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Wan-Hui Wang
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Transformation of Carbon Dioxide to Formic Acid and Methanol



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Chapter 1

Introduction

Abstract Huge amount of carbon dioxide emission poses a serious threat to our environmental and biological systems. Development of sustainable energy system based on CO₂ is highly desired. This chapter briefly introduces the approaches of CO₂ activation and transformation, and emphasizes CO₂ reduction to formic acid and methanol, which are currently considered as promising energy carriers and alternative fuels.

Keywords CO₂ emission · CO₂ activation · CO₂ reduction · Alternative fuels
Hydrogen economy · Methanol economy

In nature, plants use carbon dioxide (CO₂) to produce hydrocarbon and oxygen via photosynthesis, whereas the respiration consumes oxygen and releases CO₂. The levels of CO₂ concentration were almost constant and fluctuated minutely before the beginning of the industrial revolution. However, the balance in nature was broken since the start of the industrial revolution. Human activities, including deforestation, cement manufacture, and consumption of fossil fuels, caused the dramatic increase of CO₂ atmospheric concentration. This concentration has exceeded 400 ppm milestone in 2015 and will no longer decrease [1]. CO₂ is known as one of the important greenhouse gases. Global warming is the direct effect of increased atmospheric CO₂ concentration. The average global surface temperature has increased by 1 °C than in the 1960s [1]. The period from 2011 to 2015 has been the hottest 5-year period on record. Global warming leads to severe decline of Arctic sea ice and land ice, thus resulting in the sea level rise of 200 mm from 1870 to 2000. Another consequence of anthropogenic CO₂ emission is ocean acidification. This phenomenon causes major damage to the ocean ecosystems [2]. These combined effects have a strong influence on the biological and ecological systems worldwide.

Another major concern of our society is the depletion of fossil fuels, a nonrenewable energy resource. Since the modern society mainly relies on fossil resources to provide either energy or basic chemical resource, building a sustainable energy or chemical industry system before the depletion of fossil resources is of much

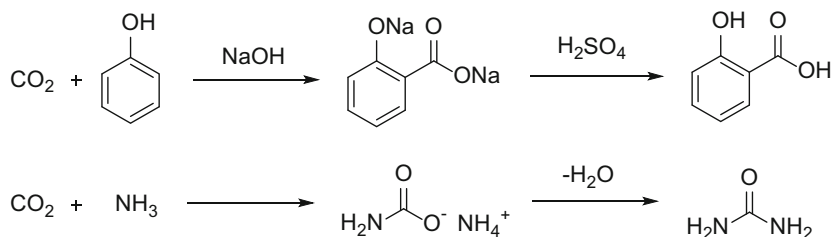


Fig. 1.1 Industrial production of salicylic acid and urea with CO_2

importance. Therefore, capture and utilization of CO_2 as fuels and chemicals is becoming an important scientific project. The use of CO_2 as an economical and abundant C1 building block to construct various chemicals and fuels has attracted increasing attention [3–8]. However, CO_2 is a thermodynamic stable molecule. Converting CO_2 into value-added chemicals and fuels is a challenging task. In the industry, CO_2 is only used to produce limited products including urea, organic carbonates, and salicylic acid (Fig. 1.1). A total of 150 million tons of urea is produced annually. This process utilizes 109.5 million tons of CO_2 , which accounts for 94% of CO_2 consumption [9]. However, urea production makes no contribution to carbon sequestration because urea emits equal amounts of CO_2 when applied to the soil as a fertilizer. Moreover, the production of the co-reactant, ammonia, from fossil resources releases more CO_2 .

The great challenge of CO_2 transformation is ascribed to the thermodynamic stability and kinetic inertness of CO_2 molecule. The length of the $\text{C}=\text{O}$ double bond in CO_2 is 116 pm, which is shorter than that of $\text{C}=\text{O}$ in carbonyl compounds (123 pm); therefore, the $\text{C}=\text{O}$ double bond of CO_2 is extremely stable.

