Theoretical study of the mechanisms for the homogenous gas-phase elimination kinetics of some 2-hydroxynitroalkanes[†]

Rafael Añez,[1] Rodolfo Izquierdo,[2] Alba Vidal,[2] Tania Cordova,[3] Aníbal Sierraalta[1] and Gabriel Chuchani[1]*

[1]Centro de Química, Instituto Venezolano de Investigaciones Científicas (I.V.I.C.), Apartado 21827, Caracas, Venezuela
[2]Departamento de Química, Facultad Experimental de Ciencias, Departamento de Química. Universidad del Zulia, Maracaibo, Venezuela
[3]Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Apartado 1020-A, Caracas, Venezuela

ABSTRACT: Theoretical studies for the kinetics of the gas phase elimination of 2-hydroxynitroalkanes were carried out at MP2/6-31G* level of theory. The mechanism for both secondary and tertiary 2-hidroxynitroalkanes thermolysis is retro-aldol type. In the case of the secondary 2-hydroxynitroalkanes, that is, 3-nitro-2-butanol and 3-nitro-2-pentanol, the elimination reaction proceeds via a six-membered cyclic transition state with the formation of actetaldehyde and the corresponding nitroalkane. In the case of the tertiary 2-hydroxynitroalkane, 2-methyl-3-nitro-2-propanol, the reaction also proceeds through a six-membered cyclic transition state to give acetone and nitromethane. The calculated kinetic and thermodynamic parameters are in reasonable agreement with the reported experimental values. NBO charges revealed that polarization of both $N^{\delta+}$—$C_\alpha^{\delta-}$ and $C_\alpha^{\delta-}$—$C_\beta^{\delta+}$ bonds are important factors in the decomposition process. The tertiary substrate is favored due to stabilization of the $C_\beta^{\delta+}$ positive charge in the TS. The NBO analysis showed that these reactions are concerted and polar in nature. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: Kinetics; unimolecular elimination; pyrolysis; 2-hydroxy nitroalkanes; "*ab initio*" calculations; reaction mechanism; transition state structure

INTRODUCTION

The gas-phase elimination of primary, secondary, and tertiary 2-hydroxyalkenes,[1–6] 2-hydroxyacetylenes,[7,8] 2-hydroxy esters,[2,9–13] 2-hydroxy ketones,[4,9,14–17] 2-hydroxynitriles,[18] and 2-hydroxyalkylbenzenes[19] were found to proceed through a concerted six-membered cyclic transition state as described in reaction (1). The C_α—C_β bond polarization, in the direction of $C_\alpha^{\delta-}\cdots C_\beta^{\delta+}$, was attributed to be rate determining step. The elimination rates increase from primary to tertiary C_β consistent with stabilization of the $\delta+$ charge. In addition to this fact, the higher the nucleophilicity of the main group the faster the rate of elimination.[4] In other words, C=O bond is a better nucleophile that C=CH$_2$ bond which accounts for the difference in reactivity in the order ketones > esters > alkenes (Scheme 1).
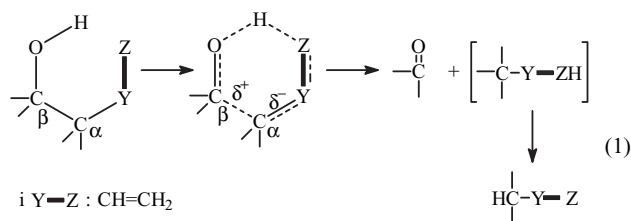
i $Y-Z$: $CH=CH_2$
ii $Y-Z$: $C\equiv CH$
iii $Y-Z$: $C(OR)=O$
iv $Y-Z$: $C(R)=O$
v $Y-Z$: $C\equiv N$
vi $Y-Z$: C_6H_5

Scheme 1

Among the compounds described in reaction (1), the gas phase elimination kinetics of several primary, secondary, and tertiary hydroxy substituent at the 2-position of a nitro group in nitroalkanes were examined.[20] According to product formation of secondary and tertiary hydroxynitroalkanes, a retro-aldol type of decomposition takes place, which is similar to the elimination process of reaction (1). Consequently, these substrates appear to proceed through a six-membered cyclic transition state as

Correspondence to: G. Chuchani, Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas, Venezuela.
E-mail: chuchani@ivic.ve

depicted in reaction (1). Consequently, the mechanisms of elimination may be described as in reactions (2) and (3).

