

# Chapter 14

## Multiphase Catalytic Reactions in/Under Dense-Phase Carbon Dioxide: Utilization of Carbon Dioxide as a Reaction Promoter

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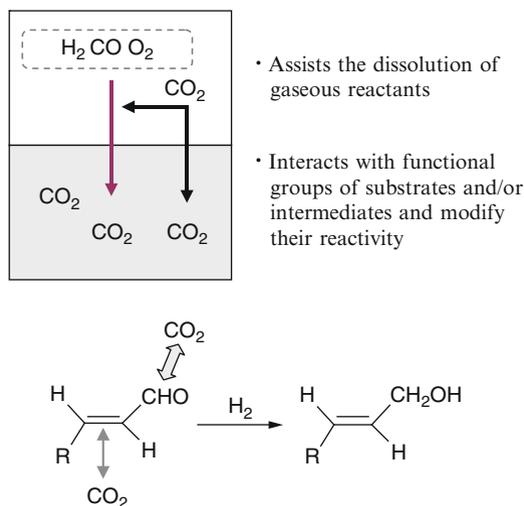
### 14.1 Introduction

Carbon dioxide serves as a building block for organic compounds, and various interesting examples are shown in the other chapters of this book. Carbon dioxide may be transformed into value-added organic compounds through chemical, photochemical, electrochemical, and biochemical reactions. In addition to the role of CO<sub>2</sub> as a useful reactant, CO<sub>2</sub> acts as a promoter/modifier in organic reactions in liquid phases although it is not involved as a reactant. In order for CO<sub>2</sub> to show such actions, pressurization is necessary to dissolve CO<sub>2</sub> in a certain quantity in an organic phase. When an organic liquid (substrate, solvent) is pressurized by CO<sub>2</sub>, its volume may increase to some extent depending on the nature of the liquid. In some cases, a considerable amount of CO<sub>2</sub> is dissolved, and this expands the volume of the organic liquid phase significantly. This phase is often called as CO<sub>2</sub>-dissolved expanded liquid phase (CXL) [1–3]. The dissolution of CO<sub>2</sub> changes the solvent properties of a liquid phase from pure organic liquid state to high-density CO<sub>2</sub> state, depending on its pressure applied. The liquid-phase dissolving CO<sub>2</sub> is beneficial to dissolution of gaseous reactants such as oxygen, hydrogen, and carbon monoxide. Thus, the pressurization with CO<sub>2</sub> would accelerate the liquid-phase chemical reactions involving gaseous reactants, including oxidation, hydroformylation, and hydrogenation. That is, CO<sub>2</sub> can act as an accelerator in organic synthetic reactions on simple pressurization of the reaction mixtures with CO<sub>2</sub>

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**Fig. 14.1** Multiphase catalytic reactions in the presence of pressurized  $\text{CO}_2$ . The liquid phase includes substrate, solvent, and catalyst (homogeneous or heterogeneous). The dissolution of  $\text{CO}_2$  may improve the dissolution of gaseous reactants and modify the reactivity of certain functional groups of organic substrates. An example given is the selective hydrogenation of carbonyl group, than carbon-carbon double bond, of  $\alpha,\beta$ -unsaturated aldehyde to unsaturated alcohol

(Fig. 14.1). Under certain conditions, however, the dissolved  $\text{CO}_2$  molecules act only as a diluent and have a negative effect of retarding the reactions. Whether the promotional effect of  $\text{CO}_2$  pressurization will appear or not depends on a relative balance between those positive and negative factors.

In addition to the above-mentioned *macro (physical)* functions,  $\text{CO}_2$  has interesting and significant *micro (chemical)* functions in organic synthetic reactions through direct interactions with reacting species in the liquid phases. The dissolved  $\text{CO}_2$  molecules interact with functional groups of substrates and/or reaction intermediates, as proved by in situ high-pressure Fourier transform infrared spectroscopy [4]. The direct interaction with  $\text{CO}_2$  changes the reactivity of certain functional groups of substrates and/or reaction intermediates, and, as a result, this may improve the selectivity to the production of desired products. That is,  $\text{CO}_2$  acts as a reaction modifier, which is expected for liquid-phase synthetic reactions including no gaseous reactants (e.g., Heck coupling) as well as those including gaseous reactants. This chapter reviews several interesting examples of *micro (chemical)* effects of  $\text{CO}_2$  in organic synthetic reactions and possible explanations for these effects observed. The reactions dealt with this chapter include oxidation, hydroformylation, hydrogenation, acid-catalyzed reactions, Heck reactions, and Diels–Alder reactions.

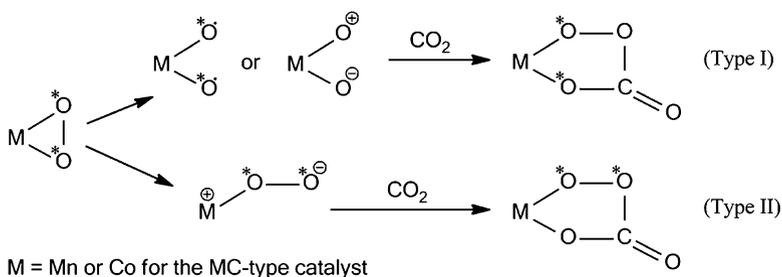
## 14.2 Multiphase Catalytic Reactions in the Presence of Dense-Phase CO<sub>2</sub>

### 14.2.1 Oxidation

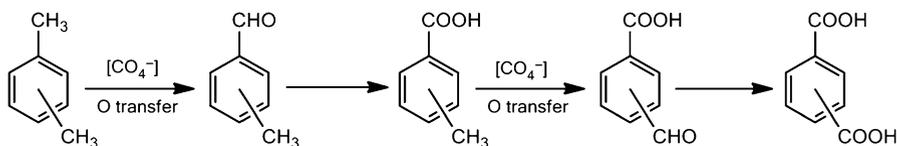
Oxidation is one of the widely investigated reactions in both academia and industry, and O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> are generally used as oxidants. The use of dense-phase CO<sub>2</sub> prevents oxidation reactions from combustion and explosion, and mass transfer limitation can be improved in multiphase catalytic oxidations using gaseous oxidants. Therefore, several researchers investigated the utilization of CO<sub>2</sub> in oxidation reactions.

