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学位論文題目	Elucidation of Metal Carbon Bond Characters in CO ₂ Multi-Electron Reduction on Metals
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論文内容の要旨

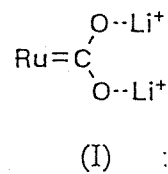
Carbon dioxide is a potential C1 source for the synthesis of future fuels and chemicals. A variety of metal complexes have proven to be active as precursors to CO and/or HC(O)OH generations in electro- and photochemical reduction of CO₂. From the viewpoint of the utilization of CO₂, however, multi-electron reduction of CO₂ accompanied with C-C bond formation is much more important than the two electron reduction of CO₂. Recently, highly reduced products containing C-C bonds are obtained in a few photo- and electrochemical CO₂ reductions mediated by transition metal complexes in both homogeneous and heterogeneous reactions. Elucidation of the reaction mechanism including the binding mode of CO₂ to metals would serve to construct a strategy for the design of catalysts, which effectively catalyze the reduction of CO₂ accompanied with C-C bond formation. In this connection, knowledge concerning the binding modes of CO₂ to metals is a fundamental importance to understand the reactivity of CO₂ ligated to metals. Among a various metal CO₂ complexes reported so far, metal complexes with an η^1 -CO₂ ligand are generally accepted as reaction intermediates for CO generation in photo- and electrochemical CO₂ reductions, since metal- η^1 -CO₂ complexes ($[M-\eta^1-CO_2]$) are subject to protonation in protic media to form metal-hydroxycarbonyls ($[M-C(O)OH]$) and -carbonyls ($[M-CO]$) as precursors to HC(O)O⁻ and CO, respectively. The molecular structures of M- η^1 -CO₂ and the conjugated acid M- η^1 -C(O)OH, therefore, are of interest in the elucidation of the CO₂/CO conversion on metals because of the lack of the data concerning the structural difference in those two complexes. Furthermore, the elucidation of the role of an M-C(O)H in the reduction of CO₂ is also interested on the basis of the proposal as the key intermediate in the multi-electron reduction of CO₂ accompanying by C-C bond formation.

The purpose of this study is to elucidate the main factor which controls the selectivity of two- and multi-electron reduction of CO₂. This would afford a strategy for designing of effective catalysts directed toward multi-electron reduction of CO₂ accompanied by C-C bond formation.

Interconversion of CO₂ and CO on metals requires an intramolecular 2-electron transfer between metals and CO₂ or CO through the metal-C bond. The two electron transfer from and to metal centered orbitals may cause serious configurational changes of metal complexes, which would strongly hamper the smooth CO₂/CO conversion. Such the change in the electronic structures of metals would be effectively depressed by participation of π -orbitals of ligands as well as d-orbitals of metals in the intramolecular electron transfer and accelerates the CO₂/CO conversion. Hydroxycarbonyl complexes (M- η^1 -C(O)OH) as the intermediate in the CO₂/CO conversion, therefore, may afford the

fundamental knowledge about the intramolecular electron transfer by the comparison of the deprotonated $M-\eta^1\text{-CO}_2$ ones. In the Chapter 2, the molecular structure of $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-C(O)OH})]^+$ is determined as the first example of a hydroxycarbonyl intermediate in CO_2 reduction. The comparison in the molecular structures between $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-C(O)OH})]^+$ and $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$ revealed that not only the Ru-CO_2 but also $\text{Ru-N}(\text{trans to CO}_2)$ bond distances are largely influenced by protonation of $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$. Thus, σ -donor and π -acceptor ability of bpy play the role in the electron reservoir to facilitate the smooth interconversion among $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$, $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-C(O)OH})]^+$ and $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ in protic media.

