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Reaction Mechanisms in Carbon Dioxide Conversion

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Preface

Carbon dioxide (CO_2) 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 CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 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 Cn energy-rich molecules.

This book covers 40 years of research efforts in understanding the reactivity of CO_2. Its aim is not to present an exhaustive list of all reactions in which CO_2 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 CO_2 molecule and gives fundamental information for understanding the chemistry of the heterocumulene. It also discusses the excited states of CO_2 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

CO_2 moiety in the products are introduced here, and applied in the following chapters.

Chapter 2 discusses the co-ordination of CO_2 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 CO_2 to a metal centre is an essential prerequisite for CO_2 conversion.

In Chap. 3 the interaction of CO_2 with selected electron-rich moieties such as: H^-, OH^-, NR_2^-, R_3C^-, 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 CO_2 with E–X bonds, where E–X=M–H, M–R, M–OH, M–OR, M–O_2, 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 CO_2. Such reactions illustrate the role of metals in initiating the reactions and give the fundamentals for understanding the use of CO_2 in synthetic chemistry under catalytic conditions.

Chapter 5 covers the topic of CO_2 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 CO_2, 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 CO_2 conversion: Dry Reforming of Methane (DRM) and the relevant general use of CO_2 as oxidant or dehydrogenating (DH) agent. The conversion of CO_2 into methanol is discussed here as it has similarities to the other processes. Such applications deal with the conversion of large volumes of CO_2 into fuels or energy-rich molecules.

Chapter 8 deals with the $1e^- - 2e^-$ transfer to CO_2 in electrochemical, photochemical, photo-electrochemical processes, a topic of great importance for the conversion of CO_2 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 CO_2. 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 CO_2 into chemicals and fuels.

Chapter 9 makes the analysis of bioprocesses (enzyme catalysed reactions) in which CO_2 is converted. Carboxylation processes and reduction of CO_2 to other C1-molecules such as HCOOH, H_2CO, CH_3OH and CH_4 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-CO_2. 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 CO_2 conversion reaction mechanisms. We believe that it will be of great help to those who are newcomers in the fascinating field of carbon-cycling (CO_2 conversion) mimicking Nature and be for all readers a guide to discovering aspects of the recent history of CO_2 chemistry, a topic of great interest today for its potential impact on avoiding CO_2 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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His scientific interests are in the fields of: Chemistry of small molecules (N_2, H_2, O_2, CO, CO_2, ethene, allene, propene, butadiene); Metals in low oxidation state (also negative); Co-ordination chemistry; Reactivity of co-ordinated molecules; Reaction mechanisms; Catalysis; CO_2 chemistry; CO_2 as building blocks for chemicals and carbon source for fuels; Photocatalysis; Utilization of biomass; Conversion of polyols; Conversion of long chain acids and esters; Polyunsaturated compounds; Valorization of polyols; New bio-sourced monomers for polymeric materials. Author of over 250 papers in international journals and of 10 books on CO_2 and biomass valorization; owner of several patents.

Founder and Honorary Chair of the International Conference on Carbon Dioxide Utilization-ICCDU.

Award of the Italian Chemical Society for "Pioneering work on carbon dioxide activation (and utilization)" 1990.

Renoir Award for the Dissemination of Science, 1990.

Award of the Société Française de Chimie, 1995 for Inorganic Chemistry.

Award of the Tianjin University, Tianjin China, for Green Chemistry 2002.

Several recognitions from the American Chemical Society for dissemination of "CO_2 Utilization".

Angela Dibenedetto Associate Professor at the University of Bari-UNIBA (IT)—Department of Chemistry. Her scientific interests are focused on carbon dioxide utilization in synthetic chemistry, catalysis, coordination chemistry and organometallic chemistry, green chemistry, marine biomass (algae) production by enhanced carbon dioxide fixation, marine biomass as source of fuels and chemicals applying the biorefinery concept.

She is director of the Interuniversity Consortium on Chemical Reactivity and Catalysis-CIRCC. In 2001 she was the winner of the RUCADI Prize for "Better Carbon Management—An Intelligent Chemical Use of CO_2" delivered by ACP-Belgium, Carburos Metalicos-Spain and ENIChem-Italy. Author of over 90 scientific papers on carbon dioxide utilization published in international journals since 1995 and several book chapters. She was invited speaker at several international conferences.

Eugenio Quaranta Graduated in Chemistry in 1983, received his Ph.D. in Chemistry in 1990 presenting a final dissertation entitled "Utilization of carbon dioxide in carboxylation reactions: the role of metal systems". Researcher at the University of Bari from 1990 to 1998, at present he is Associate Professor of General and Inorganic Chemistry at the Dipartimento di Chimica of the University of Bari. His main fields of research are coordination chemistry, organometallic chemistry, catalysis; activation of small molecules (CO_2, CO, CH_2O, C_2H_4, H_2, dimethyl carbonate, etc.); utilization of carbon dioxide in chemical synthesis; eco-sustainable synthetic methodologies.

