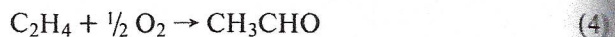
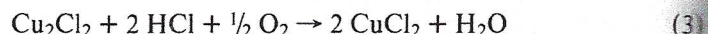
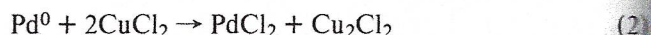


scope and practice of these reactions is in the patent literature. Few reviews are available and studies of mechanism are quite limited. The lack of academic attention may reflect the newness and the complexity of these reactions. The organometallic chemist may also find these processes unappealing because the Mo and Te atoms play such a limited part. There seems to be no convincing evidence for organometallic intermediates. In this respect these processes resemble the cobalt-catalyzed hydrocarbon oxidations discussed in Chapter 10.

## 6.1 WACKER ACETALDEHYDE SYNTHESIS

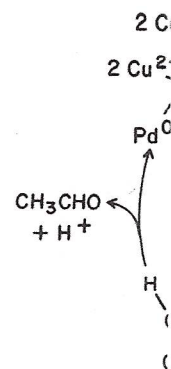
The synthesis of acetaldehyde by oxidation of ethylene, generally known as the Wacker process, was a major step in displacement of acetylene as a starting material in manufacture of organic chemicals. Acetylene-based acetaldehyde (Section 8.3) was a major intermediate for production of acetic acid and of butyraldehyde, itself a major intermediate (Section 5.5). The cost was, however, high because a large energy input is required to produce acetylene. When an efficient process for synthesis of acetaldehyde from ethylene was developed, its adoption was rapid. Ironically this development originated in the laboratories of the Consortium für Elektrochemische Industrie, a branch of Wacker-Chemie [5], which was established to promote use of acetylene. Although the Wacker process itself is now being displaced by CO-based technology (Chapter 5), it is still a major application of homogeneous catalysis.

The invention of the Wacker process was a triumph of common sense. It had been known since 1894 [6] that ethylene is oxidized to acetaldehyde by palladium chloride as a stoichiometric reagent (eq. 1). It was not until 1956, however, that this reaction was combined with the known reactions (2) and (3) to yield a catalytic acetaldehyde synthesis (eq. 4).



This sequence of reactions permits the precious metal salt to be used in a catalytic sense.

In commercial practice two modes of operation have developed [5,7]. The single-stage Hoechst process involves feeding an oxygen-ethylene mixture to an aqueous solution of  $\text{PdCl}_2$  and  $\text{CuCl}_2$  at 120–130° and 4 atmospheres' pressure. The acetaldehyde is fractionated from the gases as they exit from the reactor. In a two-stage process ethylene is stoichiometrically oxidized to acetaldehyde by a  $\text{PdCl}_2$ - $\text{CuCl}_2$  solution in one reactor. The organic-free aqueous solution leaving this reactor contains  $\text{PdCl}_2$  and  $\text{CuCl}_2$ . The copper salt is reoxidized with air in



**Figure 6.1** Major features

a separate reactor before boiling. The process gives 95% yields of acetaldehyde and 90% yields of acetyl chloride, acetic acid, chloroacetaldehyde, and acetyl acetate. The two-stage process requires more equipment than the one-stage process but permits the use of a smaller reactor, thus reducing the explosion hazards involved.

Recently halide-free cata [8]. Such systems typically salt such as a phosphomol halide-promoted corrosion tems will be used commerc

The Wacker chemistry of olefins yield methyl ketones. The reaction is rapid and clean, and the length. In a standard set of experiments at 20° to give a 90% yield of methyl ketone and gave only a 34% yield of methyl ketone. Good yields of cyclic ketones are also obtained.

The nature of the product is dependent on reaction conditions. At low temperatures, the reaction is directed to give vinyl acetate and ethyl acetate as major products. At higher temperatures,  $\text{CH}_3\text{CH}(\text{OCH}_3)_2$  can be formed. In the presence of ethanol, ethanol becomes a major product.

The major features of the

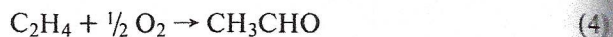
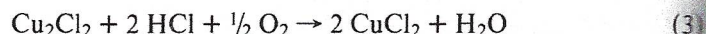
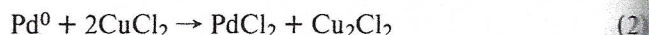


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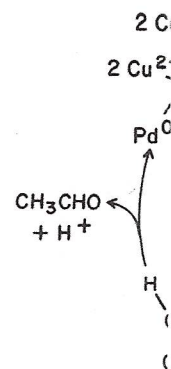


Figure 6.1 Major features

a separate reactor before butyraldehyde. The two-stage process requires a separate reactor before butyraldehyde. The two-stage process requires a separate reactor before butyraldehyde. The two-stage process requires a separate reactor before butyraldehyde.