The adjustment of the electron density of the CO_2 moiety in $M-\eta^1\text{-CO}_2$ complexes would serve the control of the reactivities in the reduction of CO_2 . In the Chapter 3, stabilization of $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$ in non protic media is described. In solid state, $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$ forms three hydrogen bondings among the oxygens of the $\eta^1\text{-CO}_2$ moiety and three hydrate water molecules. The complex dissociates CO_2 to form $[\text{Ru}(\text{bpy})_2(\text{CO})\text{H}]^+$ in CH_3CN in the presence of a small amount of H_2O . Furthermore, $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$ also reacted with O_2 with evolving CO_2 in dry CH_3CN to give $[\text{Ru}(\text{bpy})_2(\text{O}_2\text{CO})]$ possibly through an O_2 adduct intermediate ($[\text{Ru}(\text{bpy})_2(\text{CO})(\text{O}_2)]$). On the other hand, $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$ is quite stable in alcohol even in air. Thus, hydrogen bondings formed between $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$ and alcohol effectively stabilizes the complex by depression of the accumulation of excess electrons in the $\eta^1\text{-CO}_2$ moiety. Otherwise $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$ dissociates CO_2 , and the resulting $[\text{Ru}(\text{bpy})_2(\text{CO})]^0$ undergoes electrophilic attack of proton and O_2 . Stabilization of $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$ in dry CH_3CN is also achieved by the presence of Li^+ . The ^{13}C NMR of an CD_3CN solution of the carbon-13 enriched $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$ in the presence of Li^+ showed a broad and a sharp signal at δ 215 and 203 ppm assignable to CO_2 and CO groups, respectively. Furthermore low $\nu_{\text{asym}}(\text{CO}_2)$ band appeared at 1467 cm^{-1} in the solution IR spectra in CD_3CN in the presence of Li^+ . The observations that the shift of the $^{13}\text{CO}_2$ signal from δ 210 ppm in CH_3OH to δ 215 in CH_3CN and the missing of the $\nu_{\text{asym}}(\text{CO}_2)$ band in the IR spectra in CD_3CN in the presence of Li^+ , are reasonably explained by the formation of carbene like structure (I) in the medium. Thus, the bond character of a $M-\eta^1\text{-CO}_2$ complex is controlled by the intermolecular bondings. Hydrogen bondings and association of Li^+ to the oxygen atoms of the $\eta^1\text{-CO}_2$ group cause inclination of electrons to the CO_2 moiety and stabilize $[\text{Ru}(\text{bpy})_2(\text{CO})(\eta^1\text{-CO}_2)]$.



Destruction of those intermolecular bondings results in the shift of electrons to metal centers, which gives rise to dissociation of CO_2 to form unstable

$[\text{Ru}(\text{bpy})_2(\text{CO})]^\circ$.