(2)

(3)

R = CH₃ or CH₂CH₃
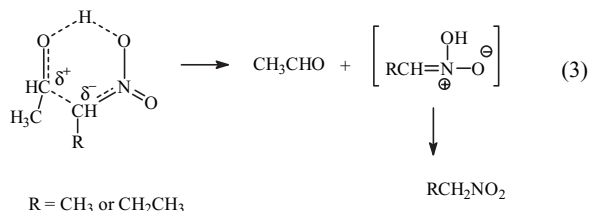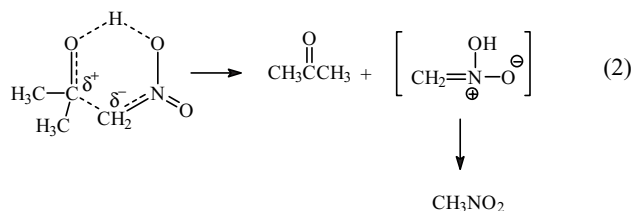
With regard to some primary 2-hydroxy groups in nitroalkane, they undergo a dehydration process and small amount of the isomer alkyl nitrate. This result differs from a retro-aldol type of elimination of compounds listed in reaction (1).

This paper is addressed at examining the quantum mechanical calculation in order to explore the nature of the reaction mechanism for the homogeneous unimolecular gas phase elimination of 3-nitro-2-butanol, 3-nitro-2-pentanol, and 2-methyl-3-nitro-2-propanol.

COMPUTATIONAL METHODS AND MODELS

The kinetics for the gas phase elimination reaction of 2-hydroxynitroalkanes have been studied at MP2/6-31G* level of theory as implemented in Gaussian 98W.[21] Transition states search was performed using Quadratic Synchronous Transit protocol. The nature of stationary points was established by calculating and diagonalizing the Hessian matrix (force constant matrix). TS structures were characterized by means of normal mode analysis. Intrinsic reaction coordinate (IRC) calculations were performed to verify transition state structures. The unique imaginary frequency associated with the transition vector (TV), that is, the eigenvector associated with the unique negative eigenvalue of the force constant matrix, has been characterized.

Frequency calculations provided thermodynamic quantities such as zero point vibrational energy (ZPVE), temperature corrections ($E(T)$) and absolute entropies ($S(T)$), and consequently, the rate coefficient can be estimated assuming that the transmission coefficient is equal to 1. Temperature corrections and absolute entropies were obtained assuming ideal gas behavior

from the harmonic frequencies and moments of inertia by standard methods[22] at average temperature and pressure values within the experimental range. Scaling factors for zero point energies were taken from the literature.[23]

The first-order rate coefficient $k(T)$ was calculated using the TST[24] and assuming that the transmission coefficient is equal to 1, as expressed in the following relation:

$$k(T) = (KT/h)\exp(-\Delta G^{\#}/RT)$$

Where ΔG is the Gibbs free energy change between the reactant and the transition state and K, h are the Boltzman and Plank constants, respectively.

$\Delta G^{\#}$ 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 and $\Delta ZPVE$ and $\Delta E(T)$ are the differences of ZPVE and temperature corrections between the TS and the reactant, respectively.

RESULTS AND DISCUSSIONS

The theoretical studies on the elimination mechanism of 2-hydroxynitroalkanes for the retro-aldol type of reaction were carried out. The secondary 2-hydroxynitroalkanes, that is, 3-nitro-2-butanol and 3-nitro-2-pentanol, undergo thermal decomposition to yield acetaldehyde and the corresponding nitroalkane. The tertiary 2-hydroxynitroalkane, 2-methyl-3-nitro-2-propanol, gives on elimination acetone and nitromethane.

Geometries for reactants, TS and products for the elimination reactions described above were optimized using MP2/6-31G* basis set. Frequency calculations were carried at the average experimental conditions (280 °C) at the same level of theory. Thermodynamic quantities such as ZPVE, temperature corrections ($E(T)$), energy, enthalpy, and free energies were obtained from vibrational analysis. Entropy values were estimated from vibrational according to the suggestion of Chuchani–Cordova[25] by using factor C^{exp}.

