

Reaction Mechanisms in Carbon Dioxide Conversion

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Preface

Carbon dioxide (CO₂) is today at the centre of attention of the scientific and technological world because of its potential role in climate change, which is supposed to be, directly or indirectly, caused by the growing level of CO₂ in the atmosphere. Policy-makers work out solutions ranging over a large number of options, including carbon capture and disposal or sequestration (CCS) or carbon capture and utilization (CCU).

The conversion of CO₂ into added-value products (chemicals, materials, fuels) is today one of the most widespread research themes, and the scientific literature presents a large number of reviews, papers and books that disclose the CO₂ chemistry or, in general, utilization. Industry is also much involved, as witnessed by the ever growing number of industrial patents and new processes.

Despite the large number of volumes published, an organized collection of information about the mechanisms concerning the many reactions in which CO₂ is involved does not exist. However, this book has been designed with the precise idea of filling the gap and collecting the knowledge we have of the *reaction mechanism* of CO₂ conversion when it is used either as a building block for the production of chemicals and materials, or as a carbon source for C₁ and C_n energy-rich molecules.

This book covers 40 years of research efforts in understanding the reactivity of CO₂. Its aim is not to present an exhaustive list of all reactions in which CO₂ can be involved, even if it shows quite a large number of them, but to analyze the thermodynamics and kinetics of its conversion.

The book is organized in ten chapters, each devoted to a particular subject. References point the reader to more specific issues or more general applications.

Chapter 1 presents the CO₂ molecule and gives fundamental information for understanding the chemistry of the heterocumulene. It also discusses the excited states of CO₂ and its radical anion and radical cation. Such species are often encountered in other chapters. The spectroscopic techniques (infrared, ultraviolet, nuclear magnetic resonance) used for collecting information about the state of the

CO₂ moiety in the products are introduced here, and applied in the following chapters.

Chapter 2 discusses the co-ordination of CO₂ to metal centres in various temperature conditions and the effects of such interaction on the heterocumulene structure. It addresses the question of whether preliminary co-ordination of CO₂ to a metal centre is an essential prerequisite for CO₂ conversion.

In Chap. 3 the interaction of CO₂ with selected electron-rich moieties such as: H⁻, OH⁻, NR₂⁻, R₃C⁻, RO⁻ and NRR'R'' is presented. This chapter discusses reactions not mediated by a metal centre, which are discussed extensively in the following chapter.

Chapter 4 is dedicated to the analysis of the interaction of CO₂ with E-X bonds, where E-X=M-H, M-R, M-OH, M-OR, M-O₂, M-M, C-C, C-O, N-H, N-C, N-P and Si-H. The analysis of such elementary steps is a bridge to the more general aspect of reactivity of CO₂. Such reactions illustrate the role of metals in initiating the reactions and give the fundamentals for understanding the use of CO₂ in synthetic chemistry under catalytic conditions.

Chapter 5 covers the topic of CO₂ interaction with multiple C-C bonds (alkenes, alkynes, cumulenes and conjugated dienes) relevant to carboxylation reactions with formation of new C-C bonds and to the synthesis of fine chemicals or intermediates.

Chapter 6 is dedicated to the synthesis of organic carbonates, linear and cyclic, molecular compounds and polymeric materials, and of polyurethanes. Organic carbonates (monomeric) find a wide use in various sectors of the chemical and energy industries. Polymers, which can be considered as chemical sinks of CO₂, find a continuously growing application in architecture and are used for making CDs, sanitary tools and laboratory glassware, among others. Polyurethanes play a key role as insulators and packaging materials.

Chapter 7 introduces the high-temperature processes of CO₂ conversion: Dry Reforming of Methane (DRM) and the relevant general use of CO₂ as oxidant or dehydrogenating (DH) agent. The conversion of CO₂ into methanol is discussed here as it has similarities to the other processes. Such applications deal with the conversion of large volumes of CO₂ into fuels or energy-rich molecules.

Chapter 8 deals with the 1e⁻-2e⁻ transfer to CO₂ in electrochemical, photochemical, photo-electrochemical processes, a topic of great importance for the conversion of CO₂ into energy-rich molecules. This chapter is relevant to the use of perennial energy sources, such as solar, wind, geothermal, hydro-energy, in the conversion of large volumes of CO₂. The use of solar energy brings about the man-made photosynthesis (direct and indirect) which is the future technology for the conversion of large volumes of CO₂ into chemicals and fuels.

Chapter 9 makes the analysis of bioprocesses (enzyme catalysed reactions) in which CO₂ is converted. Carboxylation processes and reduction of CO₂ to other C1-molecules such as HCOOH, H₂CO, CH₃OH and CH₄ are discussed here. A comparison to chemical processes discussed in previous chapters is straightforward.

Chapter 10 presents quite a new subject: the properties of hydrate-CO₂. This topic is a frontier research area and has great potential in the recovery of methane

from hydrates. Only a limited amount of information exists in the scientific and technical literature, but the interest for future applications is very high.

In its entirety, this book presents the essential knowledge of the CO₂ conversion reaction mechanisms. We believe that it will be of great help to those who are newcomers in the fascinating field of carbon-cycling (CO₂ conversion) mimicking Nature and be for all readers a guide to discovering aspects of the recent history of CO₂ chemistry, a topic of great interest today for its potential impact on avoiding CO₂ emissions and reducing fossil carbon extraction.

The authors wish to thank Prof. Sibudjing Kawi and Dr. Yasotha Kathiraser of the Department of Chemical and Biomolecular Engineering of the National University of Singapore, Singapore, for their great help, having co-authored Chap. 7, and Prof. Praven Linga, Dr. Junjie Zheng and Ponnivalavan Babu of the same Department for having co-authored Chap. 10.

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