Variational RRKM calculation of thermal rate constant for C–H bond fission reaction of nitro methane

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Abstract The present work provides quantitative results for the rate constants of unimolecular C–H bond fission reactions in the nitro methane at elevated temperatures up to 2000 K. In fact, there are three different hydrogen atoms in the nitro methane. The potential energy surface for each C–H bond fission reaction of nitro methane was investigated by ab initio calculations. The geometry and vibrational frequencies of the species involved in this process were optimized at the MP2 level of theory, using the cc-pvdz basis set. Since C–H bond fission channel is a barrierless reaction, we have used variational RRKM theory to predict rate coefficients. By means of calculated rate coefficients at different temperatures, the Arrhenius expression of the channel over the temperature range of 100–2000 K is \( k(T) = 5.9 \times 10^{19} \times \exp(-56274.6/T) \).

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1. Introduction

Thermal rate constants are of central interest not only in chemistry but also in many related subjects like simulation of atmospheric and combustion processes. To model blaze properties requires accurate kinetic data over extended ranges of temperature and pressure for a rich manifold of chemical species. Since it is foreseeable that not all of these can be done experimentally, theoretical methods have become admissible and useful remedies both with respect to accuracy and predictive power. Thus, an important goal of theoretical chemistry is to be able to accurately obtain thermal rate constants. The aim of this study is to investigate thermal C–H bond rupture channel of nitro methane. The energy specific microcanonical rate constant, \( k(E) \), for the thermal dehydrogenation of nitro methane was evaluated using variational RRKM theory.

The reactions and properties of nitro-containing compounds have been extensively investigated both experimentally and theoretically in recent years for the significant role they play in propellant ignition, combustion, and atmosphere pollution. Nitro compounds are organic compounds that contain one or more nitro functional groups. They are often highly
explosive. Nitroalkanes are of significant interest as the prototypes of high energy materials. Among the nitroalkanes, nitromethane (CH$_3$NO$_2$) is an energetic material with a wide variety of applications, such as a liquid explosive, a solvent for chemical processing and analysis, a monopropellant, and a high-performance fuel additive for internal combustion engines and pulsed detonation engines. Nitromethane is vastly employed as a model substance for ascertaining propellant combustion, deflagration phenomena and atmospheric pollution (Jacox, 1984; Hsu and Lin, 1985; Wang and Brower, 1997; Glaborg and et al., 1999; Glänzer and Troe, 1973).

Gas phase decomposition of nitromethane was investigated experimentally (Glänzer and Troe, 1974; Zhang and Bauer, 1997; Zaslonko and et al., 1997; Tricota et al., 1981; Taylor et al., 1980; Piermarini et al., 1989). Meanwhile, the unimolecular decomposition of Nitromethane has been extensively investigated theoretically (McKee, 1989; Rice and Thompson, 1990; Hu et al., 2002; Nguen et al., 2003; Denis et al., 2003; Manaa and Fried, 1998).

2. Methods and computational details

The optimized geometries and the frequencies of reactant and transition states have been calculated at the ump2/cc-pvdz level of theory along several points of the minimum energy path. All quantum mechanical calculations were done in the Gaussian 2009 program (Gaussian 09, 2009). Also, Natural bond orbital (NBO) analysis was accomplished with NBO code included Gaussian 09. Stationary and first order saddle points were acquired through the calculation of analytical harmonic vibrational frequencies, which were also utilized to evaluate the zero-point vibrational energy (ZPVE). The reactant was assessed as true minima on the potential energy surface by the absence of negative eigenvalues in the hessian matrix and also zero gradients for all coordinates. The transition state structures were identified by the presence of a single negative eigenvalue in the hessian matrix or nonzero gradient with respect to reaction coordinate. The microcanonical rate constant was calculated by means of the well known equation of RRKM theory

$$k(E) = \frac{\sigma G^{++}(E - E_0)}{h \rho(E)}$$

where $G^{++}(E - E_0)$ denotes the number of available energy levels for orthogonal modes to the reaction coordinate at the transition state configuration with energy less than or equal to $E - E_0$. $\sigma$ is the reaction path degeneracy, $E_0$ is the activation energy, i.e. the minimum energy value for which the rate constant has its minimum nonzero value and $\rho(E)$ is the density of states of reactants with energy equal to $E$. The number of vibrational states and density of states were calculated using the Beyer–Swinehart algorithm (Beyer and Swinehart, 1973) improved by Stein and Rabinovich (1973). Since C–H bond rupture pathway is a barrierless reaction and has no classical well defined transition state, we have to find its generalized transition state on the potential energy surface using microcanonical variational RRKM theory. According to the variational theory, the bottleneck of a reaction arises at the point through the minimum energy path where the minimum number of states of transition state available and the microcanonical rate constant is at the minimum.

$$\frac{\partial G^{++}(E - E_0)}{\partial R_C} = 0 \quad \text{or} \quad \frac{\partial k(E)}{\partial R_C} = 0$$

where $R_C$ is the reaction coordinate, which is the length of the breaking C–H for the aforementioned reaction. The calculations were carried out by fixing the reaction coordinate, (C–H), but allowing the full optimization of the remained structural parameters. The canonical reaction rate, $k(T)$, is calculated using integration of obtained microcanonical rate constants over the energies from 0 to 100000 cm$^{-1}$ above the ZPVE of the ground state.

