The Coordination and Insertion Chemistry of Carbon Dioxide

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The utilization of carbon dioxide as a carbon feedstock has been an area of great interest for many years. As a source of carbon, the supply of CO₂ is approximately equal to that of fossil fuels. Consequently, the degree of interest in the use of CO₂ as a C₁ starting material has increased exponentially over the past ten years. The principal problem associated with the use of CO₂ has been overcoming the kinetic activation barrier to reduction. Thus, many investigators have studied the use of transition metals as catalysts for the selective reduction of CO₂.

There has been a great deal of work focused on the homogeneous co-oligomerization of CO₂ with unsaturated organic substrates. For example, Behr has oligomerized CO₂ with butadiene to produce a series of conjugated lactones [2]. The heterogeneous catalytic reduction of CO₂ to CH₄ over alumina-supported metal atoms has been elegantly illustrated by Solymosi [3]. These researchers were able to observe large turnover numbers and very high selectivity for CH₄ as the final product in this process. Electrocatalytic reduction of CO₂ to CO with Ni(cyclam)Cl₂ as a catalyst has been effectively demonstrated by Sauvage [4]. Similarly, Löh and co-workers have shown that irradiation of a CO₂-saturated solution of Re(bipy)(CO)₂Cl with visible light leads to catalytic reduction of CO₂ to CO [5]. These catalytic accomplishments have promoted efforts to establish a foundation of mechanistic studies of CO₂ reactivity.

The initial phase in the study of transition metal-CO₂ catalysis was the investigation of the coordination of CO₂ to transition metal complexes. The three most likely fashions in which CO₂ could bind to a transition metal are shown below:

I

II

III

The first transition metal-CO₂ complex was prepared by Aresta and Nobile in 1975 [6]. Since then, only a few transition metal-CO₂ complexes have appeared in the literature [1a]. Complexes of type I have never been isolated and compounds of type II [7a-c] greatly outnumber those of type III [8a-c]. A second aspect of transition metal-CO₂ catalysis was the investigation of the insertion chemistry of CO₂ into M-E bonds. Virtually all of the examples of CO₂ insertion have been when E = NR₂, OR, R(Ar), and H [9a-d]. Although direct insertions have been proposed for E = R and H [10,11], Chisholm [12] has shown very clearly that insertion of CO₂ into M-E bonds with E = NR₂ or OR proceed via the mechanism shown below.

$$\text{Me}_2\text{NH(trace)} + \text{CO}_2 \rightleftharpoons \text{Me}_2\text{NCO}_2\text{H}$$

$$3\text{Me}_2\text{NCO}_2\text{H} + \text{Mo}_2(\text{NMe}_2)_6 \rightleftharpoons \text{Mo}_2(\text{NMe}_2)_3(\text{O}_2\text{CNMe}_2)_3 + \text{Me}_2\text{NH}$$
Recently, the electrocatalytic reduction of CO\(_2\) to give products such as carbon monoxide has received increasing attention \[13\] and is likely to become the main area of research in the future. The design of more selective and more efficient catalysts will doubtless be assisted by studies directed toward understanding the mechanistic details of metal-mediated CO\(_2\) electroreduction.

References