To overcome the high energy barrier of CO_2 activation, catalysts are required. In the linear CO_2 molecule, the carbon atom is electron deficient and thus acts a Lewis acid, whereas the oxygen atom is a Lewis base. Transition metal as a Lewis base is demonstrated to be efficient in activating the weak electrophilic CO_2 molecule. The three possible coordination modes are illustrated in Fig. 1.2a. η^1 C-bound structure is the most common mode. Besides metals in a low oxidation state, other electron-rich species, such as base and hydride, are prone to attack C by forming a σ bond. Transfer of electron to the C atom results in a bent CO_2^- anion. This process can be facilitated by the interaction of the O atom with the electrophilic atoms through the outer coordination sphere. π coordination of one $\text{C}=\text{O}$ bond to the metal center leads to a η^2 -CO bonding mode. In this mode, the electron transfers from CO_2 to the metal center and weakens the $\text{C}=\text{O}$ bonds. Transition metals such as electron-poor species with a high oxidation state attack the O atom. η^1 O-bound mode is observed, but difficult to form. η^2 -OO mode is usually found in interaction with alkali metals. In addition, organocatalysts, such as frustrated Lewis pairs (FLPs), have recently achieved great progress in CO_2 activation [10, 11]. FLPs are a combination of bulky Lewis acid and Lewis base that do not form classical adducts because of the steric or geometric constraints. FLPs are ambiphilic and thus can activate CO_2 by adduct formation (Fig. 1.2b).

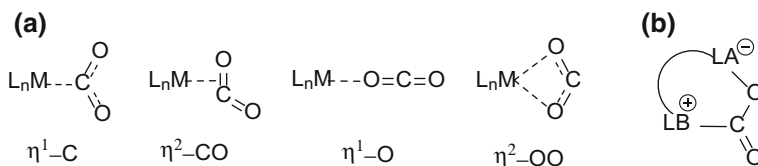


Fig. 1.2 **a** Coordination modes of CO₂ with transition metal complex. **b** Ambiphilic activation of CO₂ with FLPs

Besides using catalysts to decrease the energy barrier, using reactants of high intrinsic energy can render CO₂ transformation thermodynamically feasible. Three-membered heterocycles, especially epoxides, is typically used to incorporate the entire CO₂ molecule into products. The production of cyclic carbonate ethylene, propylene carbonate, and polycarbonate has been industrialized [7]. Nevertheless, no formal reduction is involved in this process. CO₂ is the end product of hydrocarbon combustion with the highest oxidation state. To fulfill the energy storage and convert CO₂ to fuels, CO₂ reduction is a prerequisite. CO₂ is reduced by photochemical, electrochemical, and thermal hydrogenation methods [12–14]. Photo- and electrochemical CO₂ reduction are of great interest, but this topic is beyond the scope of this book. As shown in Fig. 1.3, CO₂ can be reduced to various compounds, including aldehydes, acids, amides, alcohols, amines, and hydrocarbon.

Among these products, formic acid (FA) is recently recognized as a promising hydrogen storage material [15, 16]. Moreover, it can be directly used in the formic

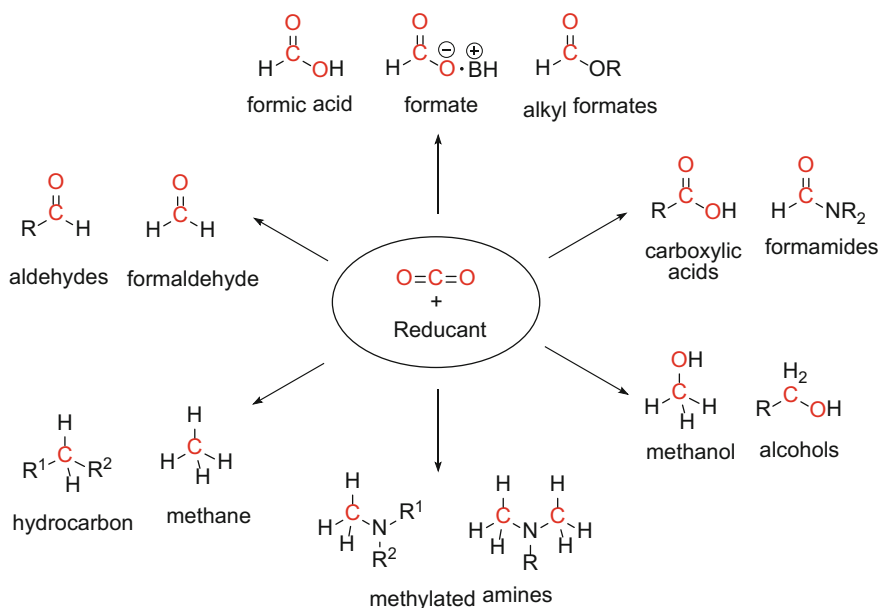
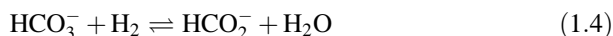
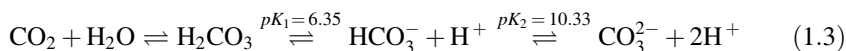
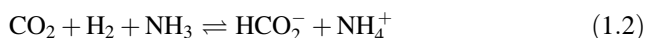
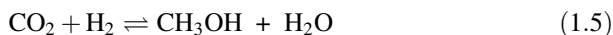


