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Quantum chemical theory calculations on the mechanism of the homogeneous, unimolecular gas-phase elimination kinetics of selected diazirines

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ABSTRACT

Theoretical calculations on the gas-phase thermal decomposition of dimethyldiazirine, diethyldiazirine and difluorodiazirine have been carried out using *ab initio* composite methods CBS-QB3 and G3, and DFT CAM-B3LYP, MPW1PW91, PBE1PBE and M062X. Reasonable agreement has been found with the experimental values by the G3 method. Two possible mechanisms were studied: Mechanism A consists the opening of the heterocyclic ring with hydrogen transfer to a nitrogen atom to form prop-1-en-2-yldiazene intermediate which later decomposes to nitrogen gas and the corresponding olefin. Mechanism B involves the extrusion of nitrogen molecule with the formation of carbene intermediate which subsequently yields the corresponding olefin. The results obtained from G3 calculations support the mechanism of a carbene intermediate. Population analysis and Wiberg's bond order show an interaction between the leaving nitrogen and the electron deficient carbon formed during the first step of the reaction.

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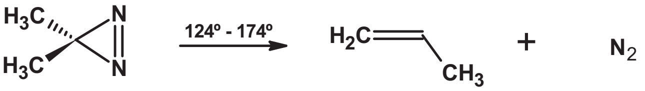
1. Introduction

Diazirines are small heterocyclic compounds whose studies revealed interesting chemical behavior [1–3]. Their nitrogen atoms with its unshared electrons do not exhibit basic properties or react with mineral acids. Diazirines have generally been found as precursors of carbene intermediates either by photolysis or by pyrolysis [4,5]. Diazirines have also been used as markers in the investigation of structures and functions of nucleic acids, proteins and other complex macromolecules [6,7]. Among practical applications are the preparation of modified heparin bags to prevent the blood from clotting and fabrication of biosensors for neuronal cerebral activity [8,9].

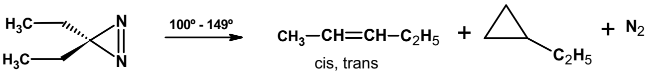
Studies reported on diazirines decomposition in the gas phase are scarce. In this sense, the present work is addressed to provide theoretical information related to the nature of the electronic reorganization that leads these small heterocyclic molecules to yield the corresponding decomposition products. This computational study aims at the elucidation of a reasonable mechanism of the gas-phase thermal decomposition of selected diazirines as depicted in Scheme 1.

The gas-phase thermal decomposition of dimethyldiazirine has been found to be unimolecular homogeneous process at the temperature range of 124–174 °C [3]. According of these authors, the low temperatures appear to indicate that the mechanism may proceed in a polar nature. This means that the decomposition does not take place as free radicals (reaction (1)).



(1)

The decomposition of diethyldiazirine [10] yielded as products *cis*-pent-2-ene 30.6%, *trans*-pent-2-ene 67.5% and ethylcyclopropane 1.6% (reaction (2)). The activation energies for alkenes formation [10] were basically the same within the experimental errors. This result supported the proposed carbene intermediate and subsequent hydrogen migration.



(2)

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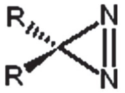
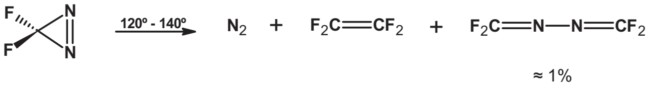


i. R = CH_3,
ii. R = CH_2CH_3,
iii. R = F

Scheme 1.

In 1967, Neuvar and Mitsch [11] reported the kinetics of the thermal decomposition of difluorodiazirine (reaction (3)). The reaction was found to be homogeneous in the temperature range between 120 and 140 °C with an activation energy of 32.5 kcal/mol.



(3)

The three reported diazirines substrates (Table 1) undergo unimolecular decomposition. The study of the reaction mechanism aimed at the characterization of the stationary points on the potential energy surface, including the transition states. Calculated kinetic and thermodynamic parameters were to compare with the experimental values in order to describe a reasonable mechanism of these elimination reactions.

