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Description of Kinetics of Propane Fragmentation with a Support of Ab Initio Simulation

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***Abstract*—**Using *ab initio* theoretical calculations, we present analysis of fragmentation process. The analysis is performed in two steps. The first step is calculation of fragmentation energies by *ab initio* calculations. The second step is application of the energies to kinetic description of process. The energies of fragments are presented in this paper. The kinetics of fragmentation process can be described by numerical models. The method for kinetic analysis is described in this paper. The result - composition of fragmentation products - will be calculated in future. The results from model can be compared to the concentrations of fragments from mass spectrum.

***Keywords*—**Ab initio, Density functional theory, Fragmentation energy, Geometry optimization.

I. Introduction

FRAGMENTATION is a process, where the larger molecules are dissociated to the smaller fragments. The fragmentation energy is the property of molecular structure, and it is defined as the required energy for separation of several chemical bonds of the large molecule and getting smaller particles (fragments) [1]. The fragmentation energy has a relation to reactivity of the compound. It determines the composition of fragmentation product. Particularly, in this paper, the fragmentation of the propane molecule near the catalyst surface is described and investigated. The molecule is first ionized in plasma, and in the next phase it is spontaneously dissociated. The products of fragmentation can be detected by mass spectrometry. Theoretical calculations can improve our knowledge about fragmentation process. In the simplest kinetic approach, the fragmentation energy and vibration frequencies are sufficient to describe the process. The results of such calculation are fractions of different product. It is similar output as a mass spectrometry and thus the theoretical findings can be compared to experimental data.

The appropriate level for calculation of fragmentation energy is quantum mechanics *ab initio* method that treats the electronic structure of molecules and is encountered in quantum mechanics (quantum chemistry), which is based on Born Oppenheimer Approximation and solving the electronic Schrödinger's equation [1]. Recent *ab initio* methods can be also used to calculate how electrons and nuclei interact and predict physical properties of compounds such as geometry of a molecule, dipole moment, energy of reaction, reaction barrier height, vibrational frequencies, IR spectra, NMR spectra, reaction rate, partition function, potential energy surfaces (PES) and free energy. According to the literature, There are many theoretical methods of *ab initio* to calculate fragmentation energy of molecules such as Hartree-Fock (HF or RHF), which is also known as the Self-Consistent Field (SCF) [2], The local spin density approximation (LSDA) with a plane-wave basis [3], semi-empirical modified neglect of differential overlap (MNDO) [4], gradient-corrected exchange-correlation density functional BLYP with HF densities [2], tight-binding methods [5]–[6], second-order Møller-Plesset perturbation theory (MP2) [7], and Density Functional Theory (DFT) [7].

In the present work, we analyze the fragmentation of propane by theoretical calculations. We have calculated energies of different fragments by *ab initio* method. The energies can be used for calculation of fragmentation kinetics. In this time, we developed method for calculation of kinetics. The composition of fragments will be presented later. We will compare the results with results from mass spectrometry method presented in the literature. Propane was selected to study because it is a simple molecule. In such simple molecule the individual aspects (atom vibration, bond dissociation) can be analyzed. When an alkane of straight chain is bombarded by high energy electrons it will lose an electron to form a radical cation. This radical cation has the same mass as the parent compound and produces the molecular ion (M^+) peak. The type of radical formed follows the stability of radicals. The alkane molecular ion can further fragment to form a homologous series of neutral alkyl radicals usually beginning with the methyl radical. The methyl radical has a mass of 15 and the next largest peak in the mass spectrum usually corresponds to the loss of methyl radical (M-15). Ethyl radical can also be lost (M-29) and so forth. Fig. 1 shows the mechanism of fragmentation for propane; the corresponding mass spectrum for propane is given in Fig. 2. Table 1 shows the typical fragments lost by straight chain alkanes and their respective masses.

This mechanism shows that propane produces a parent peak (m/z = 44) and fragments of 29 and 15. From the mass spectrum of propane, it was shown a molecular ion at m/z = 44 that is only about 30% as high as the base peak at m/z = 29. In addition, many other fragment ions are present [8].