Yoo et al. reported the chemical functions of CO<sub>2</sub> as an active component for the liquid-phase O<sub>2</sub> oxidation of *o*-, *m*-, and *p*-xylenes at 468 K with Co/Mn/HBr catalyst, which is called “MC-type O<sub>2</sub> oxidation” [5]. They showed that the amount of O<sub>2</sub> consumed in O<sub>2</sub> oxidation of *m*-xylene was enhanced by the copresence of CO<sub>2</sub>, and the purity of isophthalic acid (IPA) in the recovered solid product was also increased. Moreover, the promoting effects of CO<sub>2</sub> increased with increasing concentration of CO<sub>2</sub>, indicating that both catalytic activity and selectivity to IPA were influenced by the presence of CO<sub>2</sub> in the reaction media. The O<sub>2</sub> oxidation of *p*-toluic acid, which was produced as an intermediate from *p*-xylene, was also examined, and they concluded that there were three mechanistic interpretations of the effects of CO<sub>2</sub>. Firstly, copresence of CO<sub>2</sub> enhanced the solubility of the substrates as well as the intermediates; secondly, decarboxylation of the intermediates can be suppressed by the presence of CO<sub>2</sub>. Thirdly, a synergistic interaction of CO<sub>2</sub> and O<sub>2</sub> molecules may create a cyclic peroxocarbonate species on the metal center of the MC-type catalyst, and these species play a key role in initiating the free radical propagation via the hydrogen abstraction process and accelerating the oxidation. The possible pathways of formation of peroxocarbonate species are shown in Scheme 14.1.

The metal-O<sub>2</sub> complex is initially formed on either Co or Mn center, and the CO<sub>2</sub> molecule is then inserted into the O-O bond to produce an active species (Type I).

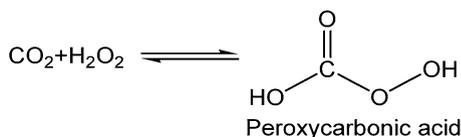


**Scheme 14.1** Possible pathways of formation of peroxocarbonate species from O<sub>2</sub> and CO<sub>2</sub> with metal center of MC-type catalyst



**Scheme 14.2** Reaction pathways of  $\text{O}_2$  oxidation of xylenes over Co/Mn/HBr catalyst in the presence of  $\text{CO}_2$

**Scheme 14.3** The formation of peroxy-carbonic acid from  $\text{CO}_2$  and  $\text{H}_2\text{O}_2$



Another type of peroxocarbonate species can also be formed by a different mode of interaction (Type II). Aresta et al. reported that the oxygen atom directly bonded to the metal center in these species can transfer to the oxophile substrates [6], indicating that the peroxocarbonate species formed from  $\text{O}_2$  and  $\text{CO}_2$  accelerated the oxidation of methyl group in aromatic compounds to corresponding aldehydes as shown in Scheme 14.2.

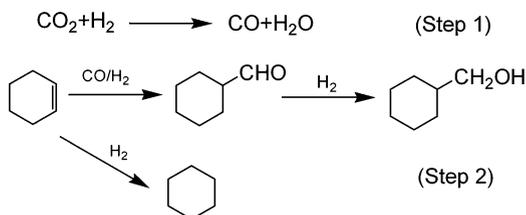
Eckert et al. have investigated the olefin epoxidations using  $\text{H}_2\text{O}_2$  as oxidant in the presence of dense-phase  $\text{CO}_2$  with no metallic catalyst [7] and mentioned the formation of peroxy-carbonic acid from  $\text{CO}_2$  and  $\text{H}_2\text{O}_2$ , which facilitates the olefin epoxidation (Scheme 14.3). The mass transfer limitation is one of the crucial problems in this reaction because the epoxidation occurs in aqueous phase. Dense-phase  $\text{CO}_2$  contributes to improve the mass transfer. Subramaniam et al. indicated that the peroxocarbonate is the most likely reactive intermediate in the olefin epoxidation [8]. In addition, they note that hydrogen bonding and polarity of CXLs are key factors in the epoxidation, which can be controlled by  $\text{CO}_2$  pressurization and the kind of organic solvent used.

### 14.2.2 Hydroformylation

Hydroformylation of olefin with  $\text{H}_2$  and  $\text{CO}$  is an industrially important reaction, and homogeneous Rh or Co complex catalysts are generally used. The cost of Rh complex catalyst is relatively expensive than Co complex catalyst, but the reaction can occur with high activity and selectivity under milder conditions. The utilization of dense-phase  $\text{CO}_2$  in hydroformylation has been investigated by several researchers [9–11]. It is indicated that the increase of the solubility of syngas into liquid phase by using CXLs as reaction media gives the most significant effect in the hydroformylation reactions.

Tominaga et al. have first shown that the hydroformylation can indeed proceed with a mixture of  $\text{H}_2$  and  $\text{CO}_2$  instead of  $\text{CO}$  [12, 13].  $\text{CO}$  can be formed from  $\text{H}_2$

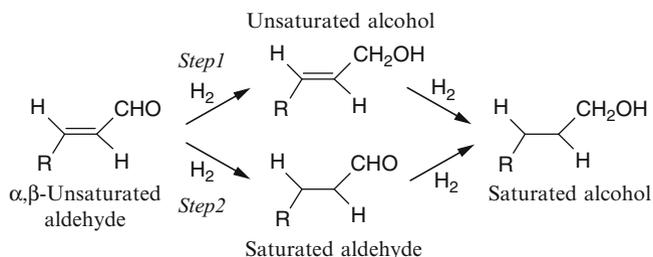
**Scheme 14.4** One-pot hydroformylation of cyclohexene using  $H_2$  and  $CO_2$



