

Density Functional Theory and *Ab Initio* Study on the Reaction Mechanism of the Gas-Phase Thermal Elimination Kinetics of Oxetan-2-one and 4-Methyl-oxetan-2-one

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Abstract- The mechanism of the thermal decomposition of oxetan-2-one (β -propiolactone) and 4-methyl-oxetan-2-one (β -butyrolactone) in the gas-phase has been revisited through the electronic structure calculations using B3LYP, B3PW91, MPW1PW91, PBEPBE, PBE1PBE, CAMB3LYP, and MP2, with basis sets 6-31G(d), 6-31G(d,p), 6-31++G(d,p), 6-311G(d,p), 6-311++G(d,p). The authors found better agreement between experimental and calculated parameters when using MWP1PW91 functional. The B3LYP functional gave lower energies of activation with errors over 15 kJ/mol for oxetan-2-one and 4-methyl-oxetan-2-one. The reactions are unimolecular and proceed through a concerted-polar four-centered transition states. The presence of a methyl group in 4-methyl-oxetan-2-one lowers significantly the energy of activation, facilitating the thermal decomposition by stabilizing the transition state. The polarization of the $\text{RHC}^{\delta+}-\text{O}^{\delta-}$ ($\text{R} = \text{H}$ or CH_3) was rate determining for these reactions. The predominant advance of the $\text{RHC}^{\delta+}-\text{O}^{\delta-}$ bond breaking in the transition state, confers intimate ion pair character. The reactions are described as unimolecular concerted non-synchronous process.

Keywords- *Ab Initio* and DFT Calculations; Thermal Decomposition; Oxetan-2-one; 4-Methyl-oxetan-2-one; Mechanism

I. INTRODUCTION

James and Wellington [1] were the firsts to carry out the kinetics of the gas-phase thermal decomposition of oxetan-2-one (β -propiolactone). The products of the reaction were ethylene and CO_2 . The process was found to be first-order and the given Arrhenius expression was $\log k = 16.07 - 191.6 \text{ kJ mol}^{-1} (2.303RT)^{-1}$. The reaction was molecular in nature, since the free-radical suppressor nitric oxide had no effect on rates. However, the authors did not examine the surface effect on the reaction glass vessel in order to establish the homogeneity of this reaction. Around fourteen years later, Frey et.al. [2, 3], in aged Pyrex reaction vessel, reported the decomposition of oxetan-2-one (β -propiolactone) and 4-methyl-oxetan-2-one (β -butyrolactone) to be homogeneous, unimolecular and to follow a first-order rate law. The Arrhenius equations were: for β -propiolactone, $\log k = (14.86 \pm 0.30) - (180.46 \pm 3.2) (2.303RT)^{-1}$, and for β -butyrolactone, $\log k = (14.39 \pm 0.10) - (163.4 \pm 1.0) (2.303RT)^{-1}$. From the results obtained in these works [2, 3], it is suggested that a biradical intermediate or a biradical-like activated complex of a four-membered strained ring system with low A factor and relatively low energy of activation may be ruled out. A concerted decomposition via an activated complex with zwitterionic character was proposed. Along this line of work, the heavy atom kinetic isotope effects in the gas-phase pyrolysis of β -propiolactone were carried out in a static system [4]. The products formed are ethylene and CO_2 . The Arrhenius expression of this reaction: $\log k = (12.32) - (154.2) (2.303RT)^{-1}$. The transition state was thought to be complex, where the C breaking bond adjacent to the $\text{C} = \text{O}$ appears to be the determining step for decomposition. An *ab initio* SCF MO calculation for ring cleavage of β -propiolactone [5] as depicted in reactions (1) and (2) reached the conclusion, from the activation barrier results, that the decomposition process mainly proceed through reaction (1) in agreement with experimental observations.



An interesting theoretical study of the thermal decarboxylation of a series of 2-oxetanones (β -lactones) has been performed by Moyano et al. [6]. They concluded from the semiempirical SCF MO methods AM1, MNDO, and MNDO/3 at the RHF that the thermal elimination of oxetan-2-one (β -propiolactone) is a concerted non-synchronous process which proceeds through a planar transition state with high zwitterionic character. An additional work of the thermal elimination of oxetan-2-ones (β -propiolactones) to yield the corresponding alkene and CO_2 has been carried out by using *ab initio* SCF-MO computational methods [7]. The decarboxylation reactions were thought to be concerted, and the saddle points connecting reactant and

products have non-Woodward-Hoffmann topologies [7]. The reaction mechanisms for the thermal elimination of β -propiolactone and β -butyrolactone was characterized by using B3LYP, MP2 and QCISD(T) level of theories [8]. In this sense, the activation enthalpy $\Delta H^\ddagger$ calculated from the more diffuse basis of MP2 and QCISD(T) methods appears to be in reasonable agreement with the experimental values obtained by Frey et al. [2, 3]. The reactions were described as a concerted non-synchronous process, where C – O bond breaking appears to be the rate-determining step. Lim et al. [9] have also examined the theoretical calculation of the thermal decarboxylation of oxetan-2-one (β -propiolactone). However, they only limited to estimate the decomposition process at B3LYP/6-31G(d,p) level of theory where the activation parameters are rather low with respect to the experimental values. They also suggested the process to be concerted non-synchronous pathway, where the C – O bond breaking is the limiting factor.