Fig. 1.3 Various chemicals and fuels from CO₂ reduction

acid fuel cell to produce electricity. Production of FA from CO₂ contributes greatly to the proposed “hydrogen economy” [17]. The hydrogenation of CO₂ into formic acid (Eq. 1.1) in the gas phase is endergonic ($\Delta G^\circ_{298} = +33 \text{ kJ mol}^{-1}$). When the reaction is carried out in the aqueous phase ($\Delta G^\circ_{298} = -4 \text{ kJ mol}^{-1}$) or with the addition of a base such as ammonia (Eq. 1.2, $\Delta G^\circ_{298} = -9.5 \text{ kJ mol}^{-1}$ in the gas phase), the CO₂ hydrogenation becomes exergonic and feasible. If base is added to the aqueous solution, the reaction is more favorable (Eq. 1.2, $\Delta G^\circ_{298} = -35 \text{ kJ mol}^{-1}$ in the aqueous phase) [18]. The solvent effects of water and deprotonation of FA with base are important for CO₂ hydrogenation. The acid/base equilibrium of CO₂ in water (Eq. 1.3) makes the reaction quite complicated. Although “hydrogenation of CO₂” is frequently used in this book and elsewhere, in basic aqueous solutions, the substrates used are HCO₃⁻ and CO₃²⁻ besides CO₂, depending on the pH of the solution. The hydrogenation of bicarbonate into formate in water (Eq. 1.4) is also known to be exergonic on the basis of the theoretical calculations ($\Delta G^\circ_{298} = -9.6 \text{ kJ mol}^{-1}$) [19].



Another product methanol is applied as liquid fuel, as well as in MeOH fuel cell. The generation of water makes the CO₂ hydrogenation to MeOH thermodynamically favorable (Eq. 1.5, $\Delta G^\circ_{298} = -9.5 \text{ kJ mol}^{-1}$) in the gas phase [20]. The thermodynamics is more favorable for this reaction in an aqueous solution (Eq. 1.5, $\Delta G^\circ_{298} = -79 \text{ kJ mol}^{-1}$) [18]. The concept of “methanol economy” has recently been put forward by Olah and co-workers [21–24].



Both in hydrogen economy and methanol economy, fossil fuels are replaced with hydrogen or methanol as a means of energy storage. In methanol economy, methanol can be regenerated from chemical recycling of CO₂. Therefore, carbon neutral process is achieved. In hydrogen economy, if H₂ is totally produced from photocatalytic water splitting, CO₂ emission is completely avoided. Both economy forms have specific advantages and disadvantages; they provide promising alternatives to the current economy based on fossil fuels. A number of previous books and reviews described the CO₂ transformation [9, 18, 25–31]. Whereas our main focus is the development of an alternative and sustainable economy involving CO₂ conversion [32]. This book discusses the transformation of CO₂ to FA and MeOH utilizing either homogenous or heterogeneous catalysts. This book covers the most recent advances in both transformations, including the design of catalysts and

catalytic mechanism. Hence, this book will help and serve as motivation for studying mechanism of CO₂ transformation and developing renewable energy sources.

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