2. Computational methods and models

Decomposition reactions of dimethyldiazirine, diethydiazirine, and difluorodiazirine in the gas phase have been examined by composite *ab initio* and DFT methods. The selected composite methods were G3 [12] and CBS-QB3 [13,14]. The DFT methods were CAM-B3LYP [15], MPW1PW91 [16], PBE1PBE [17] and M062X [18]. Two basis sets were used for the DFT methods: 6-311G(d, p) y 6-311++G(d, p). The calculations were carried out by using Gaussian 09 [19]. Transition states (TS) were found by using the quadratic synchronous transit approach (QST2) developed by H. B. Schlegel and coworkers [20,21]. The nature of the transition states was identified as saddle points of the potential energy surface (PES) when observing a negative coordinate in the Hessian matrix. They also were verified by analyzing the intrinsic reaction coordinate (IRC). Few works have reported the use of composite methods in gas-phase kinetic studies [22,23] where transition state determination is carried out at a higher level of theory. The result is then related to the energy when using the composite method. The reported difference between the calculated Energy of activation with the experimental values has been found to be approximately 4 kJ/mol. The composite methods may well be useful for direct application for Transition state studies. This idea is based in the sequence of calculations of the composite method where the Transition State is located at the first level of theory. This fact appears to be confirmed by the frequency of calculations in the second step. Thereafter, the Energy is adjusted with successive high level of theory and larger basis sets. The present results appear to be reasonable.

Table 1
Kinetic and thermodynamic parameters for the decomposition of diazirines in the gas phase.

Compound	*Ea* (kJ/mol)	Log *A* (s^{-1})	Δ*H*≠ (kJ/mol)	Δ*S*≠ (J/mol)	Δ*G*≠ (kJ/mol)	Ref.
Dimethyldiazirine	138.8	13.89	135.2	9.82	131.1	[3]
Diethyldiazirine	133.4	13.73	130.0	7.08	127.2	[10]
Difluorodiazirine	134.7	13.10	131.3	−5.15	133.4	[11]

During optimizations, Berny analytic gradient was employed with convergence in the density matrix to 10^{-9} atomic units. The maximum threshold values are for the maximum displacement, 0.0018 Å and for maximum strength, 0.00045 Hartree/Bohr. Thermodynamic quantities such as zero-point vibrational energy (ZPVE), correction of absolute temperatures and entropies, were obtained from these frequency calculations. Corrections of temperature and absolute entropies were obtained when considering the ideal gas behavior from the harmonic frequencies and moments of inertia by standard methods [24,25] at average temperature and pressure of the experiments. Frequency and zero point energy scaling factors were taken from the literature [26,27]. The results were analyzed using the calculated geometric parameters, while the charges of the natural bond orbital (NBO) [28–31] analysis were estimated at the G3 level.

3. Results and discussion

3.1. Kinetic and thermodynamic parameters

According to the experimental data of these diazirines decompositions, two possible mechanisms have been considered. Mechanism A: involves the migration of hydrogen with a concurrent breaking of the C–N bond. The nitrogen atom assists the hydrogen transfer producing prop-1-en-2-yldiazene intermediate which then decomposes into the final products. Theoretical calculations for dimethyldiazirine decomposition, using different level of theories are shown in Table 2.

Table 2
Kinetic and thermodynamic parameters for the gas phase decomposition of dimethyldiazirine at 423 K. Mechanism A.

Method	Basis	*Ea* (kJ/mol)	Log*A* (s^{-1})	Δ*H*≠ (kJ/mol)	Δ*S*≠ (J/mol)	Δ*G*≠ (kJ/mol)
Experimental[a]		**138.8**	**13.89**	**135.2**	**9.82**	**131.1**
CAM-B3LYP	6-311G(d, p)	190.5	12.73	187.0	−12.40	192.2
	6-311++G(d, p)	188.7	12.76	185.2	−11.81	190.2
mPW1PW91	6-311G(d, p)	186.5	12.72	183.0	−12.54	188.3
	6-311++G(d, p)	185.0	12.76	181.5	−11.81	186.4
PBE1PBE	6-311G(d, p)	187.0	12.76	183.5	−11.88	188.5
	6-311++G(d, p)	185.5	12.79	181.9	−11.29	186.7
CBS-QB3		191.0	12.73	187.4	−12.37	192.7
G3		193.6	13.08	190.1	−5.66	192.5
M062X	6-311G(d, p)	211.6	12.92	208.1	−8.72	211.8
	6-311++G(d, p)	209.9	13.05	206.4	−6.36	209.1

[a] See Ref. [3].

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