

Theses of Ph.D. Dissertation

**Theoretical investigation of the reactions of the OH radical with  
C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>NH<sub>2</sub> and glycine molecules**



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# 1 INTRODUCTION AND OBJECTIVES

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Over the past 50 years, quantum chemistry has undergone tremendous advancement making it possible today to study the energetics of chemical systems with more than 10 atoms using highly-accurate *ab initio* methods. To explore the dynamics of reactions, various dynamical simulations can be employed including classical trajectory and quantum dynamics computations. Among the dynamics techniques, the Quasi-Classical Trajectory (QCT) method is particularly valuable because it combines quantum mechanical principles to accurately describe the initial energy levels of the reactants with classical physics to model the motion of atoms during the reaction. This approach offers significant computational advantages over fully quantum mechanical methods, which can be prohibitively expensive for large systems or complex reactions. By using classical trajectories to simulate the paths of reacting molecules, QCT can handle a large number of trajectories, which ensures high statistical reliability and allows for accurate determination of reaction probabilities, integral and differential cross sections, energy distributions as well as product branching ratios. Building on these developments, my research has concentrated on the theoretical exploration of the reactions of the OH radical with ethane ( $C_2H_6$ ), methylamine ( $CH_3NH_2$ ) and glycine ( $H_2NCH_2COOH$ ) molecules focusing on their energetic profiles and dynamic behaviors.

Ethane is a significant component of natural gas and is also present in various industrial emissions. The OH radical plays a key role in the degradation of ethane influencing the formation of secondary pollutants and affecting the overall air quality. Therefore, studying the OH +  $C_2H_6$  reaction can enhance our knowledge of its impact on atmospheric chemistry, combustion and industrial applications contributing to better pollution control and process optimization.

Previous studies on the OH +  $C_2H_6$  reaction have primarily concentrated on the H-abstraction pathway. However, substitution can also occur during the reaction, which can happen via two ways. If the substitution reaction proceeds via the Walden-inversion mechanism, the attacking molecule approaches the other molecule from the side opposite to the leaving group. In the other case, if the substitution reaction follows the front-side mechanism, the attacking molecule approaches the other molecule from the same side where the leaving group is. The goal of my work is to map out the stationary points of the reaction

using quantum chemical methods with unprecedented accuracy taking into account both the H- and methyl-substitution pathways considering the Walden and front-side mechanisms. With the help of the identified stationary points, I aim to develop a full-dimensional, analytical potential energy surface, which allows studying the dynamics of the ground-state as well as the vibrationally-excited reactions.

Methylamine, emitted from both natural and industrial sources, undergoes degradation through its reaction with OH radicals reducing its atmospheric concentration and contributing to the formation of secondary pollutants like nitramines and organic nitrates. Beyond its atmospheric implications, studying this reaction is important from biological aspect, too. The oxidation of methylamine by OH radicals leads to the formation of reactive products like formaldehyde and formamide, which can disrupt protein function and enzyme activity making this reaction crucial for understanding oxidative stress and its effects on cellular health.

For the OH + CH<sub>3</sub>NH<sub>2</sub> reaction, similar to the OH + C<sub>2</sub>H<sub>6</sub> reaction, previous studies in the literature focused only on the H-abstraction reaction pathway. H-abstraction can occur in two ways as the OH radical can remove a hydrogen atom from either the methyl or the amino group of the CH<sub>3</sub>NH<sub>2</sub> molecule. Substitution is also a possibility in this chemical system, which can also happen with the Walden or the front-side mechanism and since both ends of methylamine (the CH<sub>3</sub> and NH<sub>2</sub> groups) can be exchanged, NH<sub>2</sub>-substitution in addition to H- and methyl-substitution also emerges as a potential reaction channel. The aim of my research regarding this reaction is to surpass previous literature results by mapping the key stationary points of the reaction considering all possible reaction pathways. Additionally, my goal is to estimate the rate coefficients for the H-abstraction reaction based on the transition state theory.

Studying the H-abstraction reaction of OH + glycine is important for both atmospheric and biochemical research. Glycine, an amino acid released from biological and industrial sources, reacts with OH radicals in the atmosphere. Understanding this reaction helps to determine the fate of glycine and its role in atmospheric processes. Additionally, this reaction provides valuable information about the reactivity of biomolecules and their transformation in biological systems.