and  $CO_2$  through the reverse water gas shift reaction, and it can be directly used for hydroformylation with  $H_2$ , indicating that one-pot hydroformylation from  $H_2$  and  $CO_2$  can be achieved. Fujita et al. investigated the effect of  $H_2$  and  $CO_2$  pressures on the hydroformylation of cyclohexene with a catalyst system of  $Ru_3(CO)_{12}$  and LiCl in *N*-methyl-2-pyrrolidone [14]. The hydroformylation with  $CO_2$  and  $H_2$  has a two-step process, as shown in Scheme 14.4, and the aldehyde produced is further reduced to the corresponding alcohol. In their work, gaseous CO was detected during the reaction, and its amount was comparable to those of aldehyde and alcohol formed. The step 1 proceeds faster compared with the step 2, which means that the hydroformylation reaction is the rate-determining step. The formation of CO was accelerated with increasing total pressure of  $H_2$  and  $CO_2$ , and the yield of cyclohexanecarboxaldehyde was also increased. However, both the hydrogenation of cyclohexanecarboxaldehyde to cyclohexane-methanol and that of cyclohexene to cyclohexane were suppressed with increasing  $CO_2$  pressure. The chemical functions of  $CO_2$  as a promoter as well as a reactant were examined by in situ high-pressure FTIR measurements, and molecular interactions of  $CO_2$  with cyclohexene and intermediates were not observed. They also examined the structure of Ru complexes at different pressures of  $H_2$  and  $CO_2$ , and the results indicated the presence of  $[H_3Ru_4(CO)_{12}]^{-1}$  and  $[HRu_3(CO)_{11}]^{-1}$  under the reaction conditions used. These species may be active for the reduction of  $CO_2$  to CO and the following hydroformylation reaction, respectively.

### 14.2.3 Hydrogenation

Liquid-phase hydrogenation is one of industrially important reactions, and different homogeneous and heterogeneous catalysts are used [15, 16]. Heterogeneous catalysts are more desirable than homogeneous ones when we consider the post-reaction treatments of catalyst separation and recycling. The reaction mixtures of our interest here are a multiphase system containing a liquid phase (substrate, solvent) and/or a gas phase ( $H_2$ ,  $CO_2$ ) with a solid phase (heterogeneous catalyst). The pressurization of organic liquid phases with  $CO_2$  may have an interesting impact on the reaction rate and/or the product selectivity for the hydrogenation reactions in these phases.

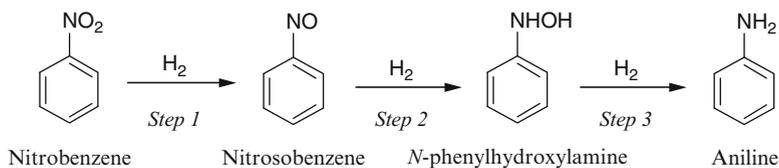


**Scheme 14.5** Reaction pathways in hydrogenation of  $\alpha,\beta$ -unsaturated aldehyde

The acceleration of hydrogenation reactions in the presence of dense-phase  $\text{CO}_2$  was reported in the literature [17–20]. For example, Chouchi et al. compared the rates of hydrogenation of  $\alpha$ -pinene with a Pd/C catalyst under different conditions at 323 K. They showed that the rate of hydrogenation in a gas–liquid system under CXL conditions was even faster compared to that in a homogeneous  $\text{scCO}_2$  system [20].

In selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes with supported Pt catalysts, the  $\text{C}=\text{C}$  group is more easily hydrogenated rather than the  $\text{C}=\text{O}$  group, and so it is difficult to produce the corresponding unsaturated alcohols in high selectivity [21] (Scheme 14.5). The high selectivity to unsaturated alcohols may be achieved by modifying the properties of supported Pt particles with Sn and other additives. Bhanage et al. revealed that the presence of dense-phase  $\text{CO}_2$  was effective for improving the hydrogenation of the carbonyl bond of cinnamaldehyde,  $\alpha$ -methyl-trans-cinnamaldehyde, and crotonaldehyde with a Pt/ $\text{Al}_2\text{O}_3$  catalyst at 323 K [22]. For crotonaldehyde, for example, the selectivity to crotyl alcohol was 46 % in neat ethanol at a  $\text{H}_2$  pressure of 4 MPa, while it was improved to >70 % in the presence of 14 MPa  $\text{CO}_2$ . For cinnamaldehyde, the selectivity to cinnamyl alcohol was enhanced from 78 % in ethanol to 93 % at a  $\text{CO}_2$  pressure of 14 MPa; in addition, the rate of hydrogenation was also improved with increasing  $\text{CO}_2$  pressure. Zhao et al. measured in situ FTIR spectra of cinnamaldehyde and benzaldehyde dissolved in pressurized  $\text{CO}_2$  gas phase at 323 K [23, 24]. They observed a significant red shift of the frequency of the stretching vibration of the  $\text{C}=\text{O}$  bond with increasing  $\text{CO}_2$  pressure for cinnamaldehyde but a marginal red shift for benzaldehyde. The frequency of the vibration of the  $\text{C}=\text{C}$  bond was found to change little with the pressure. Therefore, they assumed that  $\text{CO}_2$  molecules were able to interact with the carbonyl group, decrease the bond strength, and then increase its reactivity to hydrogenation. Those molecular interactions between  $\text{CO}_2$  species and the carbonyl group were studied and confirmed by theoretical model calculations by Zhao et al. [25]. The function of  $\text{CO}_2$  as an accelerator/modifier was also observed for the same hydrogenation reactions of  $\alpha,\beta$ -unsaturated aldehydes using homogeneous metal complex catalysts [26–28].

The dense-phase  $\text{CO}_2$  also has an impact on liquid-phase hydrogenation of aromatic nitro compounds, which is important in industry for the manufacture of aniline compounds [29], and several metals are used as active catalysts [30–34].

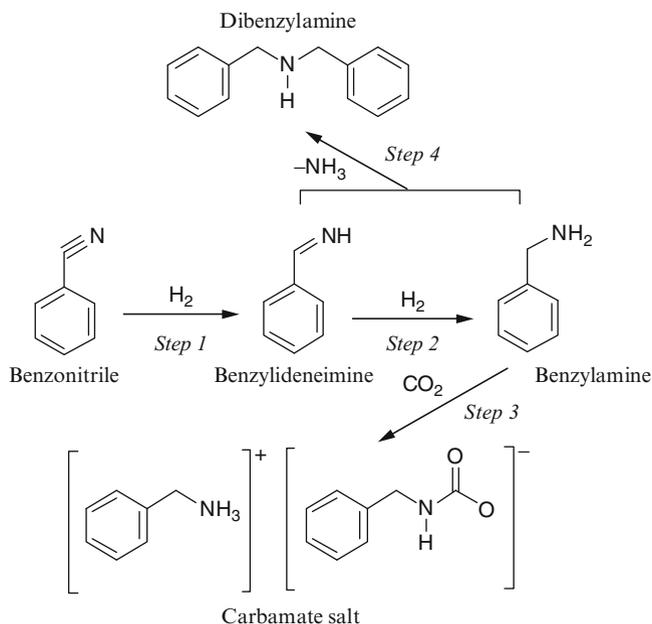


**Scheme 14.6** Hydrogenation of nitrobenzene toward aniline

In this hydrogenation (Scheme 14.6), the production of such intermediates as nitrosobenzene and *N*-phenylhydroxylamine and such coupling by-products as azoxybenzene, azobenzene, and hydrazobenzene should be avoided, and a high selectivity to aniline should be achieved at a high conversion.