Recently halide-free catalysts have been developed [8]. Such systems typically require a halide salt such as a phosphomolybdate to promote the reaction. Halide-promoted corrosion problems will be used commercially.

The Wacker chemistry of ethylene yields methyl ketones. Acetaldehyde is the palladium-catalyzed product. The reaction is rapid and clean, with a long life. In a standard set of conditions, it gave a 90% yield of acetaldehyde and gave only a 34% yield of acetaldehyde. The good yields of cyclic ketones are also noted.

The nature of the products is dependent on reaction conditions. The reaction is directed to give vinyl acetate and acetaldehyde as major products. Acetaldehyde or  $\text{CH}_3\text{CH}(\text{OCH}_3)_2$  can be produced. Ethanol becomes a major product.

The major features of the



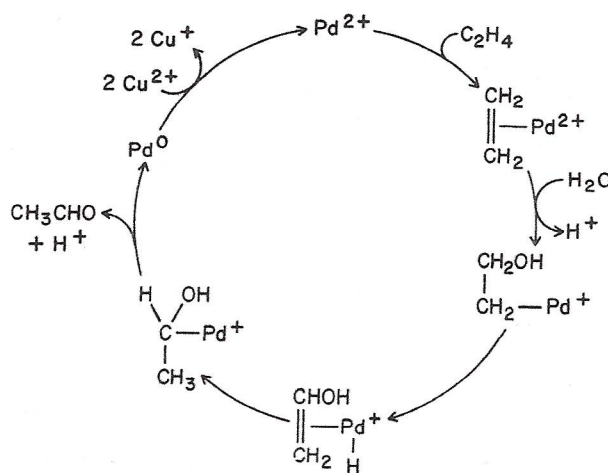


Figure 6.1 Major features of the oxidation of ethylene by palladium salts in water.

a separate reactor before being recycled to the synthesis unit. Both processes give 95% yields of acetaldehyde, along with small amounts of 2-chloroethanol, ethyl chloride, acetic acid, chloroacetaldehydes, and acetaldehyde condensation products. The two-stage process requires a higher capital investment than the single-stage process but permits the use of air rather than oxygen as the oxidant. It also avoids the explosion hazards involved in mixing oxygen and ethylene.

Recently halide-free catalyst systems for ethylene oxidation have been developed [8]. Such systems typically comprise a palladium salt along with a heteropoly acid salt such as a phosphomolybdovanadate. An obvious advantage is reduction in halide-promoted corrosion of process equipment, but it is not clear that these systems will be used commercially.

The Wacker chemistry can also be used to oxidize higher olefins. Terminal olefins yield methyl ketones. For example, one of the commercial syntheses of acetone is the palladium-catalyzed oxidation of propylene [9,10]. Although this reaction is rapid and clean, rates and yields decrease with increasing alkyl chain length. In a standard set of experiments [11] propylene was oxidized in 5 minutes at 20° to give a 90% yield of acetone. In contrast 1-decene required 1 hour at 70° and gave only a 34% yield of 2-decanone. Cyclic olefins react easily to give fairly good yields of cyclic ketones, but other internal olefins give mixtures of products.

The nature of the products in these palladium-catalyzed oxidations is strongly dependent on reaction conditions. The oxidation of ethylene in acetic acid can be directed to give vinyl acetate (Section 6.2), ethylene glycol acetates, or 2-chloroethyl acetate as major products [4]. Similarly, in methanol, either methyl vinyl ether or  $\text{CH}_3\text{CH}(\text{OCH}_3)_2$  can be made to predominate. Even in water [12], 2-chloroethanol becomes a major product at high chloride and copper concentrations.

