

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/224922681>

Kinetics and Mechanisms of the Unimolecular Elimination of 2,2-diethoxypropane and 1,1-diethoxycyclohexane in the gas Phase: Experimental and Theoretical Study

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · JULY 2012

Impact Factor: 2.69

READS

17

7 AUTHORS, INCLUDING:



Jesus Lezama

Universidad de Oriente (Venezuela)

20 PUBLICATIONS 58 CITATIONS

SEE PROFILE



Mora J.R

Venezuelan Institute for Scientific Research

52 PUBLICATIONS 148 CITATIONS

SEE PROFILE



Tania Cecilia Cordova-Sintjago

University of Florida

99 PUBLICATIONS 256 CITATIONS

SEE PROFILE



Gabriel Chuchani

Venezuelan Institute for Scientific Research

245 PUBLICATIONS 1,222 CITATIONS

SEE PROFILE

Kinetics and Mechanisms of the Unimolecular Elimination of 2,2-Diethoxypropane and 1,1-Diethoxycyclohexane in the Gas Phase: Experimental and Theoretical Study

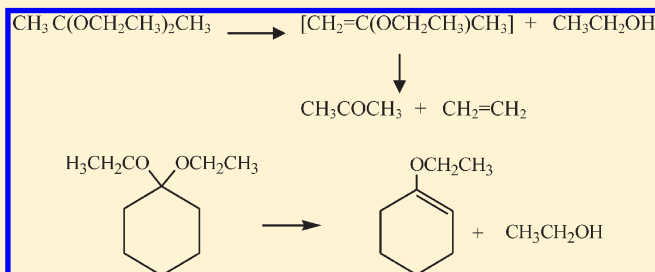
Felix Rosas,[†] Alexis Maldonado,[†] Jesus Lezama,[†] Rosa M. Domínguez,[†] José R. Mora,[†] Tania Cordova,[‡] and Gabriel Chuchani^{*,†}

[†]Centro de Química, Instituto Venezolano de Investigaciones Científicas (I.V.I.C.), Apartado 21827, Caracas 1020.A, Venezuela

[‡]Department of Medicinal Chemistry, College of Pharmacy, University of Florida, P.O. Box 100485, Gainesville, Florida 32610, United States

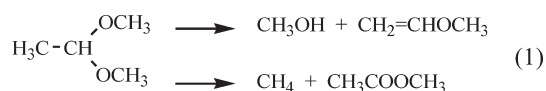
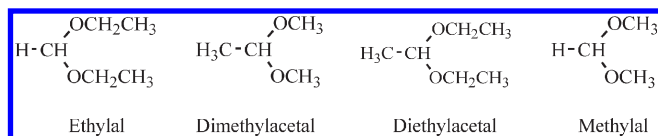
S Supporting Information

ABSTRACT: The gas-phase thermal elimination of 2,2-diethoxypropane was found to give ethanol, acetone, and ethylene, while 1,1-diethoxycyclohexane yielded 1-ethoxycyclohexene and ethanol. The kinetics determinations were carried out, with the reaction vessels deactivated with allyl bromide, and the presence of the free radical suppressor cyclohexene and toluene. Temperature and pressure ranges were 240.1–358.3 °C and 38–102 Torr. The elimination reactions are homogeneous, unimolecular, and follow a first-order rate law. The rate coefficients are given by the following Arrhenius equations: for 2,2-diethoxypropane, $\log k_1 (\text{s}^{-1}) = (13.04 \pm 0.07) - (186.6 \pm 0.8) \text{ kJ mol}^{-1} (2.303RT)^{-1}$; for the intermediate 2-ethoxypropene, $\log k_1 (\text{s}^{-1}) = (13.36 \pm 0.33) - (188.8 \pm 3.4) \text{ kJ mol}^{-1} (2.303RT)^{-1}$; and for 1,1-diethoxycyclohexane, $\log k = (14.02 \pm 0.11) - (176.6 \pm 1.1) \text{ kJ mol}^{-1} (2.303RT)^{-1}$. Theoretical calculations of these reactions using DFT methods B3LYP, MPW1PW91, and PBEPBE, with 6-31G(d,p) and 6-31++G(d,p) basis set, demonstrated that the elimination of 2,2-diethoxypropane and 1,1-diethoxycyclohexane proceeds through a concerted nonsynchronous four-membered cyclic transition state type of mechanism. The rate-determining factor in these reactions is the elongation of the C–O bond. The intermediate product of 2,2-diethoxypropane elimination, that is, 2-ethoxypropene, further decomposes through a concerted cyclic six-membered cyclic transition state mechanism.



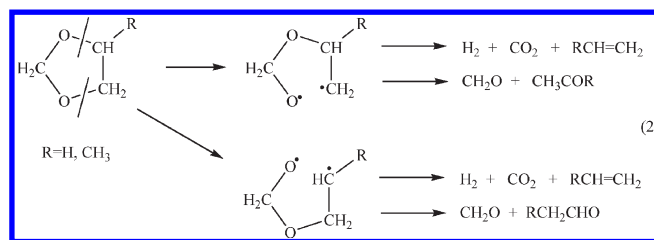
I. INTRODUCTION

Molera and co-workers¹ were first to report the gas-phase thermal decomposition of ethylal, dimethylacetal, and diethylacetal, in a static system at 389–530 °C. Ethylal was believed to decompose by a chain mechanism, whereas for dimethyl and diethylacetals a rearrangement process was assumed to be important. Thus, dimethylacetal reaction was found to follow a first-order rate law to yield the products as described in reaction 1.



Additional work on aliphatic ketals, for example, the gas-phase pyrolysis kinetics of methylal,² was carried out at 472–520 °C and was found to be a free radical chain reaction. However,

ethylene methylal and propylene methylal³ at 512–572 °C were thought to proceed through a biradical mechanism as depicted in reaction 2.



A revisited investigation of methylal thermal decomposition in a flow system^{4,5} showed again a complex radical reaction with different results due to a higher working temperature than the static system.