Meng et al. studied the selective hydrogenation of nitrobenzene to aniline with  $\text{Al}_2\text{O}_3$ -supported Ni catalysts at 323 K and at a  $\text{H}_2$  pressure of 4 MPa [35]. The reaction runs were conducted in the presence of  $\text{CO}_2$  at different pressures and no additional organic solvent. Under the conditions used, the rate of hydrogenation was observed to increase with increasing  $\text{CO}_2$  pressure up to about 12 MPa, below which the reaction mixture was a gas–liquid–solid three-phase system and the reaction occurred mainly in the liquid phase. The dissolution of a gaseous reactant of  $\text{H}_2$  should be improved by  $\text{CO}_2$  pressurization, and this effect may be superior to the dilution of the reacting species in the liquid phase. The reaction mixture changed to a gas–solid two-phase system at higher  $\text{CO}_2$  pressure, and the dilution became more significant, resulting in a decrease in the rate of reaction. It is noteworthy that the selectivity to the desired product of aniline is almost 100 % at any conversion level, and this complete selective hydrogenation can be achieved at  $\text{CO}_2$  pressures of 6–18 MPa, that is, irrespective of the phase behavior of the reaction mixture. Meng et al. measured in situ FTIR spectra of nitrobenzene, nitrosobenzene, and *N*-phenylhydroxylamine dissolved in dense-phase  $\text{CO}_2$  at different pressures. They observed that the frequency of stretching vibration of N–O bond of the nitro group was blue-shifted on  $\text{CO}_2$  pressurization and believed that the reactivity of the nitro group was reduced in the presence of dense-phase  $\text{CO}_2$ . They assumed that for nitrosobenzene and *N*-phenylhydroxylamine, in contrast, their reactivity was promoted by the action of  $\text{CO}_2$  species in the liquid phase. Thus,  $\text{CO}_2$  is believed to slow down the rate of step 1 but accelerate the rates of steps 2 and 3. As a result, aniline can be produced in 100 % selectivity with no undesired intermediates and coupling products. The dilution of intermediates of nitrosobenzene and *N*-phenylhydroxylamine by the dissolution of  $\text{CO}_2$  and  $\text{H}_2$  would contribute to the suppression of their coupling reactions.

Meng et al. made a similar study with chloronitrobenzene substrates [36]. They demonstrated that the pressurization with  $\text{CO}_2$  is also effective for the 100 % selective hydrogenation to the desired chloroaniline products at any conversion level. No dechlorination was observed to occur in this multiphase reaction system. Zhao et al. investigated the effects of metal particle size in hydrogenation of nitrobenzene with several supported noble metal catalysts in the presence of

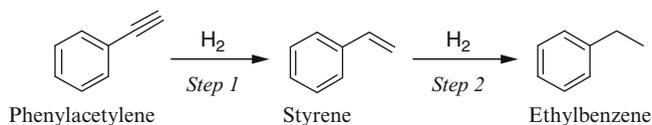


**Scheme 14.7** Reaction pathways in hydrogenation of benzonitrile

dense-phase CO<sub>2</sub> [37, 38]. They showed that the turnover frequency decreased with the degree of metal dispersion in similar fashions for the reactions in ethanol and in compressed CO<sub>2</sub>.

An interesting result was further reported by Meng et al. that the positive effect of CO<sub>2</sub> pressurization on the selective hydrogenation of nitrobenzene to aniline appeared at a low CO<sub>2</sub> pressure of about 1 MPa when an additional phase of water was also added to the reaction system [39]. Lin et al. reported the effectiveness of compressed CO<sub>2</sub>/water system for ring hydrogenation of aromatic alcohols and aldehydes [40]. The function of water added is not clear at present. The multiphase organic reaction systems including dense-phase CO<sub>2</sub> and water are interesting and worth investigating in detail. A recent review article demonstrates the significance of on-water organic reactions, in which organic-water interface is important [41]. The combination of dense-phase CO<sub>2</sub> and water could give additive or synergistic effects on the reaction rate and/or the product selectivity in organic synthetic reactions.

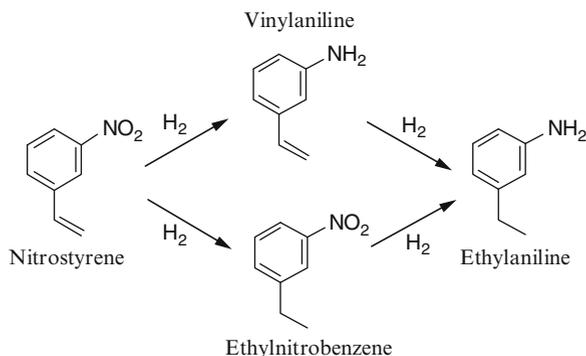
Yoshida et al. reported different CO<sub>2</sub> actions for hydrogenation of benzonitrile with a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst in multiphase media including dense-phase CO<sub>2</sub> and water at 323 K [42]. The selective hydrogenation of benzonitrile to the primary amine may be achieved in a selectivity >95 % in a medium including both CO<sub>2</sub> and water. In this system, the primary amine formed may easily transform with CO<sub>2</sub> to a water-soluble carbamate salt (Scheme 14.7), and this hinders its further hydrogenation to the secondary amine in the organic phase, resulting in the high selectivity to benzylamine. The carbamate salt is not stable, and so the benzylamine can be



**Scheme 14.8** Hydrogenation of phenylacetylene to styrene and ethylbenzene

**Scheme 14.9**

Hydrogenation of the nitro and vinyl groups of nitrostyrene



regenerated by heating [43]. When water is absent, the carbamate salt deposits on the surface of catalyst and causes its deactivation. The primary amine is soluble somewhat in water, but the production of the secondary amine cannot be avoided in the absence of  $\text{CO}_2$ .

