

Springer Theses

Recognizing Outstanding Ph.D. Research

Aims and Scope

The series “Springer Theses” brings together a selection of the very best Ph.D. theses from around the world and across the physical sciences. Nominated and endorsed by two recognized specialists, each published volume has been selected for its scientific excellence and the high impact of its contents for the pertinent field of research. For greater accessibility to non-specialists, the published versions include an extended introduction, as well as a foreword by the student’s supervisor explaining the special relevance of the work for the field. As a whole, the series will provide a valuable resource both for newcomers to the research fields described, and for other scientists seeking detailed background information on special questions. Finally, it provides an accredited documentation of the valuable contributions made by today’s younger generation of scientists.

Theses are accepted into the series by invited nomination only and must fulfill all of the following criteria

- They must be written in good English.
- The topic should fall within the confines of Chemistry, Physics, Earth Sciences, Engineering and related interdisciplinary fields such as Materials, Nanoscience, Chemical Engineering, Complex Systems and Biophysics.
- The work reported in the thesis must represent a significant scientific advance.
- If the thesis includes previously published material, permission to reproduce this must be gained from the respective copyright holder.
- They must have been examined and passed during the 12 months prior to nomination.
- Each thesis should include a foreword by the supervisor outlining the significance of its content.
- The theses should have a clearly defined structure including an introduction accessible to scientists not expert in that particular field.

More information about this series at <http://www.springer.com/series/8790>

Zhandong Wang

Experimental and Kinetic Modeling Study of Cyclohexane and Its Mono-alkylated Derivatives Combustion

Doctoral Thesis accepted by
the University of Science and Technology of China,
Hefei, China

 Springer

Author
Dr. Zhandong Wang
University of Science and Technology
of China
Hefei
People's Republic of China

Supervisor
Prof. Fei Qi
University of Science and Technology
of China
Hefei
People's Republic of China

ISSN 2190-5053 ISSN 2190-5061 (electronic)
Springer Theses
ISBN 978-981-10-5692-5 ISBN 978-981-10-5693-2 (eBook)
<https://doi.org/10.1007/978-981-10-5693-2>

Library of Congress Control Number: 2017963973

© Springer Nature Singapore Pte Ltd. 2018

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd. part of Springer Nature
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Supervisor's Foreword

The combustion of fossil fuels provides most of the energy used worldwide, and it promotes the growth of society and the economy. However, large amounts of emitted pollutants are harmful to human health and to the sustainability of human civilization. The design of high-efficiency low-emission engines and the development of detailed kinetic models of fossil fuels are crucial to alleviating the energy shortage and reducing pollution. Cycloalkanes are an important component of fossil fuels and their surrogates. In China, for example, No. 3 Kerosene has large mass fraction of cycloalkanes, and the recent discovery of oil sands may contain larger fractions of cycloalkanes. The combustion of cyclohexane and its derivatives produces large amounts of dienes (carcinogenic 1,3-butadiene) and cyclic intermediates, and it has a relatively high sooting tendency.

The object of this Ph.D. thesis is to clarify the combustion chemistry of cyclohexane and its two mono-alkylated derivatives (methylcyclohexane and ethylcyclohexane), which are commonly chosen as surrogate components for transport fuels. The pyrolysis and laminar premixed flames of these three model compounds were studied using state-of-the-art synchrotron radiation photoionization mass spectrometry. Their initial reaction pathways during combustion were calculated with high-level quantum chemistry methods, and the rate constants were evaluated. A detailed kinetic model was developed and validated against experimental data covering a wide range of combustion conditions, including pyrolysis at various pressures, flame structure at low pressures, as well as species concentrations from jet-stirred reactor oxidation at intermediate and high temperatures, ignition delay times, and laminar flame speeds. This model contributes to understanding the combustion chemistry of these cycloalkanes (initial decomposition pathways,

distribution of intermediates, and formation of air pollutants), developing combustion models for substituted cycloalkanes with long alkyl side chains and/or multiple side chains, and it has application to engine and fuel design, and emission control.

Hefei, People's Republic of China
September 2017

Prof. Fei Qi

Parts of this thesis have been published in the following journals:

- Z. Wang, Z. Cheng, W. Yuan, J. Cai, L. Zhang, F. Zhang, F. Qi, J. Wang, *Combust. Flame* 159 (2012) 2243–2253.
- F. Zhang, Z.D. Wang, Z.H. Wang, L.D. Zhang, Y.Y. Li, F. Qi, *Energy Fuels* 27 (2013) 1679–1687.
- Z. Wang, L. Ye, W. Yuan, L. Zhang, Y. Wang, Z. Cheng, F. Zhang, F. Qi, *Combust. Flame* 161 (2014) 84–100.
- Z. Wang, H. Bian, Y. Wang, L. Zhang, Y. Li, F. Zhang, F. Qi, *Proc. Combust. Inst.* 35 (2015) 367–375.
- Z. Wang, L. Zhao, Y. Wang, H. Bian, L. Zhang, F. Zhang, Y. Li, S.M. Sarathy, F. Qi, *Combust. Flame* 162 (2015) 2873–2892.

