DOI: 10.20396/revpibic.

Ab Initio And Analytic Determination of Quantum Tunneling Rates of Selenoxide Elimination Reaction

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Abstract
Quantum tunneling rate of selenoxides were determined by ab initio calculations and analytically solving the Schrödinger equation.

Key words:
DFT, Tunneling, Selenoxide.

Introduction

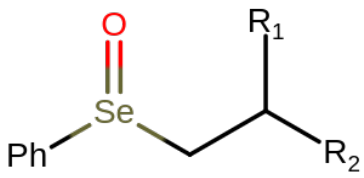
Quantum tunneling is the ability of particles, or a system of particles, of passing through a region of space wherein the energy is bigger than the energy of the particle, which is impossible by Classical Mechanics. Translating that effect to chemistry, there is a possibility of electrons, nuclei, and atoms to tunnel through an impossible to traverse classical region. This effect is important in a multitude of systems, as in chemical rates that deviate from classical behavior. Selenoxide elimination reactions have been an important method for obtaining double bonds since their development, specially with easily degradable molecules because of their mild reaction conditions. The objectives of the present work were to calculate the quantum tunneling reaction rate of selenoxides, represented on Image 1, by an *ab initio* and analytical method, determining the tunnel correction factor *Q,* which is is the factor by which the calculated classical reaction rate is multiplied to account for tunneling.

Results and Discussion

The calculations were done on the B3LYP level of theory with 6-31G(2d,p) basis set, using GAMESS software. Initially the transition states (TS) were determined, which were one or two unique TS for the molecules studied, depending on the symmetry. The intrinsic reaction coordinates (IRC) were then calculated for each TS, care being taken to allow a maximum of two steps between each optimization. The minimums at the end of the IRC curves were optimized and their frequencies calculated. The reaction coordinates were transformed to the distance between the tunneling hydrogen and the oxygen, and the curve fitted to an inverted morse potential. The inverted morse is a solvable unidimensional potential for the Schrödinger equation. It allowed the determination of the barrier permeability (G), which is the probability of tunneling of a hitting particle. The rate of tunneling for the TS is then calculated with Equation (1)[1].

$$k = \sum_i \nu_i G(W_i) \exp\left(-W_i/\mathbf{k}T\right) \qquad (1)$$

where, *G* is the barrier permeability, *W* is the energy of particle *i,* **k** is the Boltzmann constant, T is the temperature, and *v* is the frequency in which the barrier is hit. In the case of the intramolecular hydrogen tunneling, the frequency can be interpreted as the vibration levels that cause the reaction centers to approximate and accordingly *W* is the energy level of said vibration. The tunneling rate for the whole molecule is equal to the sum of the rate of each TS, weighted by the Boltzmann distribution of each starting structure.
The results can be seen on Chart 1. It's possible to notice that the tunneling rates are as high as it's expected by the experimental results, such as kinetic isotope effects.



	R1	R2
1	H	H
2	H	Ph
3	H	CH_3
4	CH_3	CH_3
5	H	Cl

Image 1. Selenoxides structure and representation .

Chart 1. Quantum tunneling rates (*k*), experimental quantum tunneling rates, and tunnel correction factor values.

	k (s^{-1})	*k* exp (s^{-1})	Q
1	$2{,}13 \times 10^{-5}$	$3{,}20 \times 10^{-5}$	2,98
2	$1{,}16 \times 10^{-3}$	$1{,}30 \times 10^{-3}$	9,25
3	$1{,}36 \times 10^{-5}$	$1{,}70 \times 10^{-5}$	3,68
4	$2{,}73 \times 10^{-6}$	$6{,}40 \times 10^{-6}$	1,74
5	$2{,}78 \times 10^{-5}$	$4{,}10 \times 10^{-5}$	3,10

Conclusions

The quantum tunneling rate and tunneling correction factor for selenoxide elimination reactions were calculated by an ab initio and analytical method. Except for **5** all the results were reasonable and close to the experimental value. The study is not finished and the next steps are using a bigger base and different functionals, and comparing the results against a multidimensional calculation.

Acknowledgement

The authors thank the Chemistry Institute for the computational infrastructure, CMP to SAE for the granted scholarship and the funding agencies CAPES, CNPq and Fapesp (project 2013/08293-7).

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