Results from MP2/6-31G* are shown in Table 1. Calculated thermodynamic and kinetic parameters are in good agreement with experimental within 3 kJ/mol for $\Delta H^{\# theo}$, Ea^{theo}, $\Delta G^{\# theo}$ Activation parameters at MP2/6-31G* level of theory follow the same reactivity order observed for experimental values.

Calculated activation parameters $\Delta H^{\#}$, Ea, $\Delta G^{\#}$, $\Delta S^{\#}$ were used to obtain log A and first order rate coefficients. Experimental values in Table 1 show that on increasing substitution at C_β increases the rate coefficient. This is also the case for calculated rates, the reactivity order being: 2-methyl-3-nitro 2-propanol (tertiary) > 3-nitro-2-

Table 1. Activation parameters for the thermal decomposition of secondary 2-hydroxynitroalkanes MP2/6-31G* at 280 °C, for retro-aldol type reaction. Experimental values are shown in parentheses

Substrate	$\Delta H^{\neq}$ (kJ mol^{-1})	Ea (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	log A	k_1 (s^{-1}) 10^4	C^{exp}
S1	147.7 (145.8)	153.3 (150.4)	−33.4 (−31.6)	166.2 (163.3)	11.31 (11.84)	6.92 (42.66)	12.9
S2	141.2 (138.9)	146.8 (143.5)	−44.3 (−42.5)	165.7 (162.4)	10.75 (11.27)	7.77 (52.00)	18.9
S3	138.0 (142.3)	143.6 (146.9)	−36.9 (−35.1)	158.4 (161.7)	11.14 (11.66)	38.10 (60.26)	14.8

S1 = 3-nitro 2-butanol, S2 = 3-nitro-2-pentanol, S3 = 2-methyl-3-nitro 2-propanol

Table 2. Structural Parameters reactants and TS of secondary 2-hydroxynitroalkanes from MP2/6-31G* calculations at 280°C, for retro-aldol type reaction. Atom distances are in Å and dihedral angles are in degrees

	S1		S2		S3	
	R	TS	R	TS	R	TS
R	Distances Å					
O1–N2	1.31	1.43	1.31	1.42	1.31	1.42
N2–C3	1.54	1.39	1.53	1.39	1.53	1.38
C3–C4	1.54	2.02	1.55	2.04	1.54	2.04
C4–O5	1.47	1.32	1.47	1.53	1.47	1.32
O5–H6	1.00	1.42	1.00	1.31	1.00	1.37
H6–O1	2.02	1.12	1.98	1.39	1.96	1.12
Dihedral angles						
O1–N2–C3–C4		TS		TS		TS
N2–C3–C4–O5		73.86		68.54		68.77
C3–C4–O5–H6		−63.58		−50.72		−51.31
C4–O5–H6–O1		33.29		22.21		22.29
		−24.78		−19.21		−19.38
Imaginary frequencies						
		TS		TS		TS
		578.30		560.33		654.78

pentanol ≅ 3-nitro-2-butanol (secondary). Values for entropy of activation (−33.4 to −44.4 J/Kmol) are in accord with a concerted process with a six-membered TS structure as indicated by experimental log A values (11.3–11.8).[26]

Structural parameters and charges for reactants, the corresponding transition states TS, and products for the three substrates under study are given in Table 2. The TS structure for thermal elimination of 2-hydroxynitroalkanes is a six-membered ring, with the hydrogen being transferred

(H6) midway between oxygen O5 in hydroxyl moiety and oxygen O1 at the nitro group (Scheme 2, Fig. 1).

Analysis of geometrical parameters revealed that all three TS structures are quite similar. Following the reaction path from reactants to TS structures, there is an increase in O1—N2 distance; N2—C3 distance decreases indicating double bond formation, C3—C4 distance diminish demonstrating a partial double bond character. The O5—H6 distance increases showing O—H bond breaking as the oxygen in the nitro group O1 abstracts the hydrogen H6, as shown in O1—H6 bond distance, which decreases indicating bond formation. The TS structure for 2-hydroxy nitroalkanes (S1, S2, S3) shows departure from planarity (maximum deviation of 74°) in a semi-chair conformation with atoms N2—O1—H6—O5 close to a planar structure and C3 out of plane.

Imaginary frequencies characterizing the TS are −578.3, −560.3, and −654.8 cm^{-1} for 3-nitro-2-butanol, 3-nitro-2-pentanol, and 2-methyl-3-nitro-2-propanol, respectively, and are associated with hydrogen transfer reaction coordinate.