The action of  $\text{CO}_2$  as a protecting agent was earlier reported for hydrogenation [44] and other synthetic reactions [45, 46] using homogeneous catalysts. Eckert et al. studied the selective hydrogenation of benzonitrile with  $\text{NiCl}_2/\text{NaBH}_4$  in ethanol at 303 K [44]. The yield of the primary amine was markedly promoted by simple pressurization of the organic phase with  $\text{CO}_2$ . This is ascribable to the formation of carbamate salt that prevents the side reaction of the primary amine with imine intermediate giving the secondary amine.

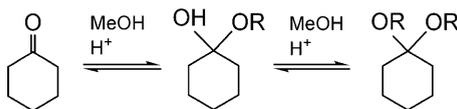
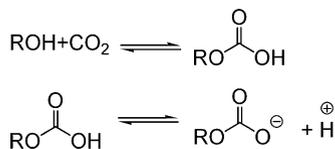
Recently Wei et al. investigated the partial hydrogenation of phenylacetylene with several monometallic and bimetallic Pd-based catalysts in hexane at 313 K [47] (Scheme 14.8). The pressurization with  $\text{CO}_2$  was shown to improve the selectivity to styrene; at a total pressure of 3.4 MPa including 20 %  $\text{CO}_2$ , styrene was produced in a selectivity of 92 % at 100 % conversion in 0.5 h with a Pd-Ag bimetallic catalyst. Further increase of  $\text{CO}_2$  partial pressure to 40 % increased the selectivity to 98 % but decreased the conversion to 74 % under the conditions used. Namely, the further hydrogenation of an alkene of styrene to an alkane of ethylbenzene can be suppressed although the function of  $\text{CO}_2$  molecules is still unclear.

The extent of impact of  $\text{CO}_2$  pressurization should be different from one organic liquid to another depending on their solvent properties; above-mentioned positive effects would be expected for some organic liquids but not for others. The dissolution of a certain amount of  $\text{CO}_2$  into a liquid is required for  $\text{CO}_2$  to have positive (or negative) effects in the liquid phase. Yoshida et al. studied the effects of  $\text{CO}_2$  for a test reaction of nitrostyrene hydrogenation (Scheme 14.9) with a Pt/TiO<sub>2</sub> catalyst

using two organic solvents of toluene and ethanol at 323 K [48]. The two solvents indicated similar degrees of volume expansion at the same CO<sub>2</sub> pressure, as confirmed by phase behavior observations at the reaction temperature. In neat toluene, neat ethanol, and ethanol pressurized by CO<sub>2</sub>, the nitro group of nitrostyrene was hydrogenated to vinylaniline in a high selectivity. In contrast, the vinyl group was selectively hydrogenated to ethylnitrobenzene in toluene pressurized by CO<sub>2</sub>. These results may be explained by relative interactions among the two functional groups, the solvent molecules, and the CO<sub>2</sub> species in the liquid phase. The interactions of the vinyl group with CO<sub>2</sub> are weak, but those of the nitro group with CO<sub>2</sub> are significant, which decrease its reactivity to hydrogenation. The interactions of the nitro group with the dissolved CO<sub>2</sub> can appear in the case of toluene, in which the nitro group is likely to be surrounded by CO<sub>2</sub> species rather than toluene molecules because of no interaction between the nitro group and toluene molecules. So, the impact of CO<sub>2</sub> pressurization appears even at low pressures, decreasing the reactivity of the nitro group and then relatively increasing the hydrogenation of the vinyl group. In the case of ethanol, however, the interactions of the nitro group with the solvent molecules are strong as compared to those with CO<sub>2</sub>, and, hence, the impact of CO<sub>2</sub> pressurization does not appear even at a high pressure of 10 MPa. These explanations are supported by molecular dynamics simulations, which determine the local composition around the nitro group of nitrostyrene in either toluene or ethanol pressurized by CO<sub>2</sub>. It is thus important to select a suitable solvent when we expect positive effects of CO<sub>2</sub> pressurization on liquid-phase hydrogenation and other organic reactions. Solvent properties of substrates, solvents, and CO<sub>2</sub> are important to consider [49].

Those results demonstrate the importance of interactions of CO<sub>2</sub> molecules with substrates and intermediates. Akiyama et al. studied these molecular interactions of CO<sub>2</sub> with various organic compounds of ketones, esters, and amides by using in situ high-pressure FTIR [4]. The results would be helpful in discussing the impact of CO<sub>2</sub> on reactions with those substrates. In the hydrogenation reactions in the presence of dense-phase CO<sub>2</sub> over supported metal catalysts, CO is formed from CO<sub>2</sub> and H<sub>2</sub> and adsorbed on the surface of supported metal particles, and this would cause the deactivation of catalysts [50–54]. The occurrence of catalyst deactivation may depend on competitive adsorption of CO, substrates, and/or intermediates. Dong et al. studied the hydrogenation of the aromatic rings of polystyrene in a CXL of decahydronaphthalene pressurized by CO<sub>2</sub> using 5 % Pd/SiO<sub>2</sub> and 5 % Pd/Al<sub>2</sub>O<sub>3</sub> catalysts at 423 K [55]. They observed the catalyst deactivation in a relatively early stage of reaction due to the formation and adsorption of CO formed from CO<sub>2</sub> and H<sub>2</sub>. They detected CO at the end of hydrogenation reaction. It is interesting to note that the catalyst deactivation can be avoided by physically mixing an additional methanation catalyst (5 % Ru/Al<sub>2</sub>O<sub>3</sub>, 65 % Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) and a hydrogenation catalyst into a single particle. The methanation catalyst could convert CO into CH<sub>4</sub> and regenerate the surface of the hydrogenation catalysts. The use of the methanation catalysts does not influence the desired reaction of the aromatic ring hydrogenation of polystyrene. Using in situ high-pressure FTIR, Yoshida et al. studied the formation and adsorption of CO

