

**EXPLORING THE PERI-, CHEMO-, AND REGIO-SELECTIVITY OF ADDITION OF
METAL OXIDES TO KETENES: A DFT COMPUTATIONAL STUDY**

KNUST

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in partial fulfillment of the requirement for the award of the degree of

MASTER OF PHILOSOPHY

in Physical Chemistry

By:

Issahaku Ahmed, HND, B.Sc. (Hons.)

August, 2015

DECLARATION

I hereby declare that this thesis is my own work towards the M.Phil. and that, to the best of my knowledge and belief, it contains no material that has been accepted for the award of any other degree in any educational institution nor material previously published or written by another person, except where due reference is made in the text of the thesis.

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Issahaku Ahmed

(Candidate)

.....

Signature

.....

Date

Certified by:

Richard Tia, B.Sc., Ph.D.

(Supervisor)

.....

Signature

.....

Date

Evans Adei, B.Sc., M.Phil., Ph.D.

(Co-Supervisor)

.....

Signature

.....

Date

and

Godfred Darko, B.Sc., M.Sc., Ph.D.

(Head of Department)

Signature

.....

Date

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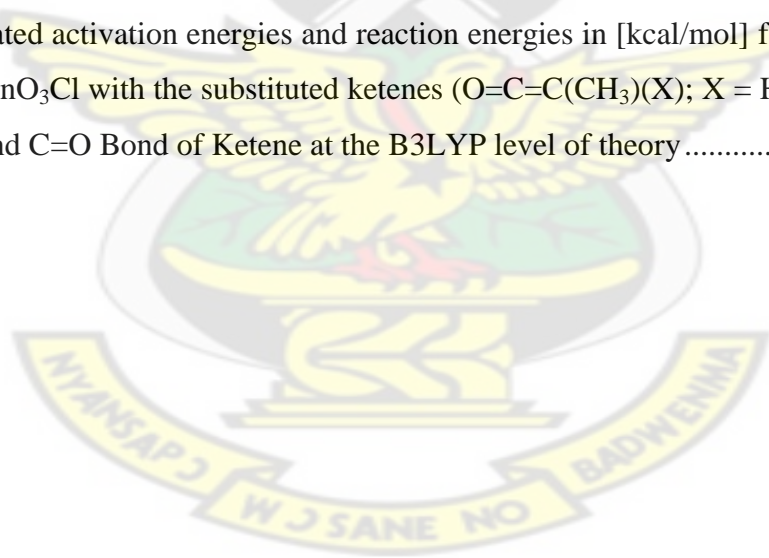