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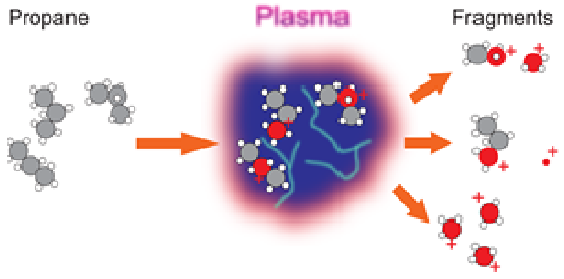

$CH_3\text{-}CH_2\text{-}CH_3 \xrightarrow{e-(fast)} CH_3\text{-}CH_2\text{-}CH_3^{\bullet +}$ (m/z = 44)

$CH_3\text{-}CH_2\text{-}CH_3^{\bullet +} \xrightarrow{M-15} CH_3^{\bullet} + CH_3\text{-}CH_2^{+}$ (m/z = 29)

$CH_3\text{-}CH_2\text{-}CH_3^{\bullet +} \xrightarrow{M-29} CH_3\text{-}CH_2^{\bullet} + CH_3^{+}$ (m/z = 15)

Fig. 1 Mechanism of fragmentation for propane

TABLE I
TYPICAL FRAGMENTS LOST FROM STRAIGHT CHAIN ALKANES

Molecular Ion -	Fragment Lost
1	$H^{\bullet}$
2	$2H^{\bullet}$
15	$CH_3^{\bullet}$
29	$C_2H_5^{\bullet}$
43	$C_3H_7^{\bullet}$
57	$C_4H_9^{\bullet}$
71	$C_5H_{11}^{\bullet}$

Peaks in the mass spectra of straight chain alkanes will usually appear in groups of 14 mass until intervals (corresponding to one CH_2 group). The most intense fragmentation peak is usually the 3 carbon fragment, with the intensities of the peaks decreasing with increasing mass. Often, the M-15 peak (loss of methyl radical) will be absent. Fragments to look for in these spectra correspond to $C_nH_{2n+1}^{+}$, $C_nH_{2n}^{+}$, and $C_nH_{2n-1}^{+}$.

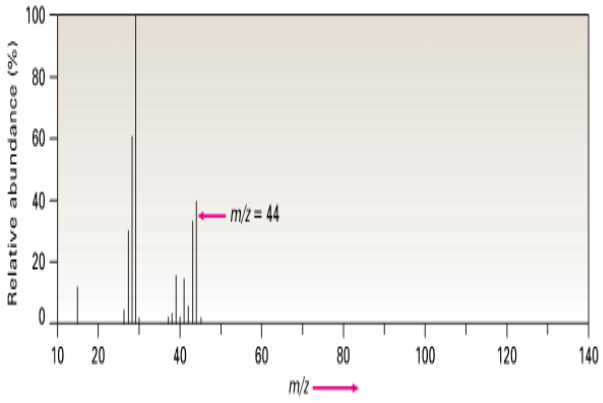

Fig. 2 Mass spectrum of propane (C_3H_8 ; MW = 44) [8]

II. RESULTS AND DISCUSSION

MOLPRO software package was used for *ab initio* quantum chemistry calculations [9]. This software is a complete system of *ab initio* programs for molecular electronic structure calculation. Using local electron correlation methods, which significantly reduce the increase of the computational cost with molecular size, *ab initio* calculations can be performed for much larger molecules than with most other programs. These methods have recently been augmented by explicitly correlated terms, which strongly reduce both the basis set truncation errors and the errors of the local approximations [10].

In the simulation *ab initio* using MOLPRO software, several calculation methods of *ab initio* can be applied, such as Hartree-Fock (HF), second-order Møller-Plesset perturbation theory (MP2), Quadratic Configuration Interaction of Single and Double excitations (QCISD), Coupled- Cluster Single, Double, and perturbative Triple excitations (CCSD (T)), and density functional theory hybrid B3LYP functional consisting of weighted combinations of various density functional together with a fraction of exact Hartree-Fock exchange DFT (B3LYP). In the basic HF (Hartree-Fock) calculation, each electron is considered in the average field caused by all the other electron and the nuclei. The next three methods try to improve the Hartree-Fock electronic wave function: the MP2 (Møller-Plesset) method, employs perturbation theory at the second order. The QCISD (Quadratic Configuration Interaction of Single and Double excitations) calculates the electronic wavefunction as a linear combination of Hartree-Fock determinants in which all the single and double excitations are included. The CCSD(T) (Coupled- Cluster Single, Double, and perturbative Triple excitations) is based on an exponential approach. B3LYP is a density functional method in which the electronic energy is expressed using the electronic density, not the wavefunction [11].

