

A Theoretical Study on Radical Reactions of Unsaturated Hydrocarbons

Theses of Ph.D. dissertation

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1. Introduction

The computational chemistry is useful tool for suggesting reaction mechanism and selecting the energetically favourable reactions. It is rather important in the case of radical reactions, since they are fast and non-selective in general. It is even true for the reaction of hydroxyl radical, since it is an aggressive oxidatizing agent.

Here, reactions of unsaturated and polyunsaturated hydrocarbons with hydroxyl radical were in my focus of interest, since this kind of reactions can occur in combustion processes, in chemical destructions of atmospheric organic compounds as well as in lipid bio-oxidation.

Formation of monoallyl and biallyl radical by hydrogen abstraction reaction is discussed mostly in my thesis since their nature is relatively unknown in the literature.

2. Applied Methods

The most crucial point in the quantum chemical calculation is the choice of the proper level of theory which should be accurate and fast. These opposing requirements are achieved in such a way that the optimization of molecular geometry (including the vibrational analysis) is treated at relatively low level of theory separately from the high level calculation of the total energy.

In order to find the proper level of theory for further optimization, the calculated geometry is compared to experimental and/or high level *ab initio* results (CCSD or QCISD). Several hibrid functionals and low level *ab initio* methods were tested to choose an appropriate methods for geometry optimization.

While a reasonable geometry can be obtained using relatively low level method, one has to choose another strategy for accurate thermochemistry, for instance, as follows:

1. carrying out single point calculation using highly accurate methods (QCISD(T) or CCSD(T)) with extended basis set.
2. usage of composite methods such as G3MP2. These methods mostly are based on the fact that the difference in treatment of correlation energy between MP2 and QCISD(T) is nearly basis set independent. In this case, one can calculate the total energy at MP2 level using an extended basis set and then the correction of correlation energy can be done at moderate basis set.

In the case of isomerization of the 1,4-pentadien-3-yl radical, the unimolecular reaction rates were carried out using conventional unimolecular transition state theory (TST). For reactions of 2,5-heptadiene, the conventional bimolecular TST was employed to calculate the reaction rate constants at room temperature.

3. New Scientific Results

Propene + •OH reactions [1,5]

- I. Benchmark calculations were carried out on the allylic hydrogen abstraction reactions of propene with hydroxyl radical using B3PW91, B1B95, B1LYP, MPW1PW91, PBE1PBE, BHH, B3LYP, BH&HLYP hybrid functionals and *ab initio* HF, MP2, CCSD methods at 6-31G(d) basis set. I found that CCSD/6-31G(d) level of theory is able to reproduce reasonably well the available experimentally observed geometries. At this level of theory, two different transition states of allylic hydrogen abstraction were explored. B3LYP/6-31G(d) was not able to characterize the indirect transition state. Amongst the remaining low-level methods, I found that only the BH&HLYP/6-31G(d) and the CCSD/6-31G(d) geometries are in good match.
- II. Using intrinsic reaction coordinate method, I have proven the existence of an indirect allylic hydrogen abstraction reaction mechanism which started from a van der Waals complex. I have found that this van der Waals complex is identical to the prereaction complex of the •OH-addition. Furthermore, I have also explored a co-existing direct allylic hydrogen abstraction reaction.
- III. The calculations at QCISD(T)/cc-pVTZ, QCISD(T)/6-311++G(3df,2p) and G3MP2 levels of theory had been able to reproduce the experimental heat of formation value for the allylic hydrogen abstraction.
- IV. My calculation at G3MP2//BH level of theory showed that the allylic hydrogen abstraction reactions have small activation enthalpy. For the direct abstraction, this barrier was found to be 0.7 kJ mol⁻¹. In the case of the indirect reaction, the enthalpy of the transition state was below by 0.9 kJ mol⁻¹ than that of the reactants (propene + •OH). Consequently, it can be regarded as a reaction with pseudo negative activation enthalpy.