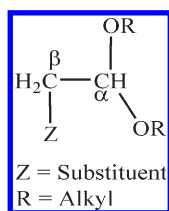
Years later, the gas-phase pyrolysis of a ketal without the presence of a H at the carbon containing the two alkoxy group

Received: October 5, 2011

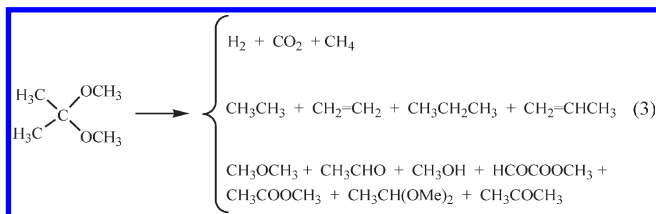
Revised: December 19, 2011

Published: December 20, 2011

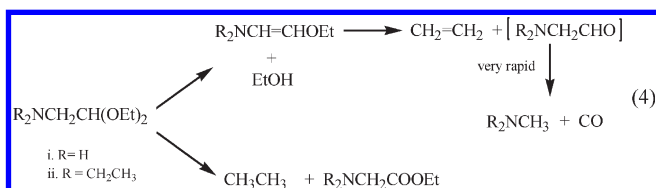
Scheme 1



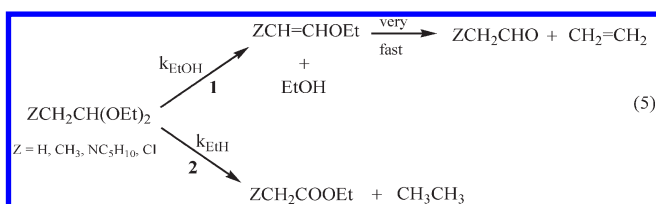
(geminal carbon), that is, 2,2-dimethoxypropane in the presence of NO gas, yielded products as described in reaction 3.⁶



These investigations led the assumption that the C—OR bond polarization may be rate determining, and because of this, a few years ago, it was examined the importance of the hydrogen atom present at the C_{β} —H bond in the transition state mechanism of ketals (Scheme 1). The work was on the gas-phase elimination kinetics of 2,2-diethoxy ethylamine and 2,2-diethoxy-*N,N*-diethyl ethylamine.⁷ The reactions undergoing two parallel processes proved to be homogeneous, unimolecular, and obey a first-order rate law [reaction 4]. According to these results, the H of the C_{β} —H bond was considered to be more favored in the elimination process.



Along these line of works, the gas-phase elimination kinetics of several β -substituted diethyl acetals were undertaken and demonstrated to be homogeneous, unimolecular, and follow first-order law kinetics [reaction 5].⁸ The decomposition processes occur via two parallel reactions as depicted in reaction 5. The comparative kinetic and thermodynamic parameters of the parallel reactions suggested two different concerted polar four-membered cyclic transition state types of mechanisms.



Recently, the homogeneous, unimolecular gas-phase elimination kinetics of 1,1-dimethoxycyclohexane was found to give 1-methoxycyclohexene and methanol.⁹ Additional data in the elucidation of the mechanism of this decomposition⁹ were the use of theoretical calculations by using DFT methods. The calculated values for energy of activation and enthalpy of activation were found

in reasonably good agreement with the experimental values using the PBEPBE/6-31G(d,p) level of theory. Both experimental results and theoretical calculations suggested a molecular mechanism involving a concerted polar four-membered cyclic transition state.

The little information on the homogeneous, unimolecular decomposition of ketals in the gas phase led us to carry out additional experiments on the elimination kinetics of selected molecules, but without an α -H at the carbon containing the two alkoxy groups. In this work, we examined the thermal decomposition reactions of 2,2-diethoxypropane and 1,1-diethoxycyclohexane with theoretical studies for a reasonable mechanistic interpretation. The theoretical calculations aim to obtain the kinetic parameters and the characterization of the potential energy surface (PES) as a means to understand the nature of the molecular mechanism of these reactions.

II. EXPERIMENTAL SECTION

The substrates 2,2-diethoxypropane (Aldrich) and 1,1-diethoxycyclohexane (Aldrich) were found better than of 98.0% purity when analyzed by GC—MS Saturn 2000, Varian, with a DB-SMS capillary column 30 m \times 0.53 mm i.d., 0.53 μm film thickness. The products ethanol and ethylene were identified in a GC—MS Saturn 2000, Varian with a DB-SMS capillary column 30 m \times 0.25 mm i.d., 0.25 μm . The impurities were traces, and their decomposition products could not be identified. The reactant 2,2-diethoxypropane was quantitatively analyzed with a capillary column VA-WAX, 30 m \times 0.53 mm i.d., 1.0 μm film thickness using a Varian 3700 gas chromatograph. For the quantitative analysis of the products, ethanol was carried out by using a Varian 3700 gas chromatograph with a Porapak R (80–100 mesh) column, while ethylene was done by employing the same Varian 3700 with a Porapak S (80–100 mesh) column. Calibration for quantitative analysis of ethanol was carried out using an internal standard of propanol, while propene was the internal standard for ethene.

Kinetics. The kinetic determinations were carried out in a static reaction system as previously reported.^{10–13} The reaction vessel was seasoned with the product of decomposition of allyl bromide at 400–420 $^{\circ}\text{C}$. At each temperature, several runs were carried out in our experiments. The rate coefficients were calculated from the pressure increase measured manometrically and by the quantitative GC analysis. The temperature was maintained within ± 0.2 $^{\circ}\text{C}$ through control with a Shinko DIC-PS 23TR resistance thermometer and was measured with a calibrated platinum—platinum—13% rhodium thermocouple. No temperature gradient was observed along the reaction vessel. The starting materials were all injected directly into the reaction vessel with a syringe through a silicone rubber septum. The amount of substrate used for each reaction was ~ 0.05 –0.2 mL.

III. RESULTS AND DISCUSSION

The products of the gas-phase elimination of 2,2-diethoxypropane and 1,1-diethoxycyclohexane, in vessels deactivated with the product of decomposition of allyl bromide, are described in reactions 6 and 7.

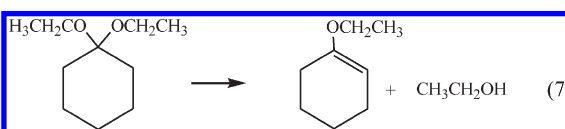
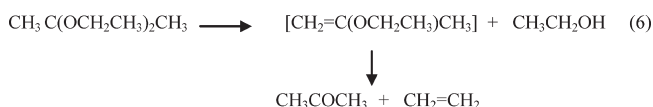


Table 1. Homogeneity of the Reaction

compound	S/V (cm ⁻¹) ^a	$10^4 k_1$ (s ⁻¹) ^b	$10^4 k_1$ (s ⁻¹) ^c
2,2-diethoxypropane	1	33.00 ± 1.15	12.63 ± 0.33
at 333.0 °C	6	50.09 ± 1.44	12.42 ± 0.46
1,1-diethoxycyclohexane	1	54.89 ± 5.20	11.05 ± 0.13
at 270.1 °C	6	65.30 ± 8.1	10.96 ± 0.17

^a S = surface area; V = volume. ^b Clean Pyrex vessel. ^c Vessel deactivated with allyl bromide.