The electronic structure of molecules can be treated only by quantum mechanics, since the electrons are very quickly moving particles. Thus each electronic structure calculation is performed for a fixed nuclear configuration, and therefore the positions of all atoms must be specified in an input file that it must be prepared before the running MOLPRO and it should contain information about geometry specification, basis set specification, and a method of calculation. The output of *ab initio* MOLPRO software is electronic energy by solving the electronic Schrödinger's equation for this fixed nuclear configuration. The electronic energy as a function of the 3N-6 internal nuclear degrees of freedom defines the potential energy surface (PES). The PES is in general very complicated and can have many minima and saddle points. The minima correspond to equilibrium structures of different isomers or molecules, and saddle points to transition states between them. The aim of most calculations is to find these structures and to characterize the potential and the molecular properties in the vicinity of the stationary points of the PES. The electronic Schrödinger's equation can not be solved exactly, except for very simple systems like the hydrogen atom. Therefore, the electronic wavefunction is represented in certain finite basis sets, and the Schrödinger's equation is transformed into an algebraic equation which can be solved using numerical methods. There are two classes of approximations: one concerning the choice of basis functions to represent the one-

electron functions called molecular orbitals, and one concerning the choice of N-electron functions to represent the many-electron electronic wavefunction. In most programs, and also in MOLPRO, Gaussian basis functions are used to approximate the molecular orbitals, since the required integrals can be computed very quickly in this basis. Many optimized basis sets are available in the MOLPRO basis set library, and in most cases the basis set can be selected using a simple keyword in the input file [12].

A basis set is a set of functions used to describe the shape of the orbitals in an atom [9]. There are several forms of basis sets used in *ab initio* methods. Used the correlation-consistent polarized basis set of Dunning and coworkers, denoted cc-pVDZ (double zeta), cc-pVTZ (triple zeta), cc-PVQZ (quadruple zeta). These names can be used directly or abbreviated by VDZ, VTZ, VQZ and so on. For computing certain properties like electron affinities, polarizabilities, or intermolecular potentials, additional diffuse basis functions are needed, and such functions are included in the augmented correlation-consistent basis set, denoted aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ etc. These names can be abbreviated by AVDZ, AVTZ, AVQZ etc. Another popular choice are the Gaussian basis sets of Pople and coworkers, e.g. 6-31G**(double zeta), 6-311G (2DF, 2PD) (triple zeta), 6-311G^{++} (2DF, 2PD) (augmented triple zeta) etc. If no basis set is specified at all, MOLPRO uses cc-pVDZ, but this is does not mean that this is a sensible choice [12]. After running the input file in MOLPRO software, output file will contain information about potential energy, atomic coordinates, dipole moment, and bond lengths and angles.

In this work, the molecular electronic structure calculations of propane molecule such as geometry optimization, and visualization of molecular orbitals and electron density have been carried out using MOLPRO software.

First, the influence of basis set and methods were tested. It was found that the results are similar when using various basis set or method. Calculations of geometry optimization (also called energy optimization or energy minimization) for propane and its fragments have been carried out using Hartree-Fock (HF) as a calculation method and valence double zeta (VDZ) as a basis set. The geometry of propane molecule, particularly, in simulation by MOLPRO, the Z-matrix that is required to form the input file and running it using MOLPRO software was created using MOLDEN software. Visual molecular dynamics (VMD) program was used to visualize the electron density and molecular orbitals for propane. Fig. 3 shows calculations of geometry optimization for propane molecule using the same method and basis set (HF/VDZ). According to the simulation by MOLPRO and visualization using visual molecular dynamics (VMD) program, it has been found that propane molecule has 23 molecular orbitals. Fig. 4 shows electron density visualized using visual molecular dynamics (VMD) program.