The glycine molecule contains three functional groups allowing the OH radical to abstract a hydrogen from the CH<sub>2</sub>, NH<sub>2</sub> and COOH groups in the H-abstraction reaction. Our research group has previously explored the conformational spaces of the reactants and products for the H-abstraction reaction providing the most accurate results in the literature to date. In the case of the glycine molecule, 8 different conformer structures have been identified along with 4-4 distinct structures for the products when the abstraction occurs at the CH<sub>2</sub> and COOH groups of glycine and 7 different structures when the abstraction takes place at the amino group of the glycine molecule. To characterize all the significant stationary points on the potential energy surface of the OH + glycine H-abstraction reaction, my research initially aimed to locate and precisely describe the transition states and post-reaction minima building upon the previous findings of our research group. With the help of these determined geometries as well as the reactant and product structures previously identified by our research group, my goal is to develop a full-dimensional, analytical potential energy surface to gain a detailed understanding of the dynamics of the OH + glycine H-abstraction reaction.

## 2 METHODS

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The geometry optimizations and harmonic frequency calculations were performed in three steps for all three chemical systems. For the OH + C<sub>2</sub>H<sub>6</sub> and OH + CH<sub>3</sub>NH<sub>2</sub> reactions, the same three theoretical levels were used. In the case of these two reactions, geometry optimization and harmonic frequency computations were first carried out at the MP2/aug-cc-pVDZ level followed by coupled cluster computations with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. A systematic search was performed to identify the transition states and minima of the OH + glycine H-abstraction reaction. For each stationary point, an MP2/3-21G structure, determined based on chemical intuition, was rotated along four different torsional modes resulting in 1296 initial structures. Geometry optimizations and harmonic frequency computations were carried out for all these structures at the MP2/3-21G theoretical level first. Then using the structures obtained in this way, we then performed geometry optimization and harmonic frequency computations at the MP2/aug-cc-pVDZ theoretical level. Finally, the same procedure was carried out at the CCSD(T)-F12b/aug-cc-pVDZ theoretical level as well.

After the geometry optimizations and harmonic frequency computations, we performed single-point energy computations on the most punctual geometries. First, we refined the energies at the CCSD(T)-F12b/aug-cc-pVQZ theoretical level, and additionally carried out five different correctional computations to approach the true energy as accurately as possible. To determine the contribution of the core electron correlation to the energy, we performed all-electron computations, and the core correction was obtained as the difference between the *all-electron* and *frozen-core* computations. To determine the T and [(Q)] corrections and thereby estimate the accuracy of the perturbative approach, we performed computations using the CCSDT(Q) method. The corrections were then derived by subtracting the CCSDT energy values from the CCSD(T) results and subtracting the CCSDT(Q) energy values from the CCSDT data. To include scalar relativistic effects, I subtracted the results of non-relativistic *all-electron* calculations from the energy values obtained with the Douglas–Kroll operator, which accounts for relativistic effects. The final correction we considered was the so-called spin-orbit correction. Spin-orbit computations were performed using the Breit–Pauli Hamiltonian in the interacting-states approach with the Davidson-corrected multi-reference configuration interaction (MRCI+Q) method.

For the OH + C<sub>2</sub>H<sub>6</sub> and OH + glycine reactions, the development of full-dimensional, analytical potential energy surfaces was carried out using the ROBOSURFER software package. In both cases, the energy points were computed with coupled-cluster quality. The fitting was performed using the monomial symmetrization approach (MSA) and the coefficients were determined through linear least-squares fitting. The reaction dynamics were studied using the QCT method in case of both reactions. The analysis of the simulations was carried out utilizing my own Fortran 90 programs.

Finally, estimates for the rate coefficients of the H-abstraction reaction channel in the OH + CH<sub>3</sub>NH<sub>2</sub> reaction were provided in the temperature range of 295-3000 K using transition state theory. The partition functions are calculated as the product of the translational, rotational, vibrational and electronic components. These factors are obtained using standard formulas, applying the rigid rotor approximation for rotational partition functions and the harmonic oscillator approximation for vibrational partition functions. The Wigner correction was used to account for the tunneling effect to increase the punctuality of the estimates.