Table 2. Effect of the Free Radical Chain Inhibitor on Rates

substrate	temp (°C)	P_s ^a (Torr)	P_i ^b (Torr)	P_i/P_s	$10^4 k_1$ (s ⁻¹)
2,2-diethoxypropane ^c	339.0	74			37.85
		60	70	1.3	34.72
		55	141	2.6	12.64
		46	142	3.1	12.82
		38	138	3.6	12.64
1,1-diethoxycyclohexane ^d	270.2	67			7.34
		55	58	1.0	11.14
		47	77.6	1.7	10.91
		50	143	2.8	11.05
		42	129	3.1	11.21

^a P_s = pressure of substrate. ^b P_i = pressure of free radical inhibitor. ^c Toluene inhibitor. ^d Cyclohexene inhibitor.

Table 3. Ratio of Final (P_f) to Initial Pressure (P_0) of the Substrate^a

substrate	temp (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	average
2,2-diethoxypropane ^b	251.4	45	126	2.8	2.8
	300.7	61	178	2.9	
	360.8	75	215	2.9	
	349.9	67	176	2.6	
	441.4	85	240	2.8	
1,1-diethoxycyclohexane ^c	250.4	82	165	2.0	2.0
	260.1	87	183	2.1	
	270.2	73	150	2.1	
	280.0	69	138	2.0	
	290.1	80	160.5	2.0	

^a Reaction vessels seasoned with allyl bromide. ^b In the presence of toluene. ^c In the presence of cyclohexene inhibitor.

Table 4. Stoichiometry of the Reaction^a

substrate	temp (°C)	parameters	value					
2,2-diethoxypropane ^b	339.0	time (min)	2	3	5	10	15	20
		reaction (%) (pressure)	14.3	20.8	31.3	53.8	67.2	76.9
		substrate (%) (GLC)	13.0	16.9	33.3	55.6	67.3	76.6
2-diethoxypropene ^b	339.0	time (min)	5	10	15	20		
		reaction (%) (pressure)	31.3	53.8	67.2	76.9		
		ethylene (%) (GLC)	17.6	20.3	33.9	46.0		
1,1-diethoxycyclohexane ^c	270.0	time (min)	2	5	8.3	10	11.7	13.3
		reaction (%) (pressure)	17.8	20.3	24.8	31.0	52.6	76.4
		substrate (%) (GLC)	18.0	20.2	25.4	30.8	52.2	76.2

^a Reaction vessels seasoned with allyl bromide. ^b In the presence of toluene. ^c In the presence of cyclohexene inhibitor.

To examine the effect of surface upon the rate of elimination, several runs, in the presence of the free radical suppressor, were carried out in a vessel with a surface-to-volume ratio of 6.0 relative to that of the normal vessel, which is equal to one. The packed and unpacked clean Pyrex vessel had a marked effect on the rates of decomposition of 2,2-diethoxypropane at 333.0 °C and 1,1-diethoxycyclohexane at 270.1 °C. However, when the packed and unpacked vessels are seasoned with allyl bromide, no significant effect on the rate coefficient of these substrates was obtained (Table 1).

The kinetic runs of 2,2-diethoxypropane were performed in the presence of at least 3 times the amount of the chain inhibitor toluene, while for 1,1-diethoxycyclohexane with at least twice the amount of cyclohexene. Apparently, a low k -value of 1,1-diethoxycyclohexane in the absence of the inhibitor may be due to a small polymerization of the product 1-ethoxycyclohexene. These processes have been undertaken as a precaution, to inhibit any possible radical chain processes. The effect of different proportions of the chain suppressor on the reactions is shown in Table 2.

The theoretical stoichiometry of reaction 6 suggests that the final pressure P_f should be 3 times the initial pressure P_0 . The average experimental results of P_f/P_0 values at five different temperatures and 10 half-lives was 2.8 (Table 3). The fact that $P_f/P_0 < 3$ for 2,2-diethoxypropane arises from the very small amount of the undecomposed intermediate 2-ethoxypropene [reaction 6]. In the case for 1,1-diethoxycyclohexane [reaction 7], the theoretical P_f/P_0 should be equal to 2, and the experimental result was found in good agreement (Table 3). An additional examination of the stoichiometry as depicted in reactions 6 and 7 is given in Table 4. In this respect, for both compounds, up to 76% reaction, there is a good agreement between the extent of decomposition as predicted from pressure measurement and from the chromatographic analyses of the reacted amount of the diethoxy substrates.

The rate coefficients were found to be independent of changes in the initial pressure, P_0 , of the substrate (Table 5), and the first-order plots are satisfactorily linear up to 70% decomposition in both reactants. The variation of the rate coefficients with temperature, in deactivated vessel with product of decomposition of allyl bromide and in the presence of the free radical inhibitor, together with the corresponding Arrhenius expression are given in Table 6 (90% confidence levels with a least-squares method).

Analysis of the experimental results of the kinetic and thermodynamic parameters of activation given in Table 7 suggests the first step 1 of both substrate eliminations is to undergo a concerted

Table 5. Invariability of the Rate Coefficients from Initial Pressure

substrate	temp (°C)	parameters		value			
2,2-diethoxypropane ^a	339.0	P_0 (Torr)	38	46	48	55	60
		$10^4 k_1$ (s ⁻¹)	12.64	12.82	12.16	12.64	12.53
1,1-diethoxycyclohexane ^b	410.8	P_0 (Torr)	48	60	77	88	102
		$10^4 k_1$ (s ⁻¹)	11.14	10.91	11.05	11.21	10.95

^a Results from GLC analysis. ^b Results from manometric measurements.

Table 6. Temperature Dependence of the Rate Coefficients

2,2-Diethoxypropane ^a						
temperature (°C)	319.0	329.7	339.0	348.6	358.3	
$10^4 k_1$ (s ⁻¹)	3.75	7.37	12.88	22.49	39.95	
$\log k_1 = (13.04 \pm 0.07) - (186.6 \pm 0.8) \text{ kJ mol}^{-1} (2.303RT)^{-1}; r = 0.9999$						
2-Ethoxypropene ^{a,b}						
temperature (°C)	319.0	329.7	339.0	348.6	358.3	
$10^4 k_1$ (s ⁻¹)	5.12	10.09	16.61	31.73	55.61	
$\log k_1 = (13.36 \pm 0.33) - (188.8 \pm 3.4) \text{ kJ mol}^{-1} (2.303RT)^{-1}; r = 0.9990$						
1,1-Diethoxycyclohexane ^c						
temperature (°C)	240.1	250.3	260.2	270.0	280.5	290.0
$10^4 k_1$ (s ⁻¹)	1.12	2.53	5.30	11.10	22.27	44.80
$\log k_1 = (14.02 \pm 0.11) - (176.6 \pm 1.1) \text{ kJ mol}^{-1} (2.303RT)^{-1}; r = 0.9998$						