**Scheme 14.10** In situ formation of alkylcarbonic acid from CO<sub>2</sub> and alcohol



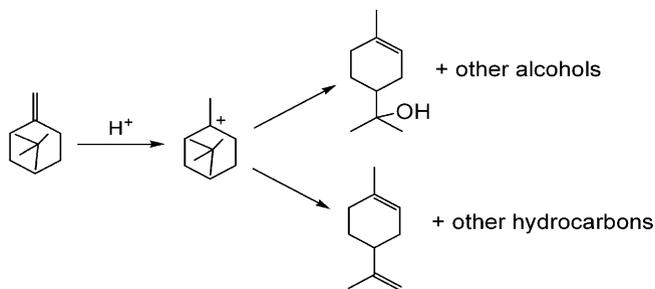
**Scheme 14.11** Formation of dimethyl acetal of cyclohexanone catalyzed by in situ generated acid in CO<sub>2</sub>-expanded methanol

from H<sub>2</sub> and CO<sub>2</sub> over Al<sub>2</sub>O<sub>3</sub>-supported Pt, Pd, Rh, and Ru catalysts at 323 K [56]. They collected FTIR spectra of adsorbed CO at different CO<sub>2</sub> pressures and in the presence and absence of water (H<sub>2</sub>O, D<sub>2</sub>O) for heat-treated and untreated noble metal catalysts. They discussed the types of CO species adsorbed on the metal particles depending on their surface structure and the influence of water vapor on the CO adsorption behavior. Water molecules may be adsorbed more preferentially on atomically rough surfaces rather than CO species. Our attention is herein given to interactions of CO<sub>2</sub> with organic substrates and intermediates. The CO<sub>2</sub> may affect the properties of supported metal particles through the formation and adsorption of CO in hydrogenation reactions, as mentioned above. Note, further, that CO<sub>2</sub> molecules could have a direct impact on supported metal particles, which was speculated from the optical absorption measurements of supported Au particles in the compressed CO<sub>2</sub> gas phase at different pressures [57]. Liu et al. recently reported that the properties and activity of a TiO<sub>2</sub> catalyst were modified by the accumulation of CO<sub>2</sub> species on its surface assisted by the action of a surfactant [58]. The photocatalytic activity of TiO<sub>2</sub> for the production of H<sub>2</sub> through water splitting was improved by about one order of magnitude.

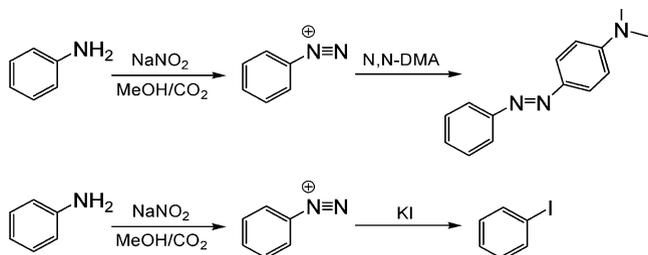
#### 14.2.4 Acid-Catalyzed Reactions

Acid-catalyzed reactions in CXLs using in situ generated catalysts from the reaction of CO<sub>2</sub> with alcohol or water were pioneered by the joint group of Eckert and Liotta [59–63]. Alkylcarbonic acids can be formed in alcohols with compressed CO<sub>2</sub> and used as acid catalysts (Scheme 14.10). This reaction system is desirable because the decomposition of the acid can automatically occur by simple depressurization after the reactions without any post-reaction neutralization and salt disposal.

They found that the formation of dimethyl acetal of cyclohexanone in methanol (Scheme 14.11) was up to 130 times faster by CO<sub>2</sub> pressurization. The greatest



**Scheme 14.12** Hydrolysis of  $\beta$ -pinene in the  $\text{CO}_2$ -expanded  $\text{MeOH}/\text{H}_2\text{O}$  mixture



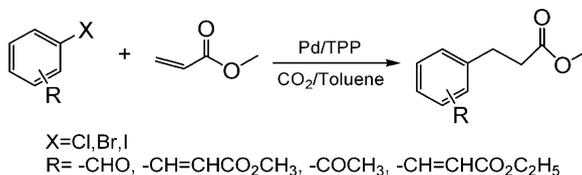
**Scheme 14.13** In situ acid catalysis for single-pot synthesis of methyl yellow and iodobenzene in  $\text{CO}_2$ -expanded methanol

enhancement was found at a pressure of 22 bar; presumably higher pressures are undesirable due to decreasing polarity of the expanded solvent inhibiting the dissociation of the acid.

The application of in situ generated alkylcarbonic acid as a catalyst for the hydrolysis of  $\beta$ -pinene to terpineol and other alcohols was also investigated [61]. Good selectivity for alcohols rather than hydrocarbons was obtained in CXLs and hot water (Scheme 14.12). Eckert et al. used several kinds of CXLs with different compositions of methanol, water, and  $\text{CO}_2$  for the reactions. A selectivity of 84.0 % for the hydrolysis product at the highest conversion (70.9 %) was achieved in the  $\text{CO}_2$ -expanded 1:1 methanol/water mixture (348 K, 3 mol%  $\text{CO}_2$ ). The reaction did not proceed when the  $\text{CO}_2$  was absent.

Eckert et al. demonstrated the catalytic performance of in situ acid catalysis for the diazotization of aniline, which is either coupled with *N,N*-dimethyl aniline to form methyl yellow or reacted with iodide to form iodobenzene (Scheme 14.13) [63]. A 97 % conversion of aniline with a 72 % yield of methyl yellow was obtained at 278 K in 72 h with an excess nitrile salt and a high  $\text{CO}_2$  loading. This reaction did not occur in the absence of  $\text{CO}_2$ . They also used THF as a solvent instead of methanol, but the yield was only 0.3 %, which may come from the lack of alkylcarbonic acid and the formation of carbamates from aniline and  $\text{CO}_2$ . These results strongly suggest that a suitable acid source like alcohol must be present for utilization of dense-phase  $\text{CO}_2$  in the acid-catalyzed reactions.