Analysis of NBO charges (Table 3) shows that the most important differences between the secondary substrates (S1, S2) and the more reactive tertiary substrate (S3) are the changes in N2—C3 and C3—C4 bond polarization. In the tertiary substrate there is an important charge separation in N2—C3 and C3—O4 that increases in the TS. Also the magnitude in C3 and C4 charges are bigger for S3. This result and the higher rate coefficient for the tertiary substrate S3 suggest that polarization of both N—C$_\alpha$ and C$_\alpha$—C$_\beta$ bonds is important in the decomposition process.

BOND ORDER ANALYSIS

To investigate the nature of the TS along the reaction pathway, the bond order calculations NBO were performed.[27–29] Wiberg bond indexes[30] were computed

S1: 3-nitro 2-butanol   S2: 3-nitro-2-pentanol   S3: 2-methyl-3-nitro 2-propanol
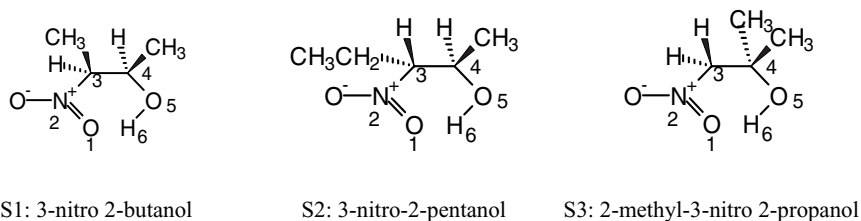
Scheme 2
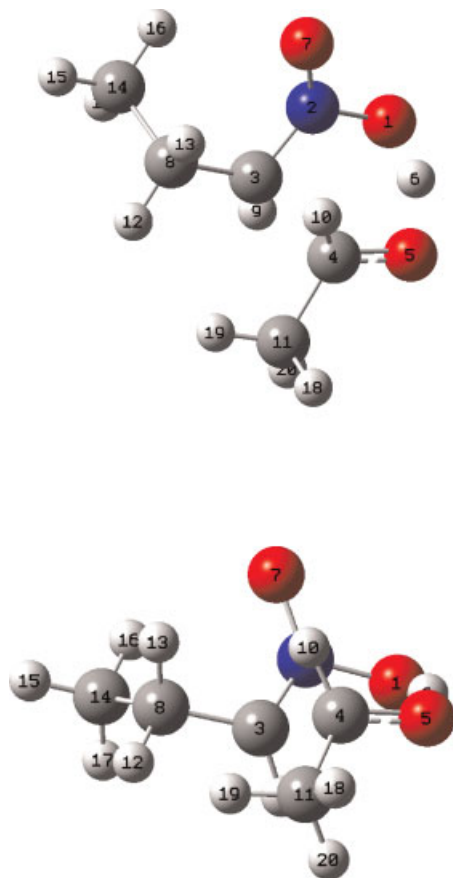
Figure 1. Two views of the TS structure for thermal decomposition of 3-nitro-2-pentanol at 280 °C are shown. A semi-chair type of structure including atoms N2, O1, H6, O5, and C4 close to a plane, while C3 is out of plane

using the natural bond orbital NBO program[31] as implemented in Gaussian 98W. Bond breaking and making process involved in the reaction mechanism can be monitored by means of the Synchronicity (Sy) concept proposed by Moyano *et al.*[32] defined by the expression:

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

n is the number of bonds directly involved in the reaction and the relative variation of the bond index is obtained from:

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

where the superscripts R, TS, P, represent reactant, transition state, and product, respectively.

The evolution in bond change is calculated as:

$$\%Ev = \delta B_i \times 100$$

The average value is calculated from:

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

Table 3. NBO charges for reactants and TS for secondary 2-hydroxynitroalkanes from MP2/6-31G* calculations at 280°C, for retro-aldol type reaction

R	S1		S2		S3	
	R	TS	R	TS	R	TS
OB_{1-}	−0.41	−0.52	−0.34	−0.51	−0.41	−0.51
NB_{2-}	0.43	0.34	0.43	0.34	0.43	0.34
CB_{3-}	−0.09	−0.13	−0.09	−0.13	−0.28	−0.34
CB_{4-}	0.06	0.34	0.06	0.34	0.24	0.53
OB_{5-}	−0.75	−0.72	−0.74	−0.72	−0.74	−0.73
HB_{6-}	0.47	0.51	0.47	0.51	0.47	0.51

Bonds indexes were calculated for those bonds involved in the reaction changes, that is: O1—H6, O5—H6, C4—O5, C3—C4, N2—C3, and N2—O1, (Scheme 2, Fig. 1), all other bond bonds remain practically unaltered during the process.