- V.** Amongst the remaining direct hydrogen abstraction reactions, the non-terminal abstraction (from the vinyl position) was found to be energetically most favoured since its activation enthalpy turned out to be only 6.3 kJ mol^{-1} .
- VI.** I have also explored the low-lying consecutive reaction channels starting from the products of the $\bullet\text{OH}$ -addition (namely, 1-propanol-2-yl and 2-propanol-1-yl). The most preferred reaction ($\Delta^\ddagger H^\circ = 125,6 \text{ kJ mol}^{-1}$) is the methyl dissociation from the 2-propanol-1-yl radical which results methyl radical and vinyl alcohol.
- VII.** The temperature dependence of the propene + $\bullet\text{OH}$ reaction was described quantitatively based on my calculated potential energy surface.

1,4-pentadiene + •OH reactions [2,3]

- VIII.** I have explored the van der Waals complexes which did correspond to the reaction of 1,4-pentadiene with •OH. I have shown that only the outer van der Waals complex can be the springboard for the terminal, non-terminal •OH-addition and biallylic hydrogen abstraction reactions.
- IX.** My calculations at QCISD(T)/cc-pVTZ//BH&HLYP/6-31G(d) level of theory did, in fact, support the concept that terminal and non-terminal •OH-addition as well as biallylic hydrogen abstraction reactions have pseudo negative activation enthalpy. So they are all expected to be fast.
- X.** I have studied possible consecutive reactions starting from the products of terminal and non-terminal •OH-additions (4-pentenyl-1-ol and 4-pentene-2-ol-1-yl). I have found that two reactions of 4-pentene-2-ol-1-yl radical were energetically favoured. The first channel is a five-membered ring closing. The second channel is bond scission, which results in an allyl radical and a vinyl alcohol. The enthalpy for transition states of both consecutive channels was found to be below that of the 1,4-pentadiene + •OH ($\Delta_{\text{rel}}H^\circ(\text{TS}) < 0$). The ring closing reaction resulted cyclopentanol-3-yl was found to be exothermic ($\Delta_r H^\circ = -78.4 \text{ kJ mol}^{-1}$). However, its activation enthalpy seemed to be as high as 70.5 kJ mol^{-1} , but its relative enthalpy was a value of 45.4 kJ mol^{-1} . My calculations had shown that the relative enthalpy of the transition state corresponded to bond scission reaction was $-25.5 \text{ kJ mol}^{-1}$. The heat of this reaction was slightly endothermic ($\Delta_r H^\circ = 20.3 \text{ kJ mol}^{-1}$).
- XI.** An analogous reaction pathway, in which arachidonic acid takes the place of 1,4-pentadiene, was suggested as an alternative radical pathways for non-enzymatic fatty acid oxidation.
- XII.** I have studied the whole conformational space of 1,4-pentadien-3-yl radical, which is the product of the biallylic hydrogen abstraction. I have found that its ring closing reaction resulted cycloopenyl radical, have four steps mechanism. The highest activation enthalpy belonged to the ring closing step ($149.0 \text{ kJ mol}^{-1}$).

2,5-heptadiene reactions [4]

XIII. Allylic hydrogen abstraction reactions of 2,5-heptadiene with hydroxyl, hydroperoxyl, methyl, and isopropyl had been explored and van der Waals complexes had been characterized in all the cases, except for the reaction with methyl, where no van der Waals complex were found. The most stable complex was the $\bullet\text{OOH}$ -heptadiene complex ($\Delta H^\circ_{\text{comp}} \approx -20 \text{ kJ mol}^{-1}$), then $\bullet\text{OH}$ -complex ($\Delta H^\circ_{\text{comp}} \approx -10 \text{ kJ mol}^{-1}$). The weakest complex belonged to the van der Waals of isopropyl radical ($\Delta H^\circ_{\text{comp}} \approx -5 \text{ kJ mol}^{-1}$).

XIV. The heat of reactions were not so sensitiv to the *cis-trans* isomer of 2,5-heptadiene, the largest difference in reaction and activation enthalpies between (*Z,Z*) and (*E,E*) isomers was found to be less than 4,5 kJ mol^{-1} . The largest activation enthalpy belonged to reactions of hydroperoxyl radical (**Table 1**). Then, methyl and isopropyl reactions had second and third largest activation enthalpies in my study, repectively. In the case of hydroxyl reactions, reactions were found to be pseudo negative activation enthalpy.