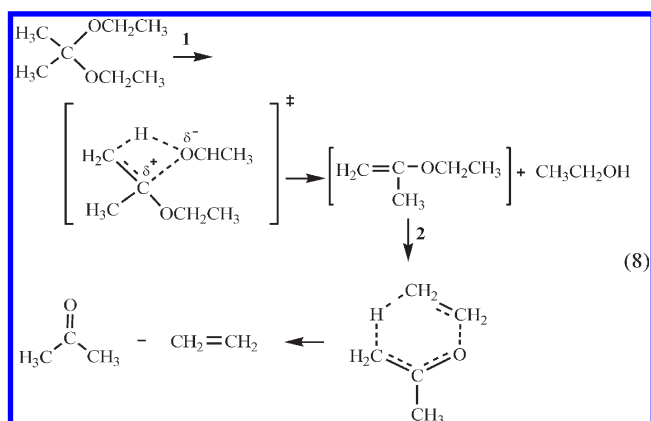
^a GLC analysis. ^b Decomposition of the intermediate. ^c Results from pressure measurements.

Table 7. Kinetic and Thermodynamic Parameters at 320 °C

Z	$k_1 \times 10^4$ (s ⁻¹)	E_a (kJ/mol)	$\log A$ (s ⁻¹)	ΔS^\ddagger (J/mol·K)	ΔH^\ddagger (kJ/mol)	ΔG^\ddagger (kJ/mol)
2,2-diethoxypropane ^a	3.98	186.6 ± 0.8	13.04 ± 0.07	-9.23	181.7	187.2
2-ethoxypropene ^{a,b}	5.37	188.8 ± 3.4	13.36 ± 0.33	-3.11	183.9	185.7
1,1-diethoxycyclohexane ^c	288.4	176.6 ± 1.1	14.02 ± 0.11	9.52	171.7	166.1

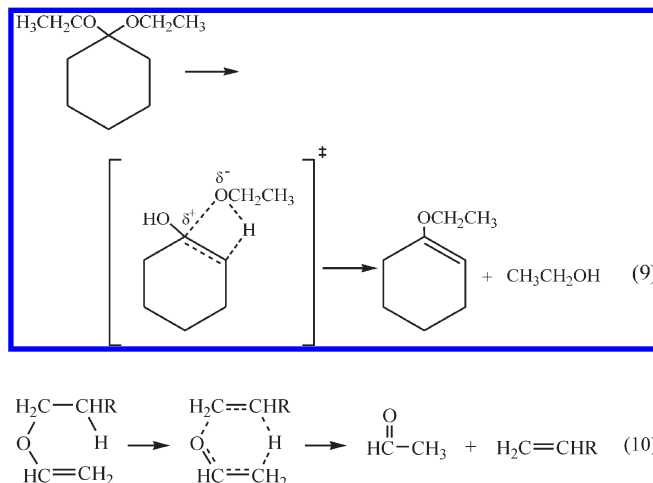
^a GLC analysis. ^b Decomposition of the intermediate. ^c Results from pressure measurements.

polar four-membered cyclic transition state type of mechanism, as shown in reactions 8 and 9.



In the case of the intermediate product of 2,2-diethoxypropane, that is, 2-ethoxypropene, under the condition of the temperature, proceeds as reported for the alkyl vinyl ethers^{14a,b} where the alkyl side contains at least a C_β -H bond, to further decompose through a six-membered cyclic transition state, step 2 (reaction 8), to a carbonyl compound

(aldehyde or ketone) and the corresponding alkene as depicted in reaction 10.



To support or modify these interpretations derived from experimental data, it was thought that a theoretical calculation was a convenient method to elucidate a reasonable mechanism of eliminations of both reactants.

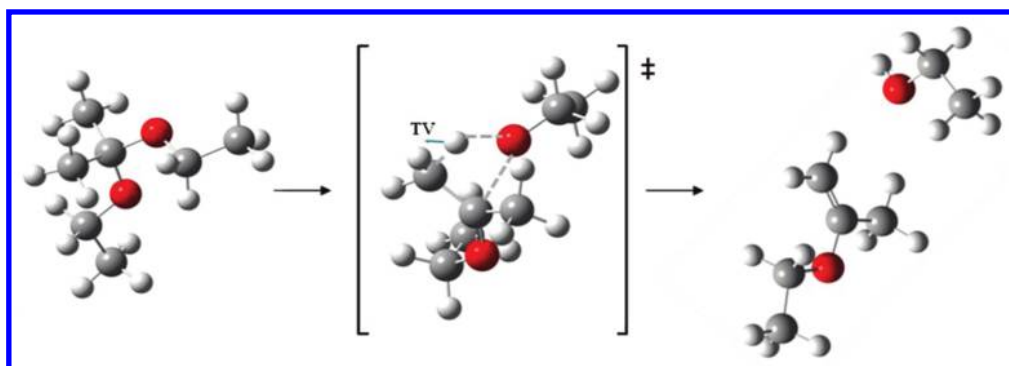


Figure 1. Structures of reactant (left), transition state TS (center), and products (right) of 2,2-diethoxypropane elimination reaction, optimized at PBEPBE/6-31++G(d,p) level of theory.

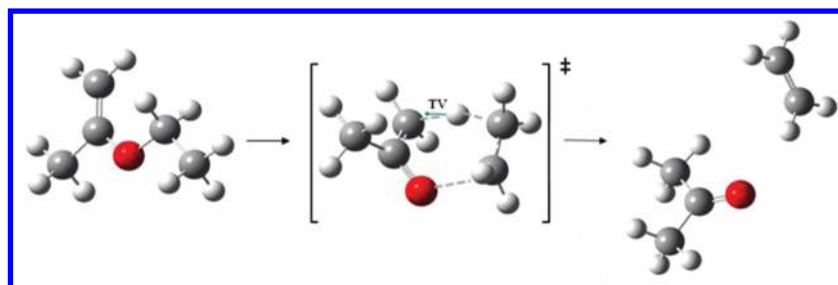


Figure 2. Structures of reactant (left), transition state TS (center), and products (right) of 2-ethoxypropene elimination reaction optimized at MPW1PW91/6-31G(d,p) level of theory.

