

GERMANY/HONG KONG JOINT RESEARCH SCHEME
THE PROJECT REPORT
(for Project Completion)

Project Number: G_HK006/10

Title

Functionalization of Carbon Dioxide in Nano-water Droplets

Particulars

	Hong Kong team				German team	
Name of Project Co-ordinator (with title)	Dr. Chi-Kit Siu				Prof. Dr. Martin K. Beyer	
Name of Co-Investigator (if any)						
Institution or Institutional affiliation	<input checked="" type="checkbox"/>	CityU	<input type="checkbox"/>	HKU	<input checked="" type="checkbox"/>	Christian-Albrechts-Universität zu Kiel Others: _____
	<input type="checkbox"/>	CUHK	<input type="checkbox"/>	HKUST	<input type="checkbox"/>	
	<input type="checkbox"/>	HKBU	<input type="checkbox"/>	LU	<input type="checkbox"/>	
	<input type="checkbox"/>	HKIEd	<input type="checkbox"/>	PolyU	<input type="checkbox"/>	
Other project team members (if any)					Dr. Robert F. Höckendorf, Dr. Christian van der Linde	

Funding Period

	1 st year	2 nd year (if applicable)
Start Date	1 January 2011	1 January 2012
Completion Date	31 December 2011	31 December 2012

Objective(s) as per original application

1. Understanding the reaction mechanism of the formation of the hydrated formate anions $\text{HCO}_2^-(\text{H}_2\text{O})_n$ from the reactions of activated carbon dioxide with methanethiol in nano-water droplets.
2. Designing chemical processes to functionalize molecular carbon dioxide in a controllable manner in the gas phase.

Details of Report [Please attach relevant document(s)]

i) Outline of proposed research and results obtained

The proposed research aims to examine the chemical properties of carbon dioxide radical anion ($\text{CO}_2^{\cdot-}$) generated from one-electron reduction of CO_2 by a free electron solvated in nano-scale water clusters in the gas phase by means of a combination of Fourier-transform ion cyclotron resonance mass spectrometry and quantum chemical calculations. The ion-molecule reactions of $\text{CO}_2^{\cdot-}$ toward some olefins and sulphur-containing compounds in water clusters have been demonstrated in the gas phase. Their reaction mechanisms have also been examined by comparing the reaction thermodynamic obtained from nano-calorimetric experiments and density functional theory calculations. These reactions include (i) the formation of C-H bond via the hydrogen-atom abstraction from methanethiol molecule (CH_3SH) to $\text{CO}_2^{\cdot-}$, producing a formate anion (OOC^--H), (ii) the formation of C-C bond by radical attack of $\text{CO}_2^{\cdot-}$ onto the olefin carbons of a methyl acrylate molecule ($\text{CH}_2=\text{CHCOOCH}_3$) or an allyl alcohol molecule ($\text{CH}_2=\text{CHCH}_2\text{OH}$) resulting, respectively, in a monomethyl succinate radical anion ($\text{OOC}^--\text{CH}_2\text{CH}^{\cdot}\text{COOCH}_3$) or a 4-hydroxybutyric acid radical anion ($\text{OOC}^--\text{CH}_2\text{CH}^{\cdot}\text{CH}_2\text{OH}$), and (iii) the formation of C-S bond from the insertion of the disulphide linkage in CH_3SSCH_3 by $\text{CO}_2^{\cdot-}$ to generate the $\text{OOC}^--\text{SCH}_3 + \text{CH}_3\text{S}^{\cdot}$.

Generation of $\text{CO}_2^{\cdot-}$ as well as $\text{O}_2^{\cdot-}$ has also been demonstrated using the redox chemistry of $\text{Mg}^+(\text{H}_2\text{O})_n$ cluster in the gas phase. The valence electron of Mg^+ being solvated out by the water clusters can reduce CO_2 or O_2 . Theoretical calculations suggested that the resulting $\text{CO}_2^{\cdot-}$ and $\text{O}_2^{\cdot-}$ can be solvated by the $\text{Mg}^{2+}(\text{H}_2\text{O})_n$ clusters to form a solvent-separated ion pair structure or directly coordinated to the Mg^{2+} centre to form a contact-ion pair structure. The hydrated electron in the $\text{Mg}^+(\text{H}_2\text{O})_n$ clusters has also recently been employed to perform one-electron reduction of acetonitrile, followed by a proton transfer, to produce $\text{CH}_3\text{CNH}^{\cdot}$ or $\text{CH}_3\text{CHN}^{\cdot}$.