NBO analysis results are shown in Table 4. Calculated Wiberg indexes B_i for reactants, TS and products for 2-hydroxy nitroalkanes show an important progress in N 2—C3 reaction coordinate (between 58 and 82 %) with the maximum progress being that of the tertiary substrate S3. For bonds O1—H6, O5—H6 and C3—C4 the advancement in the reaction coordinate varies from 60 to 66 %, while C4—O5 double bond formation evolution is midway. Small progress is observed for N2—O1 reaction coordinate in all substrates (≈21%). Considering the average progress in all reaction coordinates δB_{ave} is intermediate between reactant and products ($\delta B_{ave} \approx 0.5$). Synchronicity parameters Sy ≈ 0.7 indicate that these reactions are concerted and polar in nature as seen in NBO charges analysis.

The above-mentioned considerations provide additional evidence for polar retro-aldol type of mechanism in the gas phase elimination of 2-hydroxy nitroalkanes where the polarization of N—C_α and C_α—C_β bonds are paramount factors.

CONCLUSIONS

The thermal elimination of 2-hydroxy nitroalkanes occurs in a retro-aldol type of mechanism with a six-membered TS structure characterized by the transference of the hydroxyl hydrogen to the nitro group to give acetaldehyde and the corresponding nitroalkane for the secondary substrates and acetone and nitromethane for the tertiary substrate. Theoretical calculations suggest that the reaction proceeds in a concerted asynchronous mechanism. Activation parameters are in reasonable agreement with experimental values for MP2/6-31G* level of theory. The rate coefficients suggest that alkyl substitution on C_β favors the decomposition by stabilizing the partial positive charge

Table 4. NBO analysis for secondary 2-hydroxynitroalkanes from MP2/6-31G* calculations at 280°C for retro-aldol type reaction. Wiberg bond indexes (B_i), % evolution through the reaction coordinate (%Ev), average bond index variation (δB_{ave}) and Synchronicity parameter (Sy) are shown

Substrate		O1–H6	O5–H6	C4–O5	C3–C4	N2–C3	N2–O1	(B_{ave}	Sy
S1	B_i^R	0.0315	0.7345	0.9304	0.9804	0.8456	1.4507	0.476	0.704
	B_i^{TS}	0.4727	0.2548	1.3560	0.3930	1.2464	1.0221		
	B_i^P	0.7526	0.0102	1.8097	0.0098	1.3986	0.8946		
	%Ev	61.18	66.23	48.20	60.52	72.48	22.93		
S2	B_i^R	0.0011	0.7298	0.9418	0.9797	0.8506	1.5312	0.479	0.712
	B_i^{TS}	0.4692	0.2556	1.3627	0.3877	1.2559	1.0334		
	B_i^P	0.7078	0.0382	1.7608	0.0501	1.5464	0.9015		
	%Ev	66.23	68.57	51.39	63.68	58.25	20.94		
S3	B_i^R	0.0393	0.7276	0.9302	0.9799	0.8690	1.4380	0.496	0.708
	B_i^{TS}	0.4588	0.2657	1.3366	0.3817	1.2853	1.0357		
	B_i^P	0.7167	0.0115	1.7822	0.0106	1.3716	0.9287		
	%Ev	61.93	64.50	47.70	61.71	82.83	21.01		

in the TS. Calculated first order rate coefficients show the same tendency observed for experimental counterparts. The TS structure is a semi-chair six-membered structure in which the hydrogen being transferred, the alcohol oxygen, C_β, and the nitrogen of the nitro moiety are close to a plane and C_α is out of plane. The elimination occurs in an asynchronic fashion as suggested by synchronicity values ($Sy \approx 0.7$). NBO analysis suggests that the polarization of N—C_α and C_α—C_β bonds are important factors in the decomposition process.