Acknowledgements

This Ph.D. thesis was based on research at the National Synchrotron Radiation Laboratory, University of Science and Technology of China, from 2008 to 2014, under the supervision of Prof. Fei Qi. As my mentor in my Ph.D. studies and throughout my academic career, Prof. Qi's impressive knowledge, his enthusiasm for scientific exploration, and his constant search for excellence have influenced me significantly. I would also like to thank Prof. Frédérique Battin-Leclerc, Prof. Katharina Kohse-höinghaus, Prof. Olivier Herbinet, Prof. Lidong Zhang, Prof. Yuyang Li, and Prof. Feng Zhang for their guidance, and Prof. Mani Sarathy for the support of this work.

Finally, I wish to thank the members of the combustion and flame team for their help and companionship. Many thanks to my family for their continuous support.

September 2017

Zhandong Wang

Contents

1	Introduction	1
1.1	Background	1
1.2	Diagnostics of Laboratory Combustion System	2
1.2.1	<i>In Situ</i> Optical Spectroscopy	3
1.2.2	Product Analysis After Gas-Sampling	3
1.3	Fossil Fuel Surrogates	7
1.3.1	Surrogates for Gasoline	8
1.3.2	Surrogates for Jet Fuel	8
1.3.3	Surrogates for Diesel	9
1.4	Research on Cycloalkane Fuels	11
1.5	Thesis Content	15
	References	16
2	Experimental Method and Kinetic Modeling	23
2.1	Experimental Method	23
2.1.1	Synchrotron Radiation Beamline	23
2.1.2	Flow Reactor Pyrolysis Apparatus	24
2.1.3	Low-Pressure Laminar Premixed Flame	30
2.2	Kinetic Modeling	32
2.2.1	Thermodynamic Data	33
2.2.2	Chemical Kinetic Data	34
2.2.3	Transport Data	35
	References	36
3	Experimental and Modeling Study of Cyclohexane Combustion	39
3.1	Background	39
3.2	Kinetic Model	42
3.2.1	Unimolecular Decomposition and Isomerization of Cyclohexane	42
3.2.2	Dissociation of 1-Hexene	52

3.2.3	H-atom Abstraction of Cyclohexane	53
3.2.4	Decomposition and Isomerization of Cyclohexyl Radical	53
3.2.5	Decomposition and Isomerization of 5-Hexen-1-yl Radical	55
3.2.6	Decomposition and Dehydrogenation of Cyclohexene	57
3.3	Flow Reactor Pyrolysis of Cyclohexane	60
3.3.1	Consumption of Cyclohexane	61
3.3.2	Formation and Consumption of Cyclopentadiene and Benzene	68
3.4	Laminar Premixed Flame of Cyclohexane	70
3.5	JSR Oxidation of Cyclohexane	75
3.6	Ignition Delay Time and Laminar Flame Speed of Cyclohexane	80
3.7	Summary and Conclusions	81
	References	83
4	Experimental and Modeling Study of Methylcyclohexane Combustion	89
4.1	Background	89
4.2	Decomposition and Isomerization of Methylcyclohexane	91
4.2.1	Theoretical Method	93
4.2.2	Results and Discussion	94
4.3	H-atom Abstraction of Methylcyclohexane	100
4.4	Unimolecular Reactions of Methylcyclohexane Radicals	103
4.5	Estimation of Thermodynamic Data	105
4.6	Kinetic Model for Methylcyclohexane Combustion	109
4.7	Flow Reactor Pyrolysis	110
4.7.1	Consumption of Methylcyclohexane	110
4.7.2	Isomerization of Cyclohexyl Radical and Methylcyclohexane Radicals	120
4.7.3	Dissociation of Cyclohexyl and Methylcyclohexane Radicals	125
4.7.4	Reaction Pathway Analysis for Toluene and Benzene	129
4.8	Low-Pressure Premixed Flame of Methylcyclohexane	131
4.9	Ignition Delay Time and Laminar Flame Speed	136
4.10	Summary and Conclusions	139
	References	140

5 Experimental and Modeling Study of Ethylcyclohexane	
Combustion	145
5.1 Background	145
5.2 Preliminary Investigation of Ethylcyclohexane	
Decomposition	146
5.2.1 Dissociation and Isomerization of Ethylcyclohexane	146
5.2.2 Ring-Opening Isomerization of Ethylcyclohexane	
Radicals	149
5.2.3 Dissociation of Ethylcyclohexane Radicals	153
5.3 Kinetic Model of Ethylcyclohexane	156
5.4 Pyrolysis of Ethylcyclohexane	161
5.5 Premixed Flame of Ethylcyclohexane	171
5.6 JSR Oxidation of Ethylcyclohexane	175
5.7 Laminar Flame Speed of Ethylcyclohexane	179
5.8 Summary and Conclusions	180
References	181
6 Combustion Kinetics of Cyclohexane and C1–C2 Mono-alkyl	
Cyclohexanes	183
6.1 Flow Reactor Pyrolysis	183
6.1.1 Species Pool	184
6.1.2 Mole Fraction Distribution	188
6.2 Low-Pressure Premixed Flame	193
6.3 Laminar Flame Speed	197
References	199
7 Conclusions and Perspective	201
Appendix A	205
Appendix B	210
Appendix C	214