IV. COMPUTATIONAL METHODS AND MODEL

The reaction coordinates for the decomposition reactions of 2,2-diethoxypropane to yield products ethanol, ethylene and acetone, and of 1,1-diethoxycyclohexane to products ethanol and ethoxycyclohexene were studied. Theoretical calculations were carried out using density functional theory (DFT) methods with B3LYP, MPW1PW91, and PBEPBE methods with 6-31G(d,p), and 6-31++G(d,p) basis sets in Gaussian 03W.¹⁵ The structures of reactants and products were generated and optimized using default parameters: Berny analytical gradient optimization algorithm, requested convergence on the density matrix was 10^{-9} atomic units, the threshold value for maximum displacement was 0.0018 Å, and maximum force 0.00045 hartree/bohr. The Quadratic Synchronous Transit method was used to obtain the transition state geometries. The stationary points were characterized by means of normal-mode analysis; the transition state structures had a unique imaginary frequency that is associated with the transition vector (TV). Intrinsic reaction coordinate (IRC) calculations were performed to verify that the transition state structures connect the reactant and products in the reaction path. Vibrational analysis allowed one to obtain thermodynamic quantities such as zero-point vibrational energy (ZPVE), temperature corrections $[E(T)]$, and absolute entropies $[S(T)]$. Temperature corrections and absolute entropies were obtained assuming ideal gas behavior from the harmonic frequencies and moments of inertia by standard methods¹⁶ at average temperature and pressure values within the experimental range. Scaling factors for frequencies and zero-point energies were taken from the literature.^{17,18}

The TST¹⁹ used to estimate the first-order rate coefficients $k(T)$ was calculated using assuming that the transmission coefficient

is equal to 1, in the expression:

$$k(T) = (k_B T/h) \exp(-\Delta G/RT)$$

where ΔG is the Gibbs free energy change between the reactant and the transition state, and k_B and h are the Boltzmann and Planck constants, respectively.

ΔG^\ddagger was calculated using the following relations:

$$\Delta G = \Delta H - T\Delta S$$

and

$$\Delta H = V + \Delta ZPVE + \Delta E(T)$$

where V is the potential energy barrier, $\Delta ZPVE$ accounts for the differences of ZPVE between the transition state TS and the reactant, and $\Delta E(T)$ represents the contribution of thermal energy at a given temperature.

Theoretical Results. *Kinetic and Thermodynamic Parameters.* The gas-phase elimination reactions of 2,2-diethoxypropane and 1,1-diethoxycyclohexane [reactions 6 and 7] were studied using quantum chemical calculations to predict plausible mechanism of these molecular decomposition. The minimum energy path for the elimination reaction of 2,2-diethoxypropane and 1,1-diethoxycyclohexane to give 2-ethoxypropene, plus ethanol, and 1-ethoxycyclohexene, respectively, was characterized. The TS connecting reactant and products has four-centered geometry with elongation of the C–O bond (Figures 1 and 3). For the decomposition reaction of 2-ethoxypropene, the TS is six-centered geometry (Figure 2).

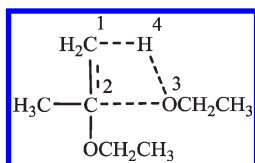
Results from theoretical calculations in these elimination reactions are given in Table 8. We found reasonable agreement with the experimental values for enthalpy and energy of activations for

Table 8. Calculated Kinetic and Thermodynamic Parameters of Activation at 270.0 °C

method	E_a (kJ mol ⁻¹)	log(<i>A</i>)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	$10^4 k_1$ (s ⁻¹)
2,2-Diethoxypropane						
experimental	186.6	13.04	-8.50	182.1	186.7	0.12
B3LYP/6-31G(d,p)	221.0	14.36	16.70	216.5	207.4	0.0013
B3LYP/6-31++G(d,p)	212.8	14.21	13.80	208.3	198.5	0.0054
MPW1PW91/6-31G(d,p)	235.3	14.41	17.70	230.8	221.2	0.00006
MPW1PW91/6-31++G(d,p)	229.6	14.97	28.40	225.1	209.7	0.00076
PBEPBE/6-31G(d,p)	192.9	14.42	17.80	188.4	178.8	0.72
PBEPBE/6-31++G(d,p)	187.8	14.91	27.20	183.3	168.5	6.92
2-Ethoxypropene ^a						
experimental	188.8	13.36	-2.40	184.3	185.6	0.16
B3LYP/6-31G(d,p)	182.6	13.29	-3.80	178.1	182.6	0.53
B3LYP/6-31++G(d,p)	178.5	13.36	-2.40	174.0	175.7	1.53
MPW1PW91/6-31G(d,p)	186.5	13.18	-5.90	181.9	185.2	0.17
MPW1PW91/6-31++G(d,p)	183.9	13.20	-5.40	179.4	182.4	0.32
PBEPBE/6-31G(d,p)	152.3	13.29	-3.70	147.8	149.9	432.4
PBEPBE/6-31++G(d,p)	148.8	13.30	-3.60	144.3	146.2	960.9
1,1-Diethoxycyclohexane						
experimental	176.6	14.02	10.23	172.1	167.3	10.66
B3LYP/6-31G(d,p)	218.6	13.77	5.48	214.1	211.1	0.00055
B3LYP/6-31G++(d,p)	213.2	14.73	23.80	208.7	195.8	0.0165
MPW1PW91/6-31G(d,p)	232.6	14.49	19.21	228.1	217.6	0.00013
MPW1PW91/6-31++G(d,p)	223.7	13.96	8.98	219.1	211.8	0.00027
PBEPBE/6-31G(d,p)	193.8	14.48	19.07	189.3	178.9	0.68
PBEPBE/6-31++G(d,p)	184.5	14.13	12.35	180.0	173.3	2.39

^a Intermediate decomposition.

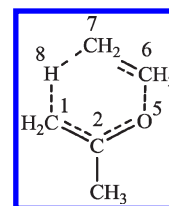
Scheme 2



the elimination reactions of 2,2-diethoxypropane and 1,1-diethoxycyclohexane, through four-membered TS, at the PBEPBE/6-31++G(d,p) level of theory. For the decomposition reaction of the intermediate 2-ethoxypropene, occurring through six-centered TS geometry, better accord between experimental and calculated enthalpy and, consequently, energy of activation was found using MPW1PW91/6-31G(d,p) method. For the elimination reactions occurring through four-centered TS, deviations in the entropy of activation and consequently the free energy of activation and log *A* values are observed, for all methods used. Typically, calculated entropies were more positive; however, for the decomposition reaction of 2-ethoxypropene, calculated entropies of activation were within an order of magnitude of experimental values. Calculated entropies of activation for these reactions were closer to the experimental values when using B3LYP functional. The performance of different electronic structure methods varies, depending on the nature of the transition state for unimolecular reaction.^{20–22}

The above results are in accord with previous works²³ where the elimination reaction through four-centered TS producing ethanol gave good results using PBE functional, in contrast with

Scheme 3



the six-centered TS elimination reaction, which gave better agreement between experimental and calculated parameters using MPW1PW91.