The major features of the mechanism of ethylene oxidation (Figure 6.1) seem

terature. Few reviews are lack of academic attention tions. The organometallic use the Mo and Te atoms g evidence for organome- nable the cobalt-catalyzed

generally known as the ene as a starting material etaldehyde (Section 8.3) l of butyraldehyde, itself ver, high because a large efficient process for syn- adoption was rapid. Iron- he Consortium für Elek- ], which was established s itself is now being dis- major application of ho-

f common sense. It had aldehyde by palladium til 1956, however, that d (3) to yield a catalytic

+ 2 HCl (1)

(2)

H<sub>2</sub>O (3)

(4)

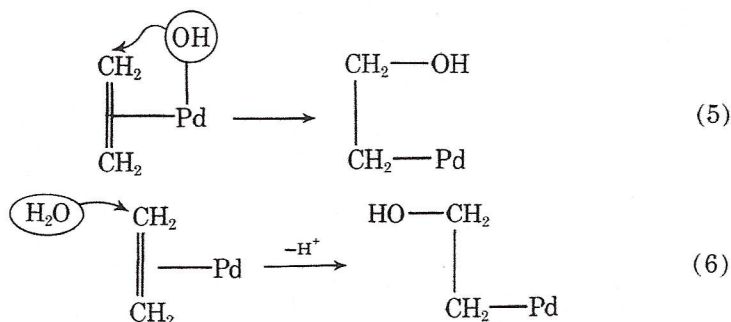
o be used in a catalytic

veloped [5,7]. The sin- hylene mixture to an atmospheres' pressure. it from the reactor. In to acetaldehyde by a eous solution leaving reoxidized with air in



to be well established, but a lively controversy about the detailed mechanism has developed recently. There is general agreement that the initial step is replacement of a chloride ion in  $[\text{PdCl}_4]^{2-}$  (shown as  $\text{Pd}^{2+}$  in the figure) by ethylene. Additionally, it is agreed that other chloride ions are replaced by water and hydroxide ligands. As a consequence the rate of the reaction is sharply decreased by high chloride concentrations.

The major point of disagreement is the mechanism of the addition of  $\text{OH}^-$  to the coordinated ethylene to give a hydroxyethylpalladium intermediate. This intermediate has never been observed but is commonly assumed to be present in the reaction mixture. Until recently, the OH addition was considered to be the result of migration of a coordinated  $\text{OH}^-$  ligand from palladium to carbon, as shown in equation 5.



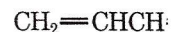
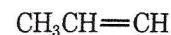
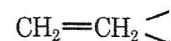
This migration (or ethylene insertion into a  $\text{Pd}\text{---OH}$  bond) is consistent with the observed kinetics. However, recent stereochemical studies [13,14] of addition to coordinated *cis*- or *trans*- $\text{CHD}=\text{CHD}$  indicate attack by an external nucleophile (eq. 6). It is quite possible that both mechanisms (*cis* and *trans* addition) operate and that reaction conditions determine which predominates.

One remarkable aspect of the ethylene oxidation is that no H/D exchange with solvent occurs. When the reaction takes place in  $\text{D}_2\text{O}$ , no deuterium appears in the product. Evidently the hydrogen migrations involved in transformation of the  $\text{HOCH}_2\text{CH}_2\text{Pd}$  intermediate to  $\text{CH}_3\text{CHO}$  occur entirely within the coordination sphere of the palladium.  $\beta$ -Hydrogen elimination to give a vinyl alcohol complex as shown in Figure 6.1 seems a likely pathway. Analogous platinum complexes of vinyl alcohol are well characterized [15]. Readdition of the hydride ligand to the coordinated vinyl alcohol gives the  $\alpha$ -hydroxyethylpalladium complex shown at the 8-o'clock position in the figure. A  $\beta$ -hydrogen elimination from OH completes acetaldehyde formation and results in formation of zerovalent palladium or a palladium hydride. Either species is rapidly reoxidized by copper(II) in a chloride-containing medium.

## 6.2 ACETOXYLATION OF OLEFINS AND DIENES

The reaction of an olefin with a palladium(II) salt in acetic acid is a versatile synthesis of vinylic and allylic acetates. These reactions are generally used industrially

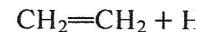
as heterogeneous processes, the analogous soluble proc following:



The chemistry of these pro closely parallels that of the

### Vinyl Acetate and Glycol

The reaction of ethylene wi ferent products under differe of the reaction was a stoichi acetate in acetic acid [16]. vinyl acetate as a major pro were needed to make 1 gram metal compound obviously l way to catalytic processes i



The two liquid-phase ca two-stage acetaldehyde pro  $\text{PdCl}_2$ ,  $\text{Cu}(\text{OAc})_2$ ,  $\text{KCl}$ , an 40–45 atmospheres and 120°

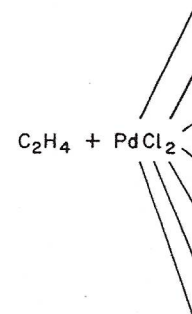


Figure 6.2 Major pro