Table 1. The thermochemistry of the allylic hydrogen abstraction reactions calculated at G3M2//BH level of theory. The $\Delta_r H^\circ$ és $\Delta^\ddagger H^\circ$ stands standard heat of reaction and activation enthalpies in kJ mol^{-1} , respectively. The standard reaction and activation entropies ($\Delta_r S^\circ$ and $\Delta^\ddagger S^\circ$) are also listed in $\text{J mol}^{-1} \text{K}^{-1}$.

	X	<i>cis – cis (Z,Z)</i>		<i>trans – trans (E,E)</i>	
		monoallyl	biallyl	monoallyl	biallyl
$\bullet\text{OH}$	$\Delta_r H^\circ$	-130.5	-178.7	-127.3	-174.3
	$\Delta^\ddagger H^\circ$	-4.6	-14.1	-3.7	-13.3
	$\Delta_r S^\circ$	12.4	11.8	12.4	8.3
	$\Delta^\ddagger S^\circ$	-113.6	-128.0	-112.9	-116.0
$\bullet\text{CH}_3$	$\Delta_r H^\circ$	-72.7	-120.9	-69.5	-116.5
	$\Delta^\ddagger H^\circ$	44.9	29.6	46.9	30.9
	$\Delta_r S^\circ$	-13.3	-13.8	-13.3	-17.3
	$\Delta^\ddagger S^\circ$	-123.5	-133.7	-126.1	-127.1
$\bullet \text{ iso-C}_3\text{H}_7$	$\Delta_r H^\circ$	-49.6	-97.8	-46.4	-93.4
	$\Delta^\ddagger H^\circ$	41.9	23.9	45.8	25.1
	$\Delta_r S^\circ$	-16.5	-17.1	-16.5	-20.6
	$\Delta^\ddagger S^\circ$	-158.6	-169.1	-152.6	-159.6
$\bullet\text{OOH}$	$\Delta_r H^\circ$	-0.5	-48.7	2.7	-44.3
	$\Delta^\ddagger H^\circ$	58.7	40.8	60.6	40.9
	$\Delta_r S^\circ$	0.2	-0.3	0.2	-3.8
	$\Delta^\ddagger S^\circ$	-143.8	-159.4	-147.1	-148.8

- XV.** The biallyl radical is found to be more stable by $47.6 \pm 0.4 \text{ kJ mol}^{-1}$ than monoallyl radical.
- XVI.** Due to the Evans-Polányi diagram, the allylic hydrogen abstraction reactions studied were classified as follows:
- (1) direct allylic hydrogen abstractions by methyl radical;
 - (2) indirect allylic hydrogen abstractions with large activation barrier. This is the case for reactions of isopropyl and hydroperoxyl radicals and
 - (3) indirect allylic hydrogen abstractions with pseudo negative activation enthalpy by $\bullet\text{OH}$ radical.
- XVII.** By means of conventional transition state theory, the reaction rates of 2,5-heptadiene reactions had been calculated at room temperature. I found that the biallylic hydrogen abstraction reactions are more than an order of magnitude faster than the monoallyl hydrogen abstraction reactions. (**Table 2**). The abstractions by hydroxyl radical were found to be about seven orders of magnitude faster than the other reactions studied.

Table 2. Calculated bimolecular reaction rates using expression of conventional transition state theory ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). In parenthesis, rates are relative to the rate for monoallylic hydrogen abstraction of (*E,E*)-heptadiene isomer.

X	<i>cis – cis (Z,Z)</i>		<i>trans – trans (E,E)</i>	
	monoallyl	biallyl	monoallyl	biallyl
$k_{\infty}^{298.15\text{K}} \text{ (G3MP2//BH)}$				
$\bullet\text{OH}$	7.65×10^{-11}	6.19×10^{-10}	5.84×10^{-11}	1.92×10^{-9}
$\bullet\text{CH}_3$	1.48×10^{-19}	2.07×10^{-17}	4.90×10^{-20}	2.80×10^{-17}
$\bullet\text{iso-C}_3\text{H}_7$	2.45×10^{-21}	9.87×10^{-19}	1.05×10^{-21}	1.94×10^{-18}
$\bullet\text{OOH}$	1.65×10^{-23}	3.48×10^{-21}	5.16×10^{-24}	1.20×10^{-20}