Because the above results show better agreement between the experimental and calculated energy of activation using PBEPBE/6-31++G(d,p) for the elimination reactions of 2,2-diethoxypropane and 1,1-diethoxycyclohexane and MPW1PW91 for the decomposition of 2-ethoxypropene, we expect that the description of the TS geometry in terms of bond formation and bond breaking can be obtained from these methods. We have selected these methods, PBEPBE/6-31G(d,p) in the case of four-membered cyclic TS eliminations and MPW1PW91/6-31G(d,p) for the six-membered cyclic TS mechanism, to study the geometrical parameters, charges, and bond orders in the transition state, and to learn about the progress in the reaction path connecting the reactant and products.

The TS nature is described by the geometrical parameters and NBO charges indicated in the following sections.

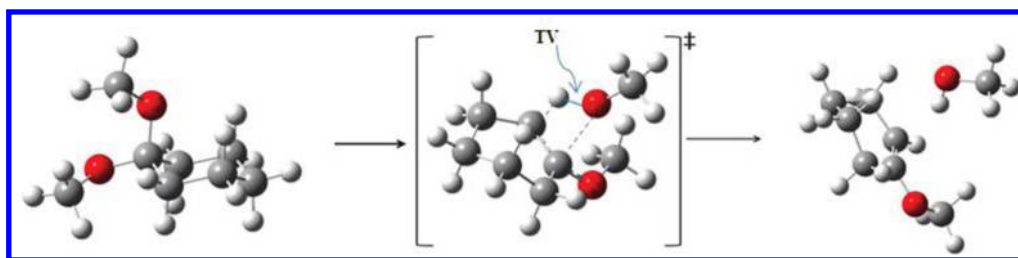
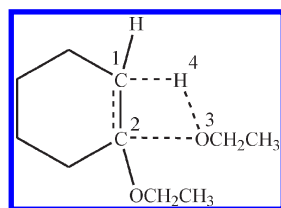


Figure 3. Structures of reactant (left), transition state (center), and products (right) of 1,1-diethoxycyclohexane elimination reaction optimized at PBEPBE/6-31++G(d,p) level of theory.

Scheme 4



Transition State and Mechanism. The transition state structures for the elimination reaction of 2,2-ethoxypropene and 1,1-diethoxycyclohexane are four-centered geometry comprising the atoms C_1 , C_2 , O_3 , and H_4 (Schemes 2, 4). The decomposition reaction of 2-ethoxypropene occurs through six-centered TS, including atoms C_1 , C_2 , O_5 , C_6 , C_7 , and H_8 (Scheme 3). The TS were verified by IRC calculations, demonstrating the TS connected to reactant and products in the minimum energy path (MEP). IRC plots are available in the Supporting Information, Figures 4–6.

For 2,2-ethoxypropene and 1,1-diethoxycyclohexane, the unique imaginary frequency of the TS is associated with the hydrogen H_4 migration from the carbon C_1 to O_3 to produce ethanol (Scheme 2, Figure 1, and Scheme 4, Figure 3). Structural parameters for the elimination reaction of 2,2-diethoxypropene (R), the transition state (TS), and products (P) are given in Table 9. Table 10 summarizes the geometrical parameters for 2-ethoxypropene decomposition, and Table 11 shows the geometrical parameters for the elimination reaction of 1,1-diethoxycyclohexane.

The 1,2-elimination reactions from 2,2-diethoxypropene (Table 9) and 1,1-diethoxy cyclohexane (Table 11), proceeding through concerted four-membered cyclic TS mechanism, show important elongation of C_2-O_3 bond in the TS (from 1.4 to 2.4 Å in the TS), while a moderate increase in H_4-C_1 distance is observed (from 1.1 to 1.2 Å in the TS). The alkene formation is observed in the decrease in C_1-C_2 distance from 1.53 to 1.54 Å in the TS. The four atoms involved in the TS are approximately in plane for 2,2-diethoxypropene, as shown by the small dihedrals in Tables 9; in the case of 2,2-diethoxycyclohexane, deviations from planarity are observed, as seen in the dihedrals in Table 11.

The geometrical parameters for the elimination of 2-ethoxypropene, Table 10, show an important increase in O_5-C_6 distance (from 1.42 to 1.98 Å in the TS) and also an increase in C_7-H_8 distance (from 1.09 to 1.34 Å in the TS) accompanied by a decrease in C_6-C_7 and C_3-O_5 distances as the double bonds form to give acetone and ethylene. The TS is a semichair configuration.

NBO Charges. The changes in electron distributions throughout the reaction were studied by means of NBO charges

Table 9. Structural Parameters for Optimized Reactant (R), Transition State (TS), and Products (P) from 2,2-Diethoxypropene Decomposition with PBEPBE/6-31++G(d,p) Method

	Atomic Lengths (Å)			
	C_1-C_2	C_2-O_3	O_3-H_4	H_4-C_1
R	1.532	1.419	2.529	1.100
TS	1.448	2.386	1.489	1.206
P	1.354	4.090	0.974	4.119

	Dihedral Angles (deg)			
	$C_1-C_2-O_3-H_4$	$C_2-O_3-H_4-C_1$	$O_3-H_4-C_1-C_2$	$H_4-C_1-C_2-O_3$
TS	1.264	−2.013	2.747	−1.292

	Imaginary Frequency (cm^{-1})	
TS	523.45	

calculations. The NBO charges of atoms involved in the reaction changes in the reactant, transition state TS, and products for 2,2-diethoxypropene, 2-ethoxypropene, and 1,1-diethoxycyclohexane elimination reactions are shown in Tables 12–14, respectively. Atom numbering corresponds to Schemes 2–4. For 2,2-diethoxypropene and 1,1-diethoxycyclohexane 1,2-elimination reactions (Tables 12 and 14), there is an important increase in electron density at the oxygen atom O_3 of the leaving ethoxy group, from −0.6 to −0.8 in the TS. The hydrogen H_4 becomes more positive, from 0.26 to 0.24 to 0.38–0.39 in the TS; the change is more significant for 1,1-diethoxycyclohexane. Also significant is the increase in negative charge in C_1 , from −0.72 to −0.82 in the TS for 2,2-diethoxypropene and from −0.5 to −0.6 in the TS for 1,1-diethoxycyclohexane. Atom C_2 is almost unchanged for 2,2-diethoxypropene and undergoes small changes, from 0.54 to 0.56 in the TS in the case of 1,1-diethoxycyclohexane.