### 3 RESULTS

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**T1. The potential energy surface of the OH + C<sub>2</sub>H<sub>6</sub> reaction was investigated using the highest theoretical level ever applied for this system resulting in the first identification of stationary points for the substitution reactions in the literature. When the adiabatic reaction enthalpies for the three product channels were compared to values from the Active Thermochemical Tables, the agreement was found to be excellent with two cases showing matching reaction enthalpies within the margin of error and in the third case showing a deviation of less than 0.2 kcal/mol.**

For the OH + C<sub>2</sub>H<sub>6</sub> reaction, we identified the transition states and minima on the potential energy surface at the CCSD(T)-F12b/aug-cc-pVTZ theoretical level considering the H-abstraction, H- and methyl-substitution reaction pathways. Using the obtained geometries, additional single-point energy computations were performed at the CCSD(T)-F12b/aug-cc-pVQZ theoretical level. To further refine the energy, post-CCSD(T), core, scalar relativistic and spin-orbit corrections were also considered. The classical relative energies were derived as the sum of the CCSD(T)-F12b/aug-cc-pVQZ energies and the five corrections. Additionally, using the harmonic frequencies obtained at the CCSD(T)-F12b/aug-cc-pVTZ theoretical level, we added the zero-point energies to the derived classical energies to obtain the adiabatic energies. Comparing our theoretical adiabatic reaction heats with the data calculated from the Active Thermochemical Tables, it can be concluded that there is excellent agreement within the error margin for the H- and methyl-substitution reactions, while for the H-abstraction case, the theoretical and experimental results show good agreement within 0.2 kcal/mol.

**T2. For the OH + C<sub>2</sub>H<sub>6</sub> reaction, dynamics simulations revealed that H-abstraction significantly dominates over the other two product channels (H- and methyl-substitution). For H-abstraction, at low collision energies, the rebound mechanism is predominant and as the collision energy increases the direct stripping mechanism becomes increasingly prominent.**

By analyzing the QCT simulations conducted for the OH + C<sub>2</sub>H<sub>6</sub> reaction, we determined the integral cross sections for the H-abstraction, H-substitution and methyl-substitution reaction channels at collision energies of 10, 20, 30, 40 and 50 kcal/mol. We found that the dominant reaction pathway is H-abstraction, as the integral cross sections for the H- and methyl-substitution pathways are only 0.02 and 0.03 bohr<sup>2</sup> even at the highest collision energy, respectively. Additionally, we determined the reaction probabilities and scattering angle distributions at various collision energies. These results show that at low collision energies, the direct rebound mechanism dominates, while as the collision energy increases, the direct stripping mechanism becomes increasingly prominent for the H-abstraction reaction.

**T3. For the reaction of OH + C<sub>2</sub>H<sub>6</sub>, dynamics simulations were performed in which a selected vibrational mode of the reactants was excited with one quantum at the start of the reaction. We observed that vibrational excitation of the CC bond led to a decrease in reactivity, excitation of the OH bond had no impact and excitation of the CH stretches in the C<sub>2</sub>H<sub>6</sub> molecule resulted in an increased reactivity for H-abstraction.**

We investigated the effect of vibrational excitation on the dynamics of the OH + C<sub>2</sub>H<sub>6</sub> reaction with the help of QCT simulations. At the beginning of the simulations, we excited five vibrational modes in ethane and one mode in the OH radical with one quantum using normal-mode sampling. The vibrational modes of C<sub>2</sub>H<sub>6</sub> included CC stretching, CH<sub>3</sub> deformation and three types of CH stretching: symmetric, asymmetric and degenerate. For the OH radical, the single vibrational mode was excited before the simulations began. By analyzing the trajectories and determining the integral cross sections, it was found that the vibrational excitation of the CC bond slightly decreased the reactivity, OH stretching had no effect, while CH stretching excitation increased the reactivity.