In the Chapter 4, reactivities of $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CHO})]^+$ and $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CH}_2\text{OH})]^+$ as models of reaction intermediates in multi-electron reduction of CO_2 are studied. Electrochemical reduction of CO_2 by $[\text{Ru}(\text{bpy})(\text{trpy})(\text{CO})]^{2+}$ in $\text{EtOH}/\text{H}_2\text{O}$ produces not only CH_2O and CH_3OH but also $\text{HO}(\text{O})\text{CCHO}$ and $\text{HO}(\text{O})\text{CCH}_2\text{OH}$ together with $\text{HC}(\text{O})\text{OH}$ as the main product. Both $[\text{Ru}(\text{bpy})(\text{trpy})(\text{CHO})]^+$ and $[\text{Ru}(\text{bpy})(\text{trpy})(\text{CH}_2\text{OH})]^+$, which are generated by two- and four-electron reduction of $[\text{Ru}(\text{bpy})(\text{trpy})(\text{CO})]^{2+}$, are proposed as the precursors to those highly reduced products. In order to elucidate the role of $[\text{Ru}(\text{bpy})(\text{trpy})(\text{CHO})]^+$ in the multi-electron reduction of CO_2 , the reactivity of $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CHO})]^+$ instead of $[\text{Ru}(\text{bpy})(\text{trpy})(\text{CHO})]^+$ toward CO_2 was examined due to the extremely thermal lability of the latter. In CH_3CN , $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CHO})]^+$ is stable below -20°C . Even such a low temperature, $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CHO})]^+$ smoothly reacted with CO_2 to form $\text{HC}(\text{O})\text{O}^-$ with generation of $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$. A strong hydride donor ability of $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CHO})]^+$ well explains the generation of $\text{HC}(\text{O})\text{OH}$ as the main product in the multi-electron reduction of CO_2 by $[\text{Ru}(\text{bpy})(\text{trpy})(\text{CO})]^{2+}$. Taking into account of the formation of $\text{HC}(\text{O})\text{O}^-$ and $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ in the reaction of $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CHO})]^+$ with CO_2 , which strongly interferes the multi-electron reduction, a decrease in a hydride ability of a formyl complex would overcome the difficulty in multi-electron reduction of CO_2 by metal complexes. Thus, a metal-formyl complex is the key intermediate as for the two- and multi-electron reduction of CO_2 . Furthermore, the observation that protonation and carboxylation of $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CH}_2\text{OH})]^+$ as a model of $[\text{Ru}(\text{bpy})(\text{trpy})(\text{CH}_2\text{OH})]^+$ produced CH_3OH and $\text{HO}(\text{O})\text{CCH}_2\text{OH}$ under electrolysis conditions, reasonably elucidates the function of $\text{Ru}-\text{CH}_2\text{OH}$ in the six-electron reduction of CO_2 .

The multi-step conversion from $\text{Ru}-\text{CO}_2$, $\text{Ru}-\text{C}(\text{O})\text{OH}$, $\text{Ru}-\text{CO}$, $\text{Ru}-\text{C}(\text{O})\text{H}$ to $\text{Ru}-\text{CH}_2\text{OH}$ is inevitably accomplished by variation in the carbon orbital of the $\text{Ru}-\text{C}$ bonds (sp^2 , sp , and sp^3), which would also give crucial influence on the formation energy of $\text{HC}(\text{O})\text{OH}$, CO , CH_2O , CH_3OH , and CH_4 in multi-electron reduction of CO_2 by metal complexes. Vibrational spectroscopy may provide useful information about the $\text{Ru}-\text{C}$ bond characters in the conversion from $\text{Ru}-\text{CO}_2$ to $\text{Ru}-\text{CH}_2\text{OH}$. In the Chapter 5, comparisons of raman spectra of a series of *cis*- $[\text{Ru}(\text{bpy})_2(\text{CO})\text{X}]^{n+}$ ($\text{X}=\text{CO}$, $\text{C}(\text{O})\text{OH}$, $\text{C}(\text{O})\text{OCH}_3$, CO_2 , CHO , and CH_2OH ; $n=0, 1, 2$) and their ^{18}O or deuterium substituted analogs permit reasonable assignments of $\nu(\text{Ru}-\text{X})$ and $\nu(\text{Ru}-\text{CO})$ bands around 500 and 470 cm^{-1} . The validity of the assignments of those bands led to identification of two configurational isomers of *cis*- $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CH}_2\text{OH})]^+$ with respect to the orientation of the CH_2-OH bond. The $\nu(\text{Ru}-\text{X})$ bands shift to higher wavenumbers with lengthening the $\text{Ru}-\text{X}$ bond distances ($d(\text{Ru}-\text{X})$). Such unusual dependence of $\nu(\text{Ru}-\text{X})$ upon $d(\text{Ru}-\text{X})$ may be

associated with multi-bond characters of the $C\equiv O$, $C=O$, and $C-O$ bonds in the Ru-X moieties.