$$k(T) = \kappa(T) \int P(E) k(E) dE$$

In the above equation, $P(E)$ is the Boltzmann energy distribution function for $s$ uncoupled harmonic oscillators and rotational motion of molecule. In fact $P(E)$ is a convolution between rotational and vibrational density of states

$$P(E) = \frac{E^{s+1} e^{-E/RT}}{(s + \frac{1}{2})!(kT)^{s+1/2}}$$

It was adopted the simple and computationally inexpensive Wigner method in the estimation of the tunneling corrections for the reactions (Engholm Henriksen and Yssing Hansen, 2008).

$$\kappa(T) = 1 + \frac{1}{24} \left(\frac{hv^{s+1}}{kT}\right)^2$$

The activation energy and exponential factor are obtained by means of plotting of ln $k(T)$ versus $1/T$ according to the well known Arrhenius equation, see Fig. 4 (Engholm Henriksen and Yssing Hansen, 2008). The above outlined procedure was performed by means of a homemade program RRKM_Dynamics designed in the VB.NET 2010 environment. The code requires the moments of inertia, vibrational frequencies and HF energies of ground state and transition states as input and calculates microcanonical and canonical rate constants according to Eqs. (1)–(3). The output of the program can be exported to the microsoft excel for further analysis. The calculations have been carried out in the range of energy from $E_0$ (the energy of transition state which is cor-

![Figure 1](image1.png)

**Figure 1** Geometric parameters for nitro methane at MP2/cc-pvdz level of theory. Bond lengths are in angstrom, bond angles are in degree. The O3N1C4H5 dihedral angle is equal to 30.09 degree.
Results and discussion

The geometry of nitro methane is illustrated in Fig. 1. There are three different hydrogen atoms in the nitro methane. The orientation of each single hydrogen atom with respect to the NO₂ group makes a main difference between three hydrogen atoms. The aim of this investigation is to obtain the rate constants for thermal C–H bond fission reactions in the nitro methane. Due to lack of the distinct transition state we have located the transition state by means of variational microcanonical transition state theory. In the variational microcanonical transition state theory, different transition states are obtained for each energy. In Fig. 2, we have curved the C4–H6 bond length of transition states versus the energy. In low available energies, the transition state structure owns the highest electronic energy but by increasing the available energy, the electronic energy of transition state and C4–H6 bond length decreases and in fact the transition state is closer to the ground state compared with lower energies (by means of structure and energy). In Fig. 3, the calculated microcanonical rate constant has been curved versus the energy. Fig. 3 shows that the k(E) increases as the available energy increases. The rotation of the CH₃ group around the C–N bond has a potential curve with six maximums equal to 0.027 kJ/mol (at the mp2/ cc-pvdz level of theory). Due to the small radius of hydrogen atoms, this rotational potential cannot be accounted for the steric effect, but also electron delocalization mainly can be considered more effective for this rotational potential. NBO analysis has shown that the LP/C₃(Ν₁) → σ₄₋₅/C₄–H₅, LP/C₃(Ν₁) → σ₄₋₆/C₄–H₆, LP/C₃(Ο₁) → σ₄₋₇/C₄–H₇ electron delocalizations have a designative effect on the optimum nitro methane structure. The above mentioned electron delocalizations have E₂ equal to 0.9, 3.58, 0.99, 1.07 and 1.08 kCal/mol, respectively. The LP/C₃(Ο₁) → σ₄₋₅/C₄–H₅ electron delocalization makes C4–H6 bond a little longer than C4–H5 and C4–H7 bonds (Alabugin, 2000). However the above mentioned electron delocalizations do not make a main difference in the rate expression of three C–H bonds in the nitro methane. In fact, due to the existence of same reactant and product for the three C–H bond fission channels of nitro methane, the minimum energy path of the channels will be the same at the adjacent of the product structure. In fact when the breaking C–H bond length is reached to 1.7 Å, the three C–H bond rupture paths were the same and small differences in the shorter C–H bond lengths did not make a main difference in the rate expression of the above mentioned C–H bond fission channels. The frequency factor, A, and the activation energy, Eₐ, for the three C–H bond rupture reactions of the nitro methane were collected in Table 1 (see Fig. 4). As can be seen from table 1, the quantum tunneling effect reduces the activation energy to about 8.7 kJ/mol (1.89%) and also the frequency factor to

### Table 1

<table>
<thead>
<tr>
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<th>Without tunneling effect</th>
<th>With tunneling effect</th>
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<tbody>
<tr>
<td>A (Hz)</td>
<td>Eₐ (kJ mol⁻¹)</td>
<td>A (Hz)</td>
</tr>
<tr>
<td>C4–H5</td>
<td>2.0E + 19</td>
<td>476.6</td>
</tr>
<tr>
<td>C4–H6</td>
<td>2.0E + 19</td>
<td>476.8</td>
</tr>
<tr>
<td>C4–H7</td>
<td>2.0E + 19</td>
<td>476.6</td>
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about 1.2E19 Hz (6.5%). To obtain the overall activation energy and frequency factor for C–H bond fission of nitro methane we have to consider all the above mentioned channels. If we take into account the C4–H5, C4–H6 and C4–H7 bond fission channels in the C–H bond rupture reaction of nitro methane, the corresponding rate expression will be as

\[ k(T) = 5.92 \times 10^{19} e^{-\frac{467.87}{T}} \]

Therefore, the activation energy and the frequency factor for C–H bond fission reaction of nitro methane are equal to 467.87 kJ/mol and 5.92E19 Hz, respectively.

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References