**T4. We identified the stationary points of the multi-channel OH + CH<sub>3</sub>NH<sub>2</sub> reaction and discovered that the energy barrier for Walden inversion in substitution reactions is higher compared to the barrier for the front-side attack mechanism.**

We mapped the transition states and minima on the potential energy surface of the OH + CH<sub>3</sub>NH<sub>2</sub> reaction using high-precision *ab initio* methods. Geometry optimizations and harmonic frequency computations were performed at the MP2/aug-cc-pVDZ, CCSD(T)-F12b/aug-cc-pVDZ and CCSD(T)-F12b/aug-cc-pVTZ theoretical levels. Subsequently, we refined the energies of the stationary points at the CCSD(T)-F12b/aug-cc-pVQZ theoretical level and performed additional energy correction computations to consider the impact of the post-(T) correlation, the effect of core electron correlation, the impact of the scalar relativistic effect and effect of the spin-orbit interaction. We obtained the classical benchmark energies as the sum of the results of the single-point energy calculations and derived the adiabatic energies by including the zero-point energies. Based on the determined energy profile of the reaction, it can be concluded that the front-side mechanism is kinetically preferred over the Walden inversion for both the H-substitution reaction occurring on the CH<sub>3</sub> group and the amino-substitution reaction.

**T5. We mapped the transition states and product-channel minima for the OH + glycine H-abstraction reaction at three different quantum chemical levels through a systematic search considering three reaction pathways: H-abstraction reactions occurring at the CH<sub>2</sub>, NH<sub>2</sub>, and COOH groups. At the highest theoretical level (CCSD(T)-F12b/aug-cc-pVDZ), we identified 5 transition states for each reaction pathway and for the product-channel complexes, we determined 2 conformers for NH<sub>2</sub>CHCOOH...H<sub>2</sub>O and 19 for H<sub>2</sub>O...HNCH<sub>2</sub>COOH.**

We performed a systematic search to identify the transition states and product-channel minima and their most possible conformers for the H-abstraction channel in the OH + glycine reaction. Since H-abstraction can occur at three different sites on the glycine molecule, we distinguished between CH<sub>2</sub>-, NH<sub>2</sub>- and COOH-H-abstraction reactions. In our systematic search, we generated 1296 initial structures by rotating a previously-obtained structure by 60° along four different torsional modes. We first carried out geometry optimizations and harmonic frequency computations at the MP2/3-21G theoretical level. From these results, we

then performed additional geometry optimizations and harmonic frequency computations at the MP2/aug-cc-pVDZ level for the identified MP2/3-21G transition states and product-channel minima. Finally, using these MP2/aug-cc-pVDZ structures, we carried out further optimizations and frequency computations at the CCSD(T)-F12b/aug-cc-pVDZ level. This process led to the identification of five distinct transition states for each of the three H-abstraction reactions and 19 H<sub>2</sub>O⋯HNCH<sub>2</sub>COOH and 2 NH<sub>2</sub>CHCOOH⋯H<sub>2</sub>O conformers for the product-channel complexes.

**T6. For the OH + glycine reaction, dynamics simulations revealed that after H-abstraction at the carboxyl group, the reaction can proceed further, ultimately leading to the formation of H<sub>2</sub>O, CH<sub>2</sub>NH<sub>2</sub> and CO<sub>2</sub> as products.**

Following the development of a full-dimensional, analytical potential energy surface, we investigated the dynamics of the OH + glycine reaction using QCT simulations. We studied the reaction at collision energies of 1, 5, 10, 15 and 20 kcal/mol. For each of the 8 reactant conformers, we ran 1000 trajectories for each combination of collision energy and impact parameter resulting in a total of 504 000 simulations. The QCT simulations revealed that after H-abstraction occurring on the COOH group, the dehydrogenated glycine molecule can decompose into CO<sub>2</sub> and CH<sub>2</sub>NH<sub>2</sub>. Additionally, based on the calculated integral cross sections, it can be concluded that in the vast majority of cases, the reaction does not stop at the carboxyl-dehydrogenated glycine molecule but continues, leading to the formation of CO<sub>2</sub>, H<sub>2</sub>O and CH<sub>2</sub>NH<sub>2</sub> products. Finally, the QCT simulations also revealed a possible mechanism in the aforementioned COOH-H-abstraction reactions of the II<sub>n</sub> and VII<sub>p</sub> glycine conformers, where the H atom from the carboxyl group first transfers to the amino group, creating a biradical structure, and in the next step, the OH radical removes one of the hydrogens from the N atom.