The NBO charges in the elimination reaction of the intermediate in the decomposition of 2,2-diethoxypropene, that is, 2-ethoxypropene, are reported in Table 13. There is an increase in negative charge at oxygen O_5 from −0.55 to −0.59, however, smaller than that observed of the 1,2-elimination reactions described above. Hydrogen H_8 develops more positive charge, from 0.25 to 0.29 in the TS. A significant change is observed for C_6 (C_6-O_5 bond breaking) and C_2 ($C_2=O_5$ double bond formation), from −0.13 to −0.26 and from 0.34 to 0.46 in the TS, respectively. Atom C_1 becomes more negative as the hydrogen is transferred to C_7 , from −0.61 to −0.69 in the TS.

Bond Order Analysis. Bond orders can be used to describe the changes in the reaction coordinate.^{24–26} Wiberg bond

Table 10. Structural Parameters for Optimized Reactant (R), Transition State (TS), and Products (P) from 2-Ethoxypropene Decomposition with MPW1PW91/6-31G(d,p) Method

	Atomic Lengths (Å)					
	C ₁ –C ₂	C ₂ –O ₅	O ₅ –C ₆	C ₆ –C ₇	C ₇ –H ₈	H ₈ –C ₁
R	1.338	1.358	1.416	1.512	1.092	4.709
TS	1.401	1.272	1.979	1.402	1.339	1.451
P	1.510	1.214	3.527	1.329	5.049	1.095

	Dihedral Angles (deg)					
	C ₁ –C ₂ –O ₅ –C ₆	C ₂ –O ₅ –C ₆ –C ₇	O ₅ –C ₆ –C ₇ –H ₈	C ₆ –C ₇ –H ₈ –C ₁	C ₇ –H ₈ –C ₁ –C ₂	H ₈ –C ₁ –C ₂ –O ₅
TS	63.313	–24.340	0.773	–22.289	49.145	–60.613

Imaginary Frequency (cm ^{–1})						
TS	1145.45					

Table 11. Structural Parameters for Optimized Reactant (R), Transition State (TS), and Products (P) from 1,1-Diethoxycyclohexane Decomposition with PBEPBE/6-31++G(d,p) Method

	Atomic Lengths (Å)			
	C ₁ –C ₂	C ₂ –O ₃	O ₃ –H ₄	H ₄ –C ₁
R	1.547	1.439	2.774	1.103
TS	1.451	2.351	1.494	1.202
P	1.359	3.428	0.983	2.494

	Dihedral Angles (deg)			
	C ₁ –C ₂ –O ₃ –H ₄	C ₂ –O ₃ –H ₄ –C ₁	O ₃ –H ₄ –C ₁ –C ₂	H ₄ –C ₁ –C ₂ –O ₃
TS	–5.913	9.409	–12.770	6.088

Imaginary Frequency (cm ^{–1})				
TS	489.8			

indexes²⁷ were calculated using the natural bond orbital NBO program²⁸ in Gaussian 03W. Bond order indexes estimate bond orders from population analysis. Bond breaking and bond making process involved in the reaction mechanism are monitored by means of the synchronicity (S_y) concept proposed by Moyano et al.²⁹ defined by the expression:

$$S_y = 1 - \left[\sum_{i=1}^n |\delta B_i - \delta B_{av}| / \delta B_{av} \right] / 2n - 2$$

where n is the number of bonds directly involved in the reaction, and the relative variation of the bond index is given by:

$$\delta B_i = [B_i^{TS} - B_i^R] / [B_i^P - B_i^R]$$

Also, the superscripts R, TS, and P denote reactant, transition state, and product, respectively.

The evolution in bond change is calculated as:

$$\%E_v = \delta B_i * 100$$

The average bond order change is calculated from:

$$\delta B_{av} = 1/n \sum_{i=1}^n \delta B_i$$

Table 12. NBO Charges of the Atoms Involved in 2, 2-Diethoxypropane Thermal Decomposition from PBEPBE/6-31++G(d,p) Calculations

	C ₁	C ₂	O ₃	H ₄
R	–0.717	0.541	–0.580	0.262
TS	–0.817	0.542	–0.804	0.380
P	–0.611	0.308	–0.769	0.494

Table 13. NBO Charges of the Atoms Involved in 2-Ethoxypropene Thermal Decomposition from MPW1PW91/6-31G(d,p) Calculations

	C ₁	C ₂	O ₅	C ₆	C ₇	H ₈
R	–0.606	0.337	–0.547	–0.129	–0.734	0.249
TS	–0.691	0.463	–0.589	–0.259	–0.742	0.292
P	–0.812	0.596	–0.552	–0.455	–0.461	0.261

Table 14. NBO Charges of the Atoms Involved in 1, 1-Diethoxycyclohexane Thermal Decomposition from PBEPBE/6-31G(d,p)++ Calculations

	C ₁	C ₂	O ₃	H ₄
R	–0.523	0.541	–0.594	0.244
TS	–0.611	0.561	–0.806	0.390
P	–0.392	0.307	–0.775	0.497

B_i values represent bond order, and δB_i represents its change in the reaction coordinate from the reactant (B_i^R), to the transition state TS (B_i^{TS}), and to products (B_i^P). The percent evolution $\% E_v$ is used to show the relative advance of the different reaction coordinates studied. The parameter S_y , or synchronicity, varies between 0 and 1 for concerted reactions; the closer is the S_y value to unity, the more synchronic is the process.

Wiberg bond indexes were calculated for those bonds involved in the reaction changes, that is, C₁–C₂, C₂–O₃, O₃–H₄, and H₄–C₁ for the elimination reaction of 2,2-diethoxypropane and 2,2-diethoxy cyclohexane (Schemes 2 and 4, Tables 15–17), and for bonds C₁–C₂, C₂–O₅, O₅–C₆, C₆–C₇, C₇–H₈, and H₈–C₁ for the decomposition reaction for 2-ethoxypropene.

Table 15. Wiberg Bond Index of Reactant (R), Transition State (TS), and Products (P) for 2,2-Diethoxypropane Thermal Decomposition from PBEPBE/6-31++G(d,p)

	C ₁ –C ₂	C ₂ –O ₃	O ₃ –H ₄	H ₄ –C ₁	S _y
B _i ^R	0.9995	0.9338	0.0021	0.9133	0.735
B _i ^{TS}	1.2058	0.2809	0.2010	0.6067	
B _i ^P	1.8099	0.0004	0.7442	0.0001	
%E _v	25.46	69.95	26.80	33.57	

Table 16. Wiberg Bond Index of Reactant (R), Transition State (TS), and Products (P) for 2-Ethoxypropene Thermal Decomposition from MPW1PW91/6-31G(d,p)