**Scheme 14.14** Heck reactions of halogenated benzene derivatives with methyl acrylate in CO<sub>2</sub>-expanded toluene with Pd/TPP catalyst



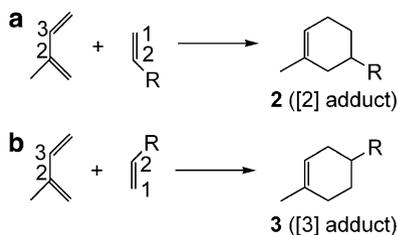
### 14.2.5 Heck and Diels–Alder Reactions

There are many advantages of using dense-phase CO<sub>2</sub> in multiphase catalytic reactions as mentioned above. Recently, some positive effects in liquid organic reactions without any gaseous reactants were also found.

scCO<sub>2</sub> has been investigated as a reaction media of Heck coupling reactions using homogeneous complex catalysts; there are some advantages such as the extraction of the product, resulting in the controlling of the product distribution. The modification of metal complex catalysts with fluorinated functional groups is effective for increasing their solubility into scCO<sub>2</sub> phase [64, 65]. Such a catalyst modification may not always be necessary for multiphase reactions, in which the solubility of the catalysts in the organic phase is not so a serious problem. Multiphase Heck reactions in the presence of dense-phase CO<sub>2</sub> were investigated [66]. Fujita et al. reported the effects of CO<sub>2</sub> pressurization on liquid-phase Heck reactions of methyl acrylate with various aryl bromides over homogeneous Pd/TPP catalyst in toluene in the presence of compressed CO<sub>2</sub> (Scheme 14.14) [67]. For the Heck reaction of iodobenzene and non-activated bromobenzene with methyl acrylate, the conversion simply decreased with CO<sub>2</sub> pressure due to the dilution effect of CO<sub>2</sub> molecules in the liquid organic phase. However, the conversion increased with CO<sub>2</sub> pressure in the range up to 3 MPa for the reaction of 2-bromoacetophenone with methyl acrylate. This promoting effect was not observed in the case of using 3- and 4-bromoacetophenone. From the results of high-pressure FTIR measurements of 2-, 3-, 4-bromoacetophenones in the presence of CO<sub>2</sub>, they conclude that the dissolved CO<sub>2</sub> molecules interact with the aryl bromide substrates in different manners depending on their structures. It is suggested that the C-Br bonds of the three substrates are modified by the presence of CO<sub>2</sub>, indirectly through interactions of CO<sub>2</sub> with the other moieties or directly with the C-Br moiety. The rate of the liquid-phase Heck reaction can be enhanced by pressurizing the reaction mixture with CO<sub>2</sub> at a low pressure of 2–4 MPa, although the enhancement effect is limited to a few bromoarenes of a certain structure.

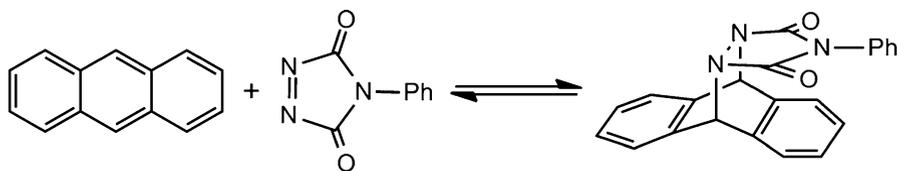
Fujita et al. studied the impact of CO<sub>2</sub> pressurization for the Diels–Alder reactions of isoprene with methyl acrylate, methyl vinyl ketone, and acrolein in the CO<sub>2</sub>-expanded toluene and ethanol at 393 K with a heterogeneous SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> catalyst [67] (Scheme 14.15). The conversion simply decreased with CO<sub>2</sub> pressure in the reactions with three dienophile substrates, which may be caused by the dilution effect of CO<sub>2</sub> molecules in the liquid phases. However, the product selectivity remarkably changed with CO<sub>2</sub> pressure; the ratio of [3] adduct to [2]

**Scheme 14.15** Two approaches (a) and (b), yielding [2] adduct and [3] adduct



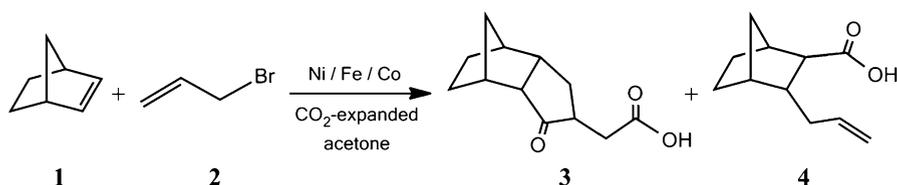
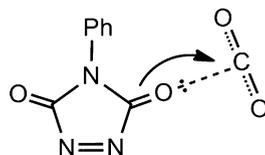
adduct could be altered, which changed most extensively for acrolein from 47:53 to 73:27 at pressure up to 16 MPa. The change was less significant for the other dienophiles, but the ratio did also change from 70:30 to 75:25 and from 63:37 to 73:27 for methyl acrylate and methyl vinyl ketone, respectively. At a high pressure of 16 MPa, very similar **3** to **2** ratios were seen for the three dienophiles, which are similar to those with Diels–Alder reactions of cyclopentadiene with methyl vinyl ketone and methyl acrylate in dense-phase  $\text{CO}_2$  reported by Tester et al. [68]. They concluded that the product selectivity was not affected by  $\text{CO}_2$  pressure, while Ikushima et al. mentioned about the effect of  $\text{CO}_2$  pressurization in the reaction of isoprene and methyl acrylate in dense-phase  $\text{CO}_2$  [69]. The pressurization and dissolution of  $\text{CO}_2$  in the toluene phase will scarcely change its features as a continuum of solvent for the reactions.  $\text{CO}_2$  molecules dissolved surround the substrate molecules inducing interactions between the substrate and  $\text{CO}_2$  molecules in the liquid phase. As the pressure is raised, the state of such a clump of substrate- $\text{CO}_2$  molecules in toluene may become similar to that in a dense-phase  $\text{CO}_2$  medium, resulting in the similar **3** to **2** ratios as obtained.

