

IN THE NEME OF GOD

A Theoretical Study on Kinetics and Dynamics of Reaction of Methyl Radical with Ethyl Radical

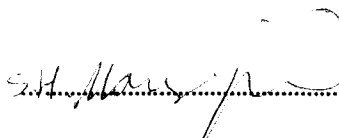
**BY
Zahra Homayoon**

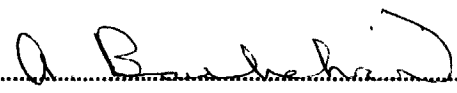
THESIS

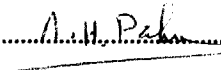
**SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES IN
PARTIAL FULFILMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE (M.Sc)**

**IN
PHYSICAL CHEMISTRY
SHIRAZ UNIVERSITY
SHIRAZ, IRAN**

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January 2002

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DEDICATED TO:

*My Dear
Mother and Father*

Σ.Σ.Νο

Acknowledgement

My hearty appreciation goes to my research advisor, Dr .S. H. Mousavipour, for his excellent guidance and for his sincerity and serenity.

I would like to thanks the members of the thesis committee, Dr. A. Boushehriy and Dr. A. H. Pakyari.

I am also under obligation to thank my group mates, Mr. A. Graily, Mr. M. A. Namdar, Ms S. Fakhraee, Mr. Sh. Ramezani and Mr. V. Sahieb whose collaborations led me to complete this work.

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ABSTRACT

A Theoretical Studies on Kinetics and Dynamics of Reaction of Methyl Radical with Ethyl Radical

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Association reaction of methyl radical and ethyl radical and hydrogen abstraction from ethyl radical by methyl radical theoretically, were studied. Ab initio calculations were carried out using the Gaussian 98. Geometries of reactants, transition states and products were optimized at HF/6-31G[D,P] and HF/6-311G[D,P] level of theory. Single point calculations at MP4SDTQ level of theory carried out to calculate the potential energy changes along the reaction coordinate.

The spin contamination has been taken into account in the calculation of the energies in the Gaussian program and noted in the results as PMP2. A harmonic force field frequency calculation establishes the nature of each stationary point. The barrier height, were calculated at the UHF/6-31G(D,P), (P)MP2/6-31G(D,P), MP4SDTQ/6-31G(D,P), and MP4SDTQ/6-311G(D,P) levels of theory corrected for zero point energy.

Kinetic parameters were calculated by canonical transition state theory (CTST) two reactions and variational transition state theory (VTST) for association reaction of ethyl radical and methyl radical by using two Fortran programs. There is no barrier height in potential energy surface of association reaction of ethyl radical and methyl radical. CVTS was used to determine the position of bottleneck for this reaction. Barrier height for hydrogen abstraction from ethyl radical by methyl radical was obtained 64.9 kJ/mol. The rate constant was calculated over the temperature range 100-3000 K. CTST was used with some modification such as tunneling

effect and hindered rotations. The tunnel correction for hydrogen abstraction from ethyl radical by methyl radical was calculated by two expressions. The first method introduced by Shavitt and the second method suggested by Brown. The tunneling factor is related to the frequency of an imaginary vibration, ν^* , in a well created by inverting the barrier. Hindered rotation is one of reasons of curvature in Arrhenius plots. To calculate the partition function for hindered rotations, we used two methods introduced by Leblance and Pacey and by Pitt, Gilbert, and Ryan.

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Chapter One

Introduction

Gas phase radical-radical reactions have been actively studied for more than 60 years. These reactions are the reverse of unimolecular decomposition, and so their rate constants can be used to quantitatively test theories of unimolecular reactions. In addition, the rate constants are valuable in understanding the chemistry of combustion, hydrocarbon cracking and air pollution.

Most experimental work has focused on the rates of radical self-addition, with $\text{CH}_3 + \text{CH}_3$ receiving the most attention. Reactions between unlike radicals have been studied less thoroughly, in part due to additional experimental complexities involved.

One of the reactions, which have been studied several times experimentally, is the decomposition of propane into ethyl radical and methyl radical. Only a few investigations of the reverse of this reaction have been done.

Teng and Jones in 1972 studied kinetics of the reactions of hydrogen atoms with ethylene and vinyl fluoride. He reported the rate constant for the combination of ethyl radical and methyl radical in a chain reaction mechanism for hydrogen atoms with ethylene as $k=41.7 \times 10^{10} \exp(-1.67\text{kJ/RT})$ (1/mol s).¹

In 1975 Lifshitz obtained the rate constant for the combination of these radicals as 2.4×10^{10} (1/mol s) at 1050-1250 K.²

Thermal decomposition of propane in 1980 was studied by IR laser absorption kinetic spectroscopy. The rate constant for combination of these radicals was 7.24×10^9 (1/mol s) at 1300-1700 K.³

In 1982 propane thermal dissociation over the temperature range 1300 to 1700 K was investigated experimentally and theoretically. The rate constant for the reverse reaction was $8 \times 10^7 \exp(47.39\text{kJ/RT})$.⁴

In 1987 Anastasi and Arthur investigated the rate constant for the reactions of CH₃ radical with C₂H₅, i-C₃H₇ and t-C₄H₉ radicals. The rate constants obtained at 308 K were (mol⁻¹s⁻¹) 9.91×10⁸ for hydrogen abstraction from ethyl radical by methyl radical and 2.7×10¹⁰ for combination of CH₃ and C₂H₅.⁵

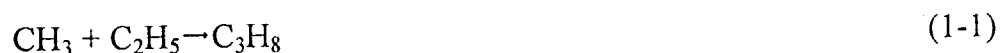
In 1984 rate constant for association of these radicals was obtained at 300-2500 K as 7×10⁹ (1/mol s).⁶

The other results obtained for association of ethyl radical and methyl radical are as: (1/mol s) k=2.72×10¹⁰ (T=308 K)⁷, 8.91×10⁹exp(7.11kJ/RT) (T=773-793 K)⁸, 2.75×10¹⁰(T=308 K)⁵, 1.93×10¹¹(T^{-0.32})(T=773-2300 K)⁹, 2.83×10¹⁰(T=300-800 K)¹⁰, 4×10¹⁰(T=290 K)¹¹.

Also in 1962 Thynne studied hydrogen abstraction from ethyl radical by methyl radicals at 351-521 K and reported the rate constant as k=5.5×10⁹.¹²

This reaction investigated also by Tsang and Hampson in 1986 at 300-2500. They obtained the rate constant as k=1.95×10¹⁰(T)^{-0.5} 1/(mol s).¹³

Because of the different results obtained in these studied the importance of theoretical study become obvious. It is the goal of this work to investigate the reaction between ethyl and methyl radicals in the two different pathways. The first is the combination of these radicals



The second reaction is hydrogen abstraction from ethyl radical by methyl radicals



Radical combination reactions are more difficult to understand than the other types of reaction. These reactions do not have a potential barrier; it

has been difficult to choose a position for the transition state along the reaction coordinate. In this work at first we used computational chemistry to investigate association of ethyl and methyl radicals and then the less important reaction of these radical, hydrogen abstraction from ethyl radical by methyl radicals was investigated.