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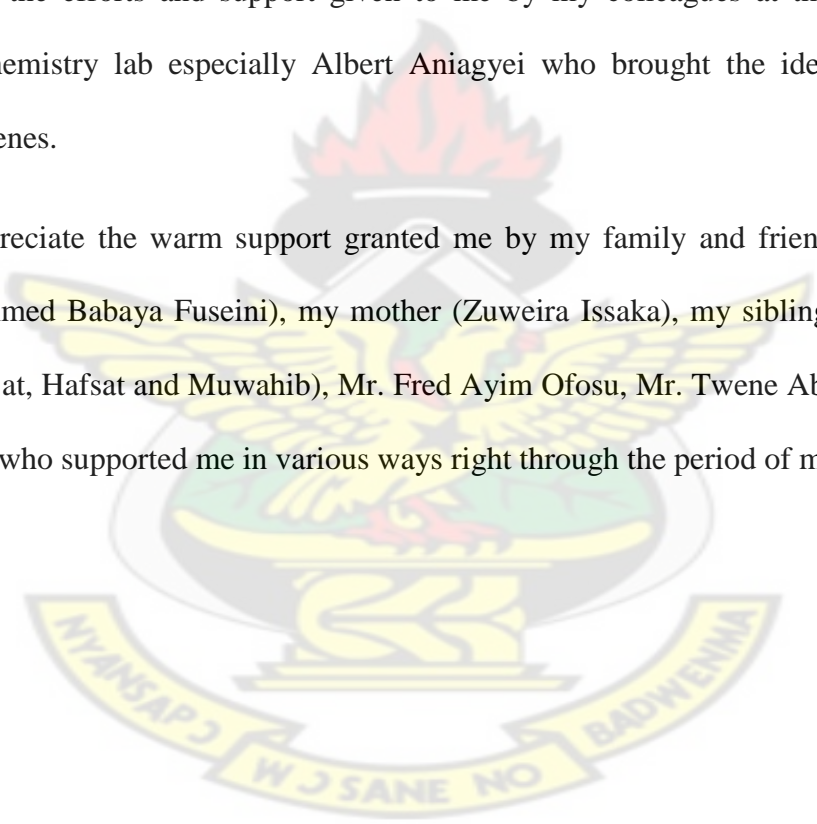
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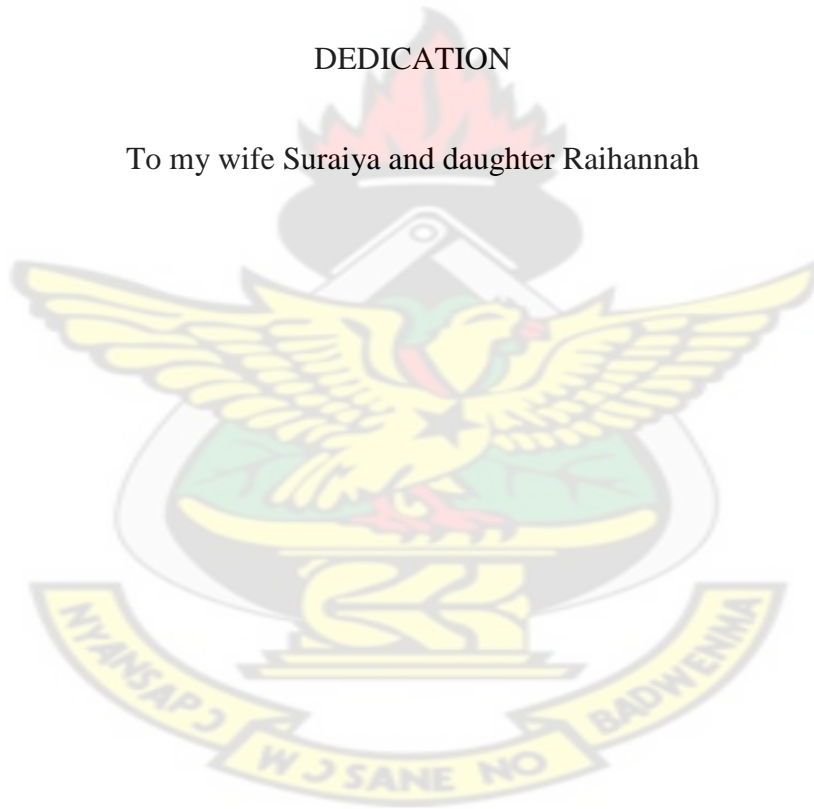
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DEDICATION

To my wife Suraiya and daughter Raihannah



Publications Arising From this Work

1. Ahmed, I.; Tia, R.; Adei, E. Density functional theory study of the mechanisms of addition of transition metal oxides ReO_3L ($\text{L} = \text{Cl}^-$, O^- , OCH_3 , CH_3) to substituted ketenes,, *Journal of Theoretical Computational Chemistry*. **2015**, 14, No. 5, 1550035: 1-29.
2. Ahmed, I.; Tia, R.; Adei, E. Exploring the Peri-, Chemo-, and Regio-selectivity of Addition of Manganese Metal Oxides MnO_3L ($\text{L} = \text{Cl}^-$, O^- , OCH_3 , CH_3) to Substituted Ketenes: A Computational Study, *Inorganica Chimica Acta*. 441 (**2016**) 57-66.
3. Ahmed, I.; Tia, R.; Adei, E. Exploring the peri-, chemo- and regio-selectivity on the mechanisms of addition of transition metal oxides of the type TcO_3L ($\text{L} = \text{Cl}^-$, O^- , OCH_3 , CH_3) to substituted ketenes $\text{O}=\text{C}=\text{C}(\text{CH}_3)(\text{X})$ ($\text{X} = \text{H}$, CH_3 , Cl^- , CN^- , Ph). *Canadian Journal of Chemistry*, DOI 10.1139/cjc-2015-0295