The molecular interaction of  $\text{CO}_2$  with three dienophiles in the presence of dense-phase  $\text{CO}_2$  was discussed using in situ high-pressure FTIR measurements, and the results indicated that the interactions of dense-phase  $\text{CO}_2$  with the carbonyl group may be stronger for acrolein compared with the other two carbonyl compounds, as estimated from the peak shift of  $\nu(\text{C}=\text{O})$  absorption band with increasing  $\text{CO}_2$  pressure. Fujita et al. speculated that  $\text{CO}_2$  molecules interact with the carbonyl group of a dienophile, and this makes its C-1 carbon more positive compared to the C-2 carbon. As a result, the approach b of Scheme 14.15 may be more favorable to occur than that between the dienophile and isoprene in which C-3 may be more positive than C-2 owing to the electron-withdrawing nature of the methyl group attached to C-2. These interactions may cause steric effects on the product selectivity, resulting in the increase of the **3** to **2** ratio with  $\text{CO}_2$  pressure. Eckert et al. also investigated the interactions between  $\text{CO}_2$  and the substrates for the Diels–Alder reaction between 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and anthracene in  $\text{CO}_2$ -expanded acetonitrile [70] (Scheme 14.16). From the reaction results, they speculate that  $\text{CO}_2$  dissolved in the liquid organic phase acts as a Lewis acid, and the interaction between Lewis acid and carbonyl oxygen of the PTAD would destabilize the azo bond, increasing the reactivity of the dienophile toward the diene (Scheme 14.17).



**Scheme 14.16** Diels–Alder reaction of anthracene and PTAD

**Scheme 14.17** Lewis acid–base interaction between  $\text{CO}_2$  and PTAD molecules

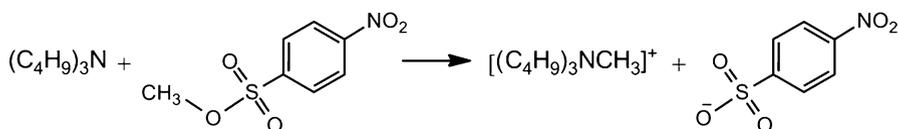


**Scheme 14.18** The catalytic carbonylative cycloaddition between norbornene **1** and allyl bromide **2** in  $\text{CO}_2$ -expanded acetone

### 14.2.6 Other Reactions

Recently, many researchers are making efforts to extend the application of dense-phase  $\text{CO}_2$  for new chemical reactions including multiphase reactions and liquid-phase organic reactions.

Moral et al. reported excellent chemoselectivity in the Ni-catalyzed cyclocarbonylation reaction with both alkynes and strained alkenes by tuning the operational parameters, using  $\text{CO}_2$ -expanded acetone as a reaction medium instead of liquid acetone [71]. The carbonylative cycloaddition between norbornene **1** and allyl bromide **2** with CO over Ni/Fe catalyst at 298 K in liquid or  $\text{CO}_2$ -expanded acetone was investigated (Scheme 14.18). The norbornene and allyl bromide tested were highly soluble in both pure  $\text{CO}_2$  and  $\text{CO}_2$ -expanded acetone, but the catalyst was only soluble in  $\text{CO}_2$ -expanded acetone under certain conditions. Thus, the reaction was feasible under homogeneous conditions in the latter medium. Cyclopentanone **3** was obtained as a main product in a selectivity of 77 % in the absence of  $\text{CO}_2$ , and the selectivity to **3** can slightly be improved to 80 % by  $\text{CO}_2$  pressurization. Interestingly, they added a certain amount of  $\text{H}_2\text{O}$  into the reaction system, and the selectivity to **3** was enhanced to 98 % with no retardation of the reaction. They speculated the acidification of reaction media with  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , which decreased the  $\text{OH}^-$  concentration, resulting in preventing hydroxyl attack at the acyl metal intermediate and interrupting the cyclization.



**Scheme 14.19** Menshutkin reaction of TBA and MNBS

Ford et al. focused on the controlling of local polarity in CXLs by changing  $\text{CO}_2$  pressure. They examined several probes as indicators of either local or bulk polarity in  $\text{CO}_2$ -expanded acetonitrile [72]. The Menshutkin reaction is a nucleophilic substitution reaction proceeding by an  $\text{S}_{\text{N}}2$  mechanism between a nitrogen base, typically a tertiary amine, and an organic electrophile such as an alkyl halide or sulfonate to form a quaternary ammonium salt. The transition state of this reaction is much more polar than the reactants, thus making the reaction kinetics strongly depend on the polarity of the surrounding medium. The Menshutkin reaction of tributylamine (TBA) with methyl *p*-nitrobenzenesulfonate (MNBS) in  $\text{CO}_2$ -expanded acetonitrile at 313 K was studied (Scheme 14.19), and it is found that at a mole fraction of  $\text{CO}_2 > 0.60$ , the value of the rate constant is significantly higher than that at a mole fraction of  $\text{CO}_2 < 0.60$ . At high  $\text{CO}_2$  loading, the charge-separated transition state of the reactant may be stabilized by acetonitrile with decreasing polarity of the liquid phase. Another factor is that the polar solutes would be clustered and/or aggregated as CXL increasingly becomes nonpolar.

### 14.3 Conclusions

Several examples described in this chapter demonstrate that  $\text{CO}_2$  can act as a promoter/modifier in organic synthetic reactions.  $\text{CO}_2$  has different macro (physical) and micro (chemical) functions depending on the reactions and conditions used. The reaction rate and/or the product selectivity in a liquid-phase reaction may be improved by the actions of  $\text{CO}_2$  dissolved in the liquid phase.  $\text{CO}_2$  interacts with organic substrates, intermediates, and/or products and changes their reactivity. Some pressure is needed for  $\text{CO}_2$  to dissolve in a certain amount, and the pressurization with  $\text{CO}_2$  is a simple procedure. When water is also present with dense-phase  $\text{CO}_2$ , the reaction mixture is more complicated, but interesting reaction outcome would be obtained through additive and/or synergistic effects of  $\text{CO}_2$  and water. The multiphase reactions in the presence of dense-phase  $\text{CO}_2$  and/or water are an interesting topic to be investigated in more detail, and the effects of  $\text{CO}_2$  and water should be explained at molecular level. For practical application, the multiphase reactions should be analyzed from the viewpoint of chemical engineering (mixing, phase behavior, mass transfer, and reaction kinetics), and the costs of  $\text{CO}_2$  pressurization and depressurization, post-purification of water, and so on should be considered.

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