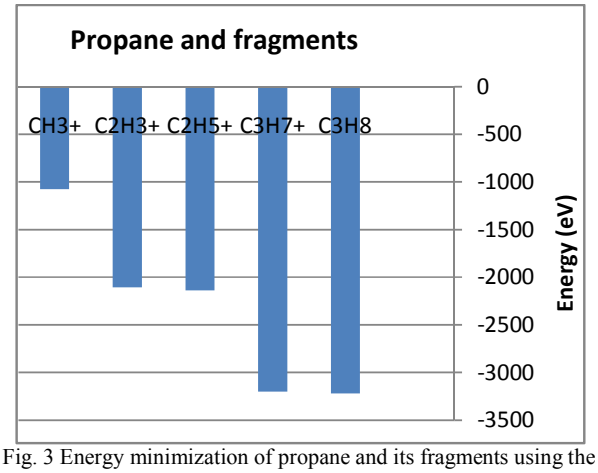

Fig. 3 Energy minimization of propane and its fragments using the same method and basis set (HF/VDZ)

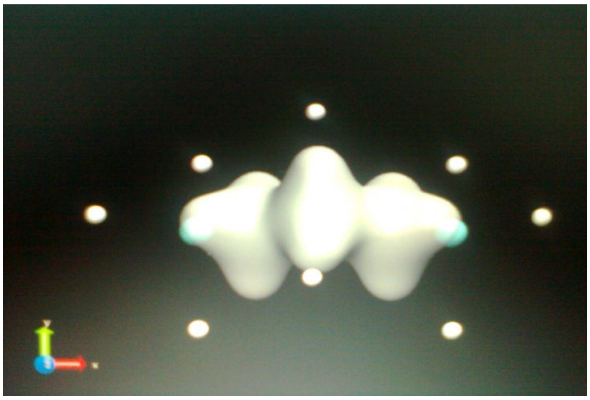

Fig. 4 Visualization of electron density of propane using visual molecular dynamics (VMD) program

We have performed the calculations of geometry optimization for propane and its fragments (CH_3^+, $C_2H_3^+$, $C_2H_5^+$, and $C_3H_7^+$) using the same calculation method and basis set (HF/VDZ). Results of simulation by MOLPRPO software reveal that values of energy minimization of propane molecule is -3218.3599 eV and (-3200.5527, -2138.4647, -2105.4382, and -1076.2407) eV for fragments of propane $C_3H_7^+$, $C_2H_5^+$, $C_2H_3^+$, and CH_3^+, respectively.

The calculated energies from Fig. 3 are the input data for kinetic description of fragmentation. The kinetics will be analyzed in future. The numerical model of kinetics is a part of software "Chemical Kinetics Simulator" (CKS) [13]–[14]. For the calculation, there is needed detailed mechanism of fragmentation. The mechanism of fragmentation of alkanes is described in literature [15]. According to this reference, we proposed the detailed mechanism for propane fragmentation.

For every partial reaction, there will be calculated activation energy. The activation energy is calculated as a difference of energies from Fig. 3.

$$\Delta E = \sum E_{prod} - \sum E_{react} \quad (1)$$

where *prod* and *react* are all products and reactants of the particular reaction. The kinetic constants depend on activation energy, and temperature.

$$k = A \exp(- \frac{\Delta E}{RT}) \quad (2)$$

where the *T* is a temperature and A is pre-exponential factor.
In the process of fragmentation, the pre-exponential factor *A* depends on the vibrations of atomic bonds. The vibrations of bonds will be calculated from infrared (IR) spectrum of propane.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \quad (3)$$

where ν is a frequency of atom vibration, *K* is the molecular force constant and μ is the reduced mass of atoms given by the following equation.

$$\mu = \frac{m1 . m2}{m1 + m2} \quad (4)$$

The molecular force constant will be calculated from energy of vibrations.

$$E = h\, c\, \nu_{IR} = \frac{1}{2} K\, x^2 \quad (5)$$

where ν_{IR} is wave number from infrared spectra. The result of the simulation of process kinetics will be the concentrations of propane fragments. The concentrations will be compared to the intensities of peaks from mass spectrometry (Fig. 2).

III. Conclusion

- Mechanism of propane fragmentation in plasma was found.
- Ionization and fragmentation energies of individual partial reactions can be calculated by the *ab initio* quantum chemistry method.
- Energies are input properties for the kinetics of the process. Concentrations of fragmentation products can be calculated.
- The final concentrations of fragments can be compared to intensities from mass spectrometry.

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