Contents

Chapter 1
The Carbon Dioxide Molecule

Abstract The basic aspects of the reactivity of carbon dioxide (CO_2) are featured in this chapter and related to the electronic structure of the molecule. The electronic properties of neutral CO_2 are compared with those of the radical ions $CO_2^{\cdot-}$ and $CO_2^{\cdot+}$. The potential of a few spectroscopic techniques (infrared, ultraviolet–visible, nuclear magnetic resonance) in the characterization of CO_2 states is also highlighted.

1.1 Introduction

The carbon dioxide (CO_2) molecule is a relatively simple molecular system. Nevertheless, much of the life on Earth, as well as the fate of our planet itself, depends heavily on the properties of this small triatomic C_1 molecule.

Large amounts of CO_2 (~700 gigatonnes/year), are involved in the natural C-cycle, which includes the production of biomass by photosynthesis, biological respiration, carbonization processes, and so on. CO_2 is the waste end product of several human activities (e.g., fossil combustion, cement manufacture, fermentation, industrial processes). Since the beginning of the industrial revolution, in the second half of the nineteenth century, anthropogenic emissions of CO_2 have been growing continuously, reaching the level of more than 35 gigatonnes/year. Together with the indiscriminate deforestation of large areas of land, this has brought about a continuous increase of CO_2 concentration in the atmosphere, which is known to contribute severely to climate change. Much effort is currently being devoted to setting up efficient strategies to reduce emission/accumulation of CO_2 in the atmosphere. CO_2 chemical utilization (CCU), which is aimed at converting the heterocumulene into fuels or other valuable products, is currently under assessment as a sustainable technology for reducing waste and making better use of both carbon and energy.

There is, however, a net dichotomy between the sophisticated facilities exploited by Nature to convert CO_2 into valuable chemicals and the difficulties experienced by chemists in converting the heterocumulene through efficient catalytic processes. CO_2 reduction, or, more generally, CCU, is a challenging task and not only mere

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chemical routes but also electrochemical, photochemical, and photoelectrochemical approaches are currently under investigation. A great deal of effort is also addressed to converting this molecule by trying to mimic Nature.

In tackling the problem of CCU, it is of fundamental importance to have a clear view of the basic features of the reactivity of this molecule, which is strictly related to its electronic configuration. This chapter confronts this issue.

1.2 Electronic Properties of CO_2

1.2.1 Ground State of Carbon Dioxide

In its electronic ground state, the CO_2 molecule is linear and belongs to the point group $D_{\infty h}$. Both carbon–oxygen bonds are equivalent with the equilibrium C–O distance of 1.1600 Å, as obtained from an analysis of infrared (IR) spectra and confirmed by electron diffraction [1, 2]. Both carbon–oxygen bonds are polar as a result of the presence of net partial charges on the carbon and oxygen atoms [3, 4]. However, the molecule has no permanent electric dipole. In fact, the dipole moments associated with each of the C–O bonds cancel each other because they have equal magnitude but opposite directions because of the linear molecular geometry (Fig. 1.1).

The molecule has an electric quadrupole [5], whose moment is -4.3×10^{-26} esu/cm^2 [6] and thus exhibits significant intermolecular interactions, which may account for the formation of neutral aggregates. Neutral clusters of $(CO_2)_n$ $(2 \leq n \leq 5)$ have been produced in a molecular beam expansion system and observed via mass spectrometry [7, 8]. The intermolecular interactions can become even stronger when a cationic or anionic CO_2 molecule interacts with other CO_2 molecules, affording positively or negatively charged intermolecular aggregates, which may be regarded, respectively, as models for solvated CO_2^{+} radical cations or solvated $CO_2{}^{-}$ radical anions [7–11]. Positively charged aggregates of $(CO_2)_n{}^{+}$ $(2 \leq n \leq 10)$ have been generated by nucleation of neutral CO_2 molecules to $CO_2{}^{+}$ radical cation in a superionic expansion [9]. The stability of these clusters is significantly higher than that of neutral aggregates. The anionic clusters are also rather stable [10]. In contrast to the $CO_2{}^{-}$ radical anion, which is unstable with respect to electron detachment (see Sect. 1.4), the dimeric species $(CO_2)_2{}^{-}$ is stable by 0.9 eV, and stability increases with increasing cluster size.

The electronic configuration of the linear ground state, ${}^1\Sigma_g{}^{+}$, of CO_2 is as shown below.

$$
{}^1\textstyle\sum_g^+ \ (\text{ground state}) : 1\sigma_u^2\ \ 1\sigma_g^2(-541.1\ \text{eV})\ 2\sigma_g^2(-297.5\ \text{eV})\ 3\sigma_g^2(-37.6\ \text{eV})
$$

$$
2\sigma_u^2(-37.6\ \text{eV})\quad 4\sigma_g^2(-19.4\ \text{eV})\ 3\sigma_u^2(-18.1\ \text{eV})\ 1\pi_u^4(-17.6\ \text{eV})\ 1\pi_g^4(-13.8\ \text{eV})
$$