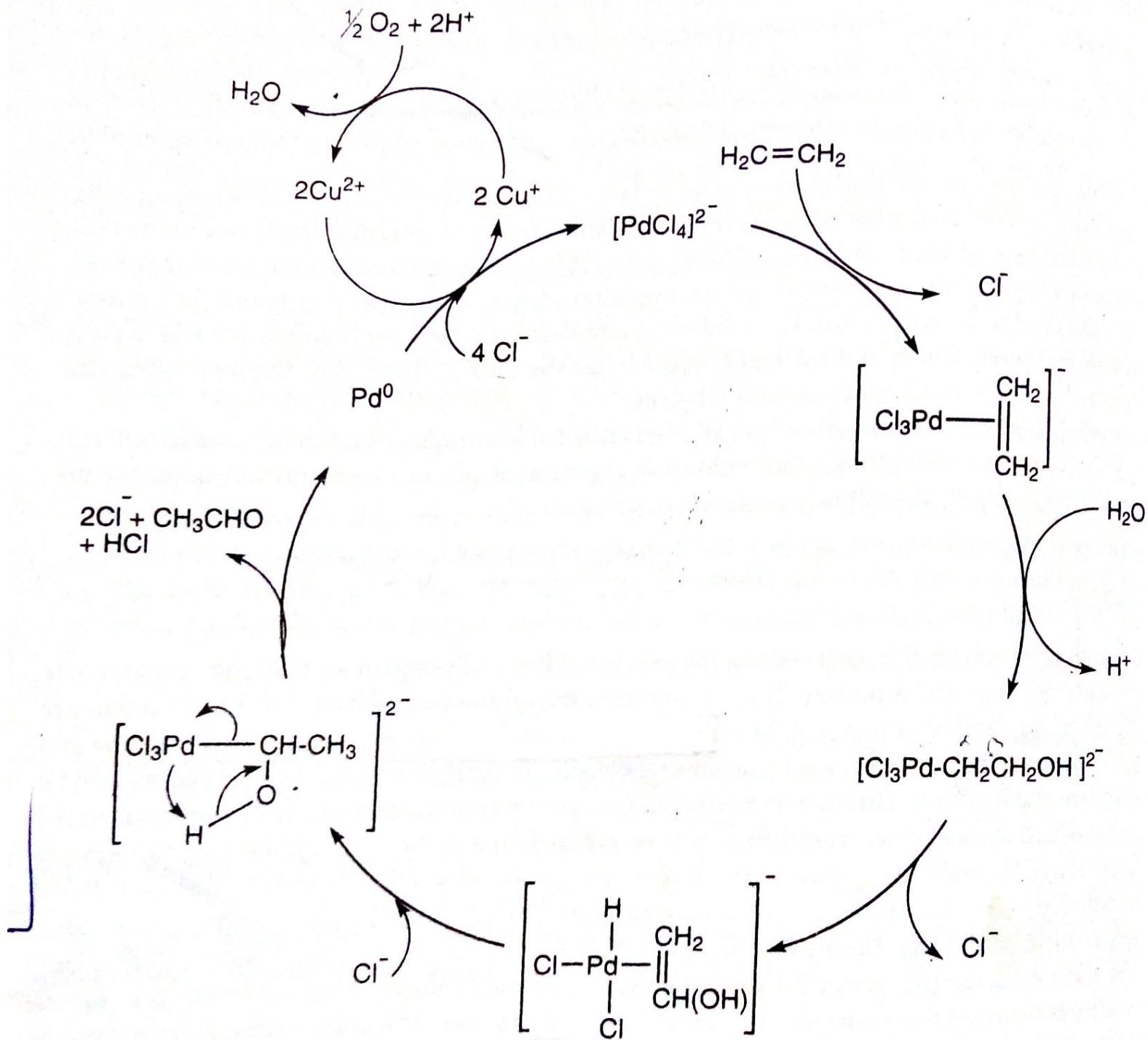
$$[PdCl_4]^{2-} + C_2H_4 + 2\, CH_3COONa \longrightarrow \begin{array}{l} CH_2{=}CHOC(O)CH_3 + Pd + \\ CH_3COOH + 2NaCl + 2\, Cl^- \end{array} \qquad (14.7)$$

Fig. 14.5 Catalytic cycle for Wacker oxidation