ABSTRACT

Ketenes are excellent precursors for catalytic asymmetric reactions, creating chiral centers mainly through addition across their C=C bonds and C=O bonds. Density functional theory calculations at the MO6/LACVP* and B3LYP/LACVP* levels of theory have been employed in a systematic investigation of the peri-, chemo- and regio- selectivity of the addition of transition metal oxo complexes of the type MO_3L ($\text{M} = \text{Re}, \text{Tc}, \text{Mn}$; $\text{L} = \text{Cl}, \text{O}^-, \text{OCH}_3, \text{CH}_3$) to substituted ketenes $\text{O}=\text{C}=\text{C}(\text{CH}_3)(\text{X})$ [$\text{X} = \text{CH}_3, \text{H}, \text{CN}, \text{Ph}$] with the aim of elucidating the effects of substituents on the mechanism of the reactions. The [2 + 2] addition pathway, across the C=C or C=O (depending on the ligand), is the most preferred in the reactions of dimethyl ketene with all the metal complexes studied. The [2 + 2] pathway is also the most preferred in the reactions of ReO_3Cl with all the substituted ketenes studied except when $\text{X} = \text{Cl}$. Thus of all the reactions studied, it is only the reaction of ReO_3Cl with $\text{O}=\text{C}=\text{C}(\text{CH}_3)(\text{Cl})$ that prefers the [3 + 2] addition pathway. Reactions of dimethyl ketene with ReO_3L favours addition across C=O bonds of the ketene when $\text{L} = \text{O}^-$ and CH_3 but favours addition across C=C bonds when $\text{L} = \text{OCH}_3$ and Cl . In the reactions of ReO_3Cl with substituted ketenes, addition across C=O bonds is favoured only when $\text{X} = \text{H}$ while addition across C=C bonds is favoured when $\text{X} = \text{CH}_3, \text{Cl}, \text{Ph}, \text{CN}$. The order in the activation energies of the reactions of dimethyl ketenes with the metal complexes ReO_3L with respect to changing ligand L is $\text{O}^- < \text{CH}_3\text{O}^- < \text{Cl}^- < \text{CH}_3$ while the order in reaction energies is $\text{CH}_3 < \text{CH}_3\text{O}^- < \text{O}^- < \text{Cl}^-$. For the reactions of substituted ketenes with ReO_3Cl , the order in activation barriers is $\text{CH}_3 < \text{Ph} < \text{CN} < \text{Cl} < \text{H}$ while the reactions energies follow the order $\text{Cl} < \text{CH}_3 < \text{H} < \text{Ph} < \text{CN}$. In the reactions of dimethyl ketenes with ReO_3L , the trend in the selectivity of the reactions with respect to ligand L is $\text{Cl}^- < \text{CH}_3\text{O}^- < \text{CH}_3 < \text{O}^-$ while the trend in selectivity is $\text{CH}_3 < \text{CN} < \text{Cl} < \text{Ph}$ in the reactions of ReO_3Cl with substituted ketenes. In the reactions of TcO_3L ($\text{L} = \text{Cl}, \text{O}^-, \text{OCH}_3, \text{CH}_3$) to substituted ketenes $\text{O}=\text{C}=\text{C}(\text{CH}_3)(\text{X})$ [$\text{X} = \text{H}, \text{CH}_3, \text{Cl}, \text{CN}, \text{Ph}$] the [2 + 2] addition across the C=C bond of the ketenes is the preferred pathway while the [3 + 2] addition across the C=C bond of the ketenes is the preferred pathway for $\text{L} = \text{Cl}, \text{OCH}_3$. The order in the activation energies of the preferred [3 + 2] and [2 + 2] pathways for addition of dimethyl ketenes to the metal complexes TcO_3L with respect to changing ligand L is $\text{O}^- < \text{Cl} < \text{CH}_3 < \text{CH}_3\text{O}^-$ while the order in reaction energies is $\text{CH}_3 < \text{CH}_3\text{O}^- < \text{O}^- < \text{Cl}$. For the reactions of substituted ketenes with TcO_3Cl , the order in activation barriers for the preferred addition pathways is $\text{CH}_3 < \text{Ph} < \text{H} < \text{Cl} < \text{CN}$ while the reactions energies follow the order $\text{Cl} < \text{CH}_3 < \text{H} < \text{Ph} < \text{CN}$. In the reactions of dimethyl