## 4 PUBLICATIONS COVERED IN THE THESIS

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[<sup>1</sup>] **B. Gruber** and G. Czakó: *Benchmark ab initio characterization of the abstraction and substitution pathways of the OH + CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> reactions*, Phys. Chem. Chem. Phys., 22, 14560 (2020) IF: 3.676

[<sup>2</sup>] **B. Gruber**, V. Tajti and G. Czakó: *Full-dimensional automated potential energy surface development and dynamics for the OH + C<sub>2</sub>H<sub>6</sub> reaction*, J. Chem. Phys., 157, 074307 (2022) IF: 3.945

[<sup>3</sup>] **B. Gruber** and G. Czakó: *High-level ab initio mapping of the multiple H-abstraction pathways of the OH + glycine reaction*, Phys. Chem. Chem. Phys., 25, 5271 (2023) IF: 3.3

[<sup>4</sup>] **B. Gruber**, V. Tajti and G. Czakó: *Vibrational mode-specific dynamics of the OH + C<sub>2</sub>H<sub>6</sub> reaction*, J. Phys. Chem. A, 127, 7364 (2023) IF: 2.9

[<sup>5</sup>] G. Czakó, **B. Gruber**, D. Papp, V. Tajti, D. A. Tasi and C. Yin: *First-principles mode-specific reaction dynamics*, Phys. Chem. Chem. Phys., 26, 15818 (2024) IF: 3.3

[<sup>6</sup>] **B. Gruber** and G. Czakó: *High-level ab initio characterization of the OH + CH<sub>3</sub>NH<sub>2</sub> reaction*, Phys. Chem. Chem. Phys., 26, 28543 (2024) IF: 2.9

**∑IF = 20.021**

## 5 ADDITIONAL PUBLICATIONS

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[<sup>7</sup>] D. Papp, **B. Gruber** and G. Czakó, *Detailed benchmark ab initio mapping of the potential energy surfaces of the X + C<sub>2</sub>H<sub>6</sub> [X = F, Cl, Br, I] reactions*, Phys. Chem. Chem. Phys., 21, 396 (2019) IF: 3.430

**∑IF = 3.430**

**∑∑IF = 23.451**

## 6 CONFERENCE TALKS

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- [<sup>1</sup>] **B. Gruber** and G. Czakó: *A OH + CH<sub>4</sub> és C<sub>2</sub>H<sub>6</sub> reakciók tanulmányozása a standard kvantumkémián túl*, Online, National Student Research Conference (2021)
- [<sup>2</sup>] **B. Gruber** and G. Czakó: *Az OH gyök reakciója metán, etán és glicin molekulákkal*, Mátrafüred, MTA Reaction Kinetics and Photochemistry Working Group Meeting (2021)
- [<sup>3</sup>] **B. Gruber**, V. Tajti and G. Czakó: *Az OH + C<sub>2</sub>H<sub>6</sub> reakció dinamikája egy automatikusan fejlesztett potenciálisenergia-felületen*, Mátrafüred, MTA Reaction Kinetics and Photochemistry Working Group Meeting (2022)
- [<sup>4</sup>] **B. Gruber** and G. Czakó: *Csatolt-klaszter minőségű potenciálisenergia-felület fejlesztése és a dinamika tanulmányozása teljes (30) dimenzióban: a glicin + OH reakció*, Mátrafüred, MTA Material and Molecular Structure Working Group Meeting (2023)
- [<sup>5</sup>] **B. Gruber** and G. Czakó: *Az OH gyök reakcióinak elméleti vizsgálata C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>NH<sub>2</sub> és glicin molekulákkal: a glicin + OH reakció*, Szeged, KeMoMo-QSAR Symposium (2024)

## 7 POSTERS

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- [<sup>1</sup>] **B. Gruber**, V. Tajti and G. Czakó: *Theoretical investigation of the reactions of OH with ethane and glycine*, Snowbird, Utah, USA, Dynamics of Molecular Collisions (2023)
- [<sup>2</sup>] **B. Gruber** and G. Czakó: *Exploring the dynamics of the OH + glycine H-abstraction reaction using an in-house-developed analytical potential energy surface*, Edinburgh, UK, New directions in molecular scattering Faraday Discussion (2024)