審査結果の要旨

豊原清綱君は、金属錯体が触媒する二酸化炭素の電気化学的還元機構について研究を行った。二酸化炭素固定化は、現在非常に関心が持たれており、触媒反応過程における中間体の諸性質を明らかにすることは、新たな反応系構築の足掛かりを与えることが期待される。本論文は、還元反応中間体の合成、構造決定、反応性の検討を行い、触媒反応の諸性質を明らかにしたものである。以下に本論文の内容をまとめる。

(1) $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ は、金属上で二酸化炭素を二電子還元し、一酸化炭素およびギ酸を生成する。この反応について、二酸化炭素付加体のプロトン化によって、ヒドロキシカルボニル錯体を経由して、18電子状態のカルボニル錯体を与える機構が提案されている。豊原君は、二酸化炭素の電気化学的還元中間体である $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COOH})](\text{CF}_3\text{SO}_3)$ の結晶構造を明らかにした。ヒドロキシカルボニル錯体におけるRu-L(L=bpy or C)結合の距離を CO_2 錯体のそれと比べると、すべての結合が0.06~0.03オングストロームの範囲で短くなっていることが明らかとなった。

(2) 二酸化炭素付加体の有機溶媒中でのカルベン構造生成について、各種スペクトルを用いて検討を行った。その結果、乾燥した有機溶媒中では、二酸化炭素は容易に放出されてしまうが、二酸化炭素残基の酸素にルイス酸であるリチウムイオンが付加した場合には有機溶媒中でも、金属イオンと二酸化炭素の炭素間の結合が多重結合性を帯び、安定なカルベン型の構造をとることを見いだした。

(3) ルテニウムポリピリジル錯体による電気化学的な CO_2 の還元機構を分子レベルで検討した。アルデヒド類を与える二酸化炭素還元反応では、その反応の途中で、不安定なホルミル錯体を生成すると考えられる。そこで、多電子還元反応における不安定反応中間体であるホルミル錯体を合成し、その反応性について検討を行った。その結果、ホルミル錯体は、系中に存在する二酸化炭素に対して強力なヒドリド供与体として作用し、ギ酸を生成した。ホルミル中間体は、多電子還元反応中間体であると同時に、ギ酸生成中間体としても作用するという知見は、今後、多電子還元触媒系探索のための重要な手がかりとなるものである。

(4) 電気化学的多電子還元では、二酸化炭素の活性化及び還元反応は、常に金属炭素結合を介して起こる。豊原君は、反応サイクルのモデル錯体として、 $[\text{Ru}(\text{bpy})_2(\text{CO})(\text{X})]^{n+}$ ($\text{X}=\text{CO}_2, \text{COOMe}, \text{COOH}, \text{CO}, \text{CHO}, \text{CH}_2\text{OH}$; $n=0\sim 2$)を合成した。これらの金属炭素結合を、振動スペクトルと構造解析によって評価を行い、還元に伴う金属炭素間結合の距離伸長と、結合間の分極に伴う振動波数の上昇を見いだした。

以上のように、本論文は二酸化炭素固定反応の反応中間体の反応性、物性の検討を通して、触媒サイクルの全体像を明確にし、反応条件を含めた触媒系設計の指針を得ることに成功したものであり、学位論文としての十分な価値があると判断された。

また、口述試験では、約1時間論文の内容について口頭で発表を行い、さらに1時間その内容について質疑応答および試問を行った。口頭発表は、研究の目的、内容、成果、今後の展望についてよく整理されたものであり、重要なポイントを押さえた大変わかりやすい発表であった。口頭発表後には、主に、(1)ホルミル錯体のヒドリド移動の機構、(2)還元反応のpH依存性、(3)カルボキシル錯体の反応性とカチオンの効果、(4)

ラマン測定における同位体効果、などについての質問や、今後の研究の展望などの幅広い質問がなされたが、豊原君はそれぞれの質問に対して的確な回答を行っており、本研究分野について十分に学習し理解していることがうかがえた。また、論文は英文で作成されているが、英語の能力についても高い評価を得た。

以上により、審査委員全員一致で、口述試験に合格であると判断した。