ketenes with TcO_3L , the trend in the selectivity of the reactions is $Cl < CH_3O^- < CH_3 < O^-$ while the trend in selectivity is $CH_3 < H < CN < Cl < Ph$ in the reactions of TcO_3Cl with substituted ketenes. In the reactions of MnO_3L ($L = Cl, O^-, OCH_3, CH_3$) to substituted ketenes $O=C=C(CH_3)(X)$ [$X = H, CH_3, Cl, CN, Ph$] the $[3 + 2]$ addition across the $C=C$ is the preferred pathway for all the reactions studied irrespective of the ligand or substituents on the ketene except for $L = O$ which undergo stepwise addition pathway. In the reaction of MnO_3Cl with the substituted ketenes ($O=C=C(CH_3)(X)$; $X = H, CH_3, Cl, CN, Ph$), the $[2 + 2]$ addition across the $C=O$ of the ketene is preferred for $L = OCH_3$ over $C=C$ of the ketene. No $[2 + 2]$ addition pathways were located except for $L = OCH_3$. The order in the activation energies of the preferred $[3 + 2]$ and $[2 + 2]$ pathways for addition of dimethyl ketenes to the metal complexes MnO_3L with respect to changing ligand L is $O^- < Cl < CH_3 < CH_3O^-$ while the order in reaction energies is $CH_3 < CH_3O^- < Cl < O^-$. For the reactions of substituted ketenes with MnO_3Cl , the order in the activation energies for the preferred addition pathways is $O^- < Cl < CH_3 < CH_3O^-$ while the order in reaction energies is $CH_3 < CH_3O^- < Cl < O^-$. For the reactions of substituted ketenes with MnO_3Cl , the order in activation barriers for the preferred addition pathways is $Cl < H < CN < CH_3 < Ph$ while the reactions energies follow the order $H < CH_3 < CN < Ph < Cl$. In the reactions of dimethyl ketenes with MnO_3L , the trend in the selectivity of the reactions is $Cl^- < CH_3O^- < CH_3 < O^-$ while the trend in selectivity is $H < Cl < CH_3 < CN < Ph$ in the reactions of MnO_3Cl with substituted ketenes ($O=C=C(CH_3)(X)$; $X = H, CH_3, Cl, CN, Ph$). Generally, reactions involving a change in oxidation state of metal from the reactant to the product have high activation barriers while reactions that do not involve a change in oxidation state have low activation barriers. The changes in oxidation state were observed for substituents or ligands with inductive effect. A triplet zwitterionic intermediate is formed in the reactions of the MO_3L with the substituted ketenes for all the metals. The reactions of dimethyl ketene with MO_3L ($L = Cl, O^-, OCH_3, CH_3$) will most likely lead to the formation of an ester precursor for each metal. For both $[3 + 2]$ and $[2 + 2]$ addition, low activation barriers are obtained when the substituent on the ketene is electron-donating while high activation barriers are obtained when the substituent is electron-withdrawing. The results show that the reactions of ketenes with MnO_3L complexes have lower activation barriers for the preferred $[3 + 2]$ and $[2 + 2]$ addition pathways than those of the ReO_3L and TcO_3L complexes reported in the literature. Thus the MnO_3L complexes may be better catalysts for the activation of the $C=C$ bonds of substituted ketenes than the reported ReO_3L and TcO_3L complexes and is in the order $Mn < Tc < Re$.