	C ₁ –C ₂	C ₂ –O ₃	O ₃ –C ₆	C ₆ –C ₇	C ₇ –H ₈	H ₈ –C ₁	S _y
B _i ^R	1.8306	1.0011	0.8848	1.0337	0.9200	0.0001	0.931
B _i ^{TS}	1.3870	1.3947	0.3843	1.4203	0.4771	0.3675	
B _i ^P	1.0139	1.8169	0.0049	2.0364	0.0000	0.9054	
%E _v	54.32	48.25	56.88	38.56	48.14	40.58	

Table 17. Wiberg Bond Index of Reactant (R), Transition State (TS), and Products (P) for 1,1-Diethoxycyclohexane Thermal Decomposition from PBEPBE/6-31G(d,p)

	C ₁ –C ₂	C ₂ –O ₃	O ₃ –H ₄	H ₄ –C ₁	S _y
B _i ^R	0.9762	0.8958	0.0023	0.9049	0.761
B _i ^{TS}	1.1888	0.2830	0.2037	0.5886	
B _i ^P	1.7433	0.0082	0.7120	0.0203	
%E _v	27.71	69.04	28.38	35.76	

Calculated bond orders indicate that the most advanced reaction coordinate is the breaking of C–O bond, being more important for the 1,2-elimination processes of 2,2-diethoxypropane and 2,2-diethoxycyclohexane, 69–70%, than the decomposition of 2-ethoxypropene, 57%. In the 1,2-elimination reaction, the other reaction coordinates are less advanced as compared to the C–O bond breaking, indicating a nonsynchronous process, S_y values 0.74–0.76. Conversely, in the 2-ethoxypropene decomposition, the progress is intermediate in reaction coordinates C₁–C₂, C₂–O₃, O₃–C₆, and C₇–H₈ and somewhat less advanced for C₆–C₇ and H₈–C₁; overall, the process is more synchronic, S_y = 0.93.

V. CONCLUSIONS

The thermal decomposition reactions of 2,2-diethoxypropane and 1,1-diethoxy-cyclohexane have been studied by experimental and theoretical methods to propose a reasonable mechanism. These reactions were demonstrated to be unimolecular, homogeneous, and follow first-order kinetics under the experimental conditions used. These compounds undergo 1,2-elimination reactions through nonsynchronous four-membered cyclic TS processes. The 2,2-diethoxypropane gives ethanol and the intermediate compound 2-ethoxypropene, which further decomposes through a concerted six-membered cyclic TS mechanism to give acetone and ethylene. The 2-ethoxypropene decomposition is more synchronic than the 1,2-elimination reactions. The rate-determining step of these elimination reactions is the polarization of the C–O bond, in the sense of C^{δ+}...O^{δ-}, in the transition state.

■ ASSOCIATED CONTENT

S Supporting Information. IRC obtained from gas-phase elimination reaction kinetics of 2,2-diethoxypropane and 1,1-diethoxy-cyclohexane. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chuchani@ivic.gob.ve.

■ REFERENCES

- (1) Molera, M.; Centeno, J.; Orza, J. *J. Chem. Soc.* **1963**, 2234–2241.
- (2) Molera, M.; Fernandez-Biarge, J.; Centeno, J.; Arévalo, L. *J. Chem. Soc.* **1963**, 2311–2320.
- (3) Molera, M.; Dominguez, G. *An. Real. Soc. Esp. Fis. Quim.* **1963**, 11, 639–648.
- (4) Molera, M.; Pereira, G. *An. Fis. Quim.* **1966**, 62, 661–666.
- (5) Molera, M.; Pereira, G. *An. Fis. Quim.* **1966**, 62, 667–675.
- (6) Garcia Dominguez, J. A.; Molera, M. *J. An. Fis. Quim.* **1970**, 70, 186–188.
- (7) Mora, J. R.; Dominguez, R. M.; Herize, A.; Tosta, M.; Chuchani, G. *J. Phys. Org. Chem.* **2008**, 21, 359–364.
- (8) Mora, J. R.; Maldonado, A.; Domínguez, R. M.; Chuchani, G. *J. Phys. Org. Chem.* **2010**, 23, 845–852.
- (9) Rosas, F.; Domínguez, R. M.; Tosta, M.; Mora, J. R.; Márquez, E.; Córdova, T.; Chuchani, G. *J. Phys. Org. Chem.* **2010**, 23, 743–750.
- (10) Maccoll, A. *J. Chem. Soc.* **1955**, 965–973.
- (11) Swinbourne, E. S. *Aust. J. Chem.* **1958**, 11, 314–330.
- (12) Dominguez, R. M.; Herize, A.; Rotinov, A.; Alvarez-Aular, A.; Visbal, G.; Chuchani, G. *J. Phys. Org. Chem.* **2004**, 17, 399–408.
- (13) Espitia, L.; Meneses, R.; Domínguez, R. M.; Tosta, M.; Herize, A.; Lafont, J.; Chuchani, G. *Int. J. Chem. Kinet.* **2009**, 41, 145–152.
- (14) (a) Smith, G. G.; Kelly, F. W. *Prog. React. Kinet.* **1971**, 8, 75–234. (b) Awan, I. A.; Flowers, M. C. *J. Chem. Soc. Pak.* **1988**, 10, 363–368.
- (15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (16) McQuarrie, D. *Statistical Mechanics*; Harper & Row: New York, 1986.
- (17) Foresman, J. B.; Frish, A. E. *Exploring Chemistry with Electronic Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.
- (18) (a) Scale factors in <http://cccbdb.nist.gov/vibscalejust.asp>. (b) Database of Frequency Scaling Factors for Electronic Structure Methods; http://comp.chem.umn.edu/truhlar/freq_scale.htm.
- (19) Benson, S. W. *The Foundations of Chemical Kinetics*; McGraw-Hill: New York, 1960.
- (20) Maldonado, A.; Mora, J. R.; Subero, S.; Loroño, M.; Córdova, T.; Chuchani, G. *Int. J. Chem. Kinet.* **2011**, 43, 292–302.
- (21) Tosta, M.; Mora, J. R.; Córdova, T.; Chuchani, G. *J. Phys. Chem. A* **2010**, 114, 7892–7897.
- (22) Rotinov, A.; Domínguez, R. M.; Córdova, T.; Chuchani, G. *J. Phys. Org. Chem.* **2005**, 18, 1–9.
- (23) Mora, R. M.; Tosta, M.; Cordova, T.; Chuchani, G. *J. Phys. Org. Chem.* **2009**, 22, 367–377.
- (24) Lendvay, G. *J. Phys. Chem.* **1989**, 93, 4422–4429.
- (25) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, 83, 735–746.
- (26) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899–926.
- (27) Wiberg, K. B. *Tetrahedron* **1968**, 24, 1083–1096.
- (28) Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO version 3.1*.
- (29) Moyano, A.; Pericá, M. A.; Valenti, E. *J. Org. Chem.* **1989**, 54, 573–582.