4. Publications Related to the Subject of the Dissertation

1. M. Szori, C. Fittschen, I. G. Csizmadia, B. Viskolcz: Allylic H-Abstraction Mechanism: The Potential Energy Surface of the Reaction of Propene with OH Radical *J. Chem. Theory Comput.*, **2006**, 2, 1575-1586. **IF= 3,627**
2. M. Szori, B. Viskolcz: Conformation Analysis of 1,4-Pentadien-3-yl Radicals by Ab Initio and DFT Methods. *J. Mol. Struct. (THEOCHEM)*, **2003**, 153, 666-667. **IF= 1,027**
3. M. Szori, I. G. Csizmadia, B. Viskolcz: Non-enzymatic Pathway of PUFA Oxidation. A First Principles Study on the Reactions of OH Radical with 1,4-Pentadiene and Arachidonic Acid *J. Chem. Theory Comput.* **2008**, (accepted), **IF= 4,308**
4. M. Szori, T. Abou-Abdo, C. Fittschen, I. G. Csizmadia, B. Viskolcz: Allylic H-Abstraction II. Hydrogen Abstraction from 1,4 type Polyalkenes as a Model for Free Radical Trapping by Polyunsaturated Fatty Acids (PUFAs) *Phys. Chem. Chem. Phys.* **2007**, 9, 1931-1940. **IF= 3,343**
5. M. Szori, I. G. Csizmadia, B. Viskolcz: Reaction of •OH radical with propene in temperature range between 200 K and 1500 K: a theoretical study *Phys. Chem. Chem. Phys.* **2008**, (in preparation)

5. Further Publications

1. I. L. Hegedűs, M. A. Sahai, M. Labádi, M. Szőri, G. Paragi, B. Viskolcz, A. Bottoni: Selenocysteine derivatives I. Side-chain Conformational Potential Energy Surface of N-acetyl-selenocysteine-N-methylamide (MeCO-L-Sec-NHMe) in its β_L Backbone Conformation, *J. Mol. Struct. (THEOCHEM)*, **2005**, 725, 111-125. **IF= 1,045**
2. G. Tasi, M. Szőri, A. G. Császár, Semispectroscopic and Quantitative Structure-Property Relationship Estimates of the Equilibrium and Vibrationally Averaged Structure and Dipole Moment of 1-Buten-3-yne, *J. Phys. Chem. A*, **2005**, 109, 4824-4828. **IF= 2,898**
3. B. Viskolcz, S. N. Fejer, M. Szori, I. G. Csizmadia: Thermodynamic Functions of Conformational Changes I. A Comparative First Principle Study on 1,2-Disubstituted Ethanes, *Mol. Phys.*, **2006**, 104, 795-803. **IF= 1,690**

4. J. M. S. Law, M. Szori, R. Izsak, B. Penke, I. G. Csizmadia, B. Viskolcz: Folded and Unfolded Conformations of ω -3 Polyunsaturated Fatty Acid Family: $\text{CH}_3\text{-CH}_2\text{-[CH=CH-CH}_2\text{-]}_B\text{-[CH}_2\text{]}_M\text{-COOH}$. First principles Study. *J. Phys. Chem. A* **2006**, 110, 6100-6111 **IF= 3,047**
5. B. Viskolcz, M. Szori, R. Izsak, S. N. Fejer, I. G. Csizmadia: Thermodynamic Functions of Conformational Changes: Functional Analysis of Conformational Entropy of Substituted Ethane and Methanol *Int. J. Quan. Chem.*, **2007**, 107, 1826-2834. **IF= 1,368**
6. M. A. Sahai, M. Szori, B. Viskolcz, E. F. Pai, I. G. Csizmadia, Transition State Infrared Spectra for the Trans \rightarrow Cis Isomerization of a Simple Peptide Model, *Journal of Physical Chemistry A*. **2007**, 111, 8384–8389. **IF= 2,918**
7. T. Bentz, B. R. Giri, H. Hippler, M. Olzmann, F. Striebel, M. Szöri, The Reaction of Hydrogen Atoms with Propyne at High Temperatures – An Experimental and Theoretical Study, *J. Phys. Chem. A*. **2007**, 111, 3812-3818. **IF= 2,918**
8. Z. Mucsi, A. Tsai, M. Szori, G. A. Chass, B. Viskolcz, I. G. Csizmadia, A Quantitative Scale for the Extent of Conjugation of the Amide Bond. Amidity Percentage as a Chemical Driving Force *J. Phys. Chem. A*. **2007**, 111, 13245-13254. **IF= 2,918**
9. M. F. Andrada, J. C. G. Martínez, M. Szori, G. N. Zamarbide, F. T. Vert, B. Viskolcz, Mario R. Estrada, I. G. Csizmadia: Thermodynamics of Competing Oxidation Reactions of Allyl-Methyl Disulfide by Hydrogen Peroxide. A First Principle Molecular Computational Study on the Conformations of Allyl-Methyl Disulfide and its Oxidized Products *J. Phys. Org. Chem.* **2008**, 21, 1-11. **IF= 1.593**