ii) Significance of research results

Carbon dioxide is a promising carbon feedstock. With the growing interest in using CO_2 a C1 building block in chemical synthesis and as a potential hydrogen-storage material, the molecular principles of CO_2 activation have attracted considerable attention in the gas phase. The $\text{CO}_2^{\cdot-}(\text{H}_2\text{O})_n$ clusters with finite number of water molecules provide controllable model systems allowing us to investigate the solvation effects of the reactions of $\text{CO}_2^{\cdot-}$ in aqueous media at the molecular level. Our experimental and theoretical results in the gas phase provide a mechanistic understanding of the observations from condensed phase electrochemistry; the carboxylation of olefins, such as methyl acrylate, can be performed in two ways: by addition of $\text{CO}_2^{\cdot-}$ to neutral methyl acrylate or by addition of neutral CO_2 to the methyl acrylate radical anion. The decay of the product will preferentially occur as the reverse reaction of the second pathway. The

results show that the chemistry of CO₂ in the presence of an extra electron is very subtle. The good news is that C–C bond formation between CO₂^{•-} and olefins readily occurs, with significant bond strengths and moderate barriers. In order to have the intact products, they need to be stabilized before elimination of neutral CO₂ takes place.

iii) Research output

1. Christian van der Linde, Amou Akhgarnusch, Chi-Kit Siu,* Martin K. Beyer* “Hydrated Magnesium Cations Mg⁺(H₂O)_n, n ≈ 20 – 60, Exhibit Chemistry of the Hydrated Electron in Reactions with O₂ and CO₂” *J. Phys. Chem. A* **2011**, *115*, 10174-10180.
2. R. F. Höckendorf, Q. Hao, Z. Sun, B. S. Fox-Beyer, Y. L. Cao, O. P. Balaj, V. E. Bondybey, C. K. Siu,* M. K. Beyer,* “Reactions of CH₃SH and CH₃SSCH₃ with Gas-Phase Hydrated Radical Anions (H₂O)_n^{•-}, CO₂^{•-}(H₂O)_n, and O₂^{•-}(H₂O)_n” *J. Phys. Chem. A* **2012**, *116*, 3824-3835.
3. A. Akhgarnusch, R. F. Höckendorf, Q. Hao, K. P. Jäger, C.-K. Siu,* Martin K. Beyer,* “Carboxylation of Methyl Acrylate by Carbon Dioxide Radical Anions in Gas-Phase Water Clusters” *Angew Chem. Int. Ed.* (Submitted on 5 April 2013).
4. R. F. Höckendorf, K. Fischmann, Q. Hao, C. van der Linde, O. P. Balaj, C.-K. Siu,* M. K. Beyer,* “C–C Bond Formation between CO₂^{•-} and Allyl Alcohol in Water Clusters: A Mechanistic Study” *Int. J. Mass Spectrom.* (Submitted on 15 April 2013).
5. T.-W. Lam, C. van der Linde, A. Akhgarnusch, Q. Hao, M. K. Beyer,* C.-K. Siu,* “Reduction of CH₃CN in Hydrated Magnesium Cations Mg⁺(H₂O)_n, n ≈ 20 – 60, in the Gas Phase” *ChemPlusChem* (Submitted on 30 April 2013).

iv) Potential for or impact on further research collaboration

Fruitful research outputs resulted from the synergy of the collaboration between the experimental mass spectrometric research group led by Prof. Dr. Beyer and the theoretical chemistry research group led by Dr. Siu have been produced in this two-year funding supports by the Germany/Hong Kong Joint Research Scheme. The collaborative researches between the two complementary research groups will continue. Currently, the reaction mechanisms for the one-electron reduction of alcohol by hydrated electron are being investigated. In addition, as an extension of the proposed research, the redox chemistry of metal ions in aqueous media at the molecular level is also being examined.