REFERENCES

1. Smith GG, Yates BL. *J. Chem. Soc*. 1965; 7242–7246.
2. Arnold RT, Smolinsky G. *J. Am. Chem. Soc*. 1959; **81**: 6443–6445.
3. Smith GG, Taylor R. *Chem. Ind*. 1961; 949–950.
4. August R, McEwen I, Taylor R. *J. Chem. Soc. Perkin Trans*. 1987; **2**: 1683–1689.
5. Failes RL, Shapiro JS, Stimson VR. *The Chemistry of Hydroxy Group*. Patai S (ed.). Wiley: Chichester, 1980; 449–468.
6. Quijano J, David J, Sanchez C, Rincon E, Guerra D, Leon LA, Notario R, Abboud JL. *J. Mol. Struct. Theochem*. 2002; **580**: 201–2057.
7. Viola A, MacMilan JH, Proverb RJ, Yates BL. *J. Am. Chem. Soc*. 1971; **93**: 6967–6974.
8. Quijano J, Sanchez C, David J, Leon LA, Notario R, Abboud JL. *J. Mol. Struct. Theochem*. 2001; **572**: 135–139.
9. Quijano J, Rodriguez M, Yepes M, del S, Gallego LH. *Tetrahedron Lett*. 1987; **28**: 3555–3558.
10. Yates BL, Quijano J. *J. Org. Chem*. 1970; **35**: 1239–1240.
11. Yates BL, Ramirez A, Velazquez O. *J. Org. Chem*. 1961; **36**: 3579–3582.
12. Quijano J, Restrepo I, Gallego LH, Yepes M. del S. *Tetrahedron Lett*. 1994; **35**: 4735–4738.
13. Dominguez RM, Chuchani G, Quijano J, Orozco LJ, Restrepo I. *React. Kinet. Catal. Lett*. 1996; **57**: 191–196.
14. Smith GG, Yates BL. *J. Org. Chem*. 1965; **30**: 2067.
15. Yates BL, Quijano J. *J. Org. Chem*. 1969; **34**: 2506–2508.
16. Rotinov A, Chuchani G, Machado R, Rivas C, Quijano J, Yepes M, del S, Restrepo I. *Int. J. Chem. Kinet*. 1992; **24**: 909–915.
17. Feng W, Wang Y, Zhang S. *Int. J. Quantum Chem*. 1997; **62**: 297–3027.
18. Chuchani G, Dominguez RM, Rotinov A, Quijano J, Valencia C, Vicente B, Franco D. *J. Phy. Org. Chem*. 1999; **12**: 19–23.
19. Chuchani G, Rotinov A, Domínguez RM. *Int. J. Chem. Kinet*. 1999; **31**: 401–407.
20. Dominguez RM, Herize A, Rotinov A, Alvarez-Auslar A, Visbal G, Chuchani G. *J. Phy. Org. Chem*. 2004; **17**: 399–408.
21. Gaussian 98, Revision A.3, Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople J. Gaussian, Inc.: Pittsburgh, PA, 1998.
22. McQuarrie D. *Statistical Mechanics*. Harper & Row: New York, 1986.
23. Foresman JB, Frish Æ, *Exploring Chemistry with Electronic Methods* (2nd edn), Gaussian, Inc: Pittsburg, PA, 1996.
24. Benson SW. *The Foundations of Chemical Kinetics*. McGraw-Hill: New York, 1960.
25. Rotinov A, Dominguez RM, Córdova T, Chuchani G. *J. Phys. Org. Chem*. 2005; **18**: 616–624.
26. (a) O'Neal HE, Benson SW. *J. Phys. Chem*. 1967; **71**: 2903–2921; (b) Benson SB. *Thermochemical Kinetics*. John Wiley & Sons: New York, 1968.
27. Lendvay G. *J. Phys. Chem*. 1989; **93**: 4422–4429.
28. Reed AE, Weinstock RB, Weinhold F. *J. Chem. Phys*. 1985; **83**(2): 735–746.
29. Reed AE, Curtiss LA, Weinhold F. *Chem. Rev*. 1988; **88**: 899–926.
30. Wiberg KB. *Tetrahedron* 1968; **24**: 1083–1095.
31. Gaussian NBO version 3.1.
32. Moyano A, Periclas MA, Valenti E. *J. Org. Chem*. 1989; **54**: 573–582.