6. Posters Related to the Dissertation

1. THE ROLE OF CHEMISTRY IN THE EVOLUTION OF MOLECULAR MEDICINE
27-29 June, 2003, Szeged, Hungary
Ab Initio Study on the 1,4-Pentadienyl radical
2. 18TH INTERNATIONAL SYMPOSIUM ON GAS KINETICS
7-12 August, 2004, Bristol, UK
Allylic H-abstraction II. Ab initio study of allylic hydrogen abstraction reaction from polyalkenes

7. Talks Related to the Dissertation

1. MTA REAKCIÓKINETIKAI ÉS FOTOKÉMIAI MUNKABIZOTTSÁGI ÜLÉSE
29 April 2004, Balatonalmádi, Hungary
Szőri Milán: *Allyl helyzetű H-atom leszakítási reakciók ab initio vizsgálta*
2. SUMMER WORKSHOP, SZEGED, HUNGARY
26 August 2006, Szeged, Hungary
Milan Szőri: *H-abstraction Reaction of Hepta-2,5-diene with a Variety of Radicals. Molecule-Radical Interaction*

8. Further Posters

1. THE ROLE OF CHEMISTRY IN THE EVOLUTION OF MOLECULAR MEDICINE
27-29 June, 2003, Szeged, Hungary
What is the Real Permanent Dipole Moment of 1-Butene-3-yne?
2. 18TH INTERNATIONAL SYMPOSIUM ON GAS KINETICS
7-12 August, 2004, Bristol, UK
The β bond dissociation reactions of "biallyl" type of radicals
3. COMPUTATIONAL TOOLS FOR MOLECULES, CLUSTERS AND NANOSTRUCTURES
23-26 January, 2005, Karlsruhe, Germany
Stability and secondary structures of isomeric long lifetime radicals formed from docosahexaenoic acid (DHA)
4. 19TH INTERNATIONAL SYMPOSIUM ON GAS KINETICS

22-27 July 2006, Orleans, France

First principle modeling of the reaction between isobutene and OH radical

5. HUNGARIAN COMBUSTION MEETING - HCM2006

6 October 2006, Szeged, Hungary

First principle modeling of the reaction between isobutene and OH radical

6. WATER INTERFACES IN PHYSICS, CHEMISTRY AND BIOLOGY: A MULTI-DISCIPLINARY APPROACH

8-13 December 2007, Obergurgl, Austria

Molecular modeling of water adsorption on mixed self-assembled monolayers as proxies for atmospheric organic surface

7. EUROPEAN GEOSCIENCES UNION GENERAL ASSEMBLY

13-18 April 2008, Vienna, Austria

Molecular modeling of water adsorption on hydrophobic and hydrophilic self-assembled monolayers as proxies for atmospheric organic surfaces

9. Further Talks

1. KOHLENSTOFF AUS DER GASPHASE: ELEMENTARREAKTIONEN, STRUKTUREN, WERKSTOFFE (SFB 551) WORKSHOP

11 November, 2005, Karlsruhe, Germany

H. Hippler, M. Olzmann, F. Striebel, M. Szori: *Theoretical Study on $C_3H_4 + H$ system*

2. WORKSHOP OF THE REACTION KINETICS COMMITTEE OF ACADEMY OF HUNGARY

27 April 2006, Balatonalmádi, Hungary

H. Hippler, M. Olzmann, F. Striebel, M Szori: *Complex Kinetics Study on $C_3H_4 + H$ system*

3. ECONET MEETING

3 May 2007, Szeged, Hungary

M. Szori: *High level ab initio potential energy surface of $HOO + SO$ and $HOO + ClSO$ reactions*