From the theoretical considerations described above, the authors believe that the work of Safont et al. [8] seems to suggest a rational mechanism of the oxetanones decomposition by the use MP2/6-31++G(d,p) calculation level, and QCISD(T)/6-31++G(d,p)//MP2/6-31++G(d,p) approaches. A good agreement between theoretical and experimental values was obtained. The C – O bond-breaking appears to be more advanced in the TS, consequently is the rate-determining step for the decarboxylation process.

Unfortunately, the B3LYP, a DFT level of theory, was the only method used in theoretical calculations of these oxetanones. The B3LYP functional has been reported inadequate to treat a number of organic reactions [9]. These results need to be examined and contrasted with experimental results with different theory levels. In this work, the authors investigate the reaction mechanism in the thermal elimination of oxetan-2-one (β -propiolactone) and 4-methyl-oxetan-2-one (β -butyrolactone) in the gas-phase by using an ample level of theories, thus, B3LYP, B3PW91, MPW1PW91, PBEPBE, PBE1PBE, CAMB3LYP, and in addition the *ab initio* MP2 quantum chemical calculations. The estimation of the kinetic and thermodynamic parameters in the elucidation of these reactions mechanisms was followed according to previous reported in theoretical calculations [10-13].

II. COMPUTATIONAL METHODS AND MODELS

The thermal elimination reaction of oxetan-2-one (β -propiolactone) and 4-methyl-oxetan-2-one (β -butyrolactone) was studied using electronic structure methods to gain more insight on the kinetics and mechanisms. Methods used included B3LYP, B3PW91, MPW1PW91, PBEPBE, PBE1PBE, CAMB3LYP, and MP2, with basis sets 6-31G(d), 6-31G(d,p), 6-31++G(d,p), 6-311G(d,p), 6-311++G(d,p), implemented in Gaussian 09 [14]. In all calculations the authors have used the default parameters, e.g., Berny analytical gradient optimization routines with convergence on the density matrix was 10^{-9} atomic units, threshold value for maximum displacement 0.0018 Å, and maximum force was 0.00045 Hartree/Bohr. Transition state structures (TS) were obtained using the Quadratic Synchronous Transit (QST) method. The identification of the TS structures was obtained through the normal-mode analysis by having a single imaginary frequency and the corresponding transition vector (TV). The authors verified the transition state structures associating the reactant and products in the minimum energy path by means of Intrinsic Reaction Coordinate (IRC) calculations. Thermodynamic values of zero-point vibrational energy (ZPVE), temperature corrections (E(T)) and absolute entropies (S(T)), assuming ideal gas behavior from the harmonic frequencies and moments of inertia by standard methods [15] at average temperature and pressure values within the experimental range. Scaling factors for frequencies and zero point energies were cited from the literature [16, 17].

First order rate coefficient k was calculated using the transition state theory TST [18] assuming that the transmission coefficient is equal to 1 as expressed in the following Eq. (1):

$$k = (k_B T/h) \exp(-\Delta G^\ddagger/RT) \quad (1)$$

where $\Delta G^\ddagger$ is the Gibbs free energy change between the reactant and the transition state, k_B , h are the Boltzmann and Planck constants, respectively. $\Delta G^\ddagger$ was calculated using the following relations [Eqs. (2) and (3)]:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (2)$$

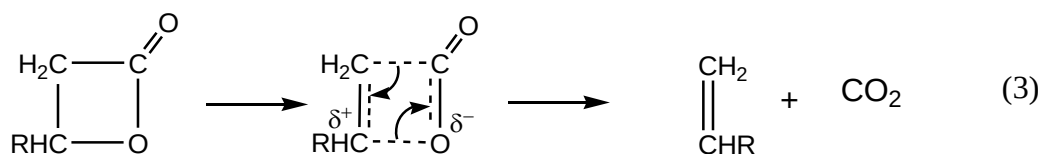
$$\text{and} \quad \Delta H^\ddagger = V^\ddagger + \Delta ZPVE + \Delta E(T) \quad (3)$$

$V^\ddagger$ 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.

III. RESULTS AND DISCUSSIONS

A. Kinetic and Thermodynamic Parameters

The proposed mechanism for thermal decomposition of oxetan-2-one (β -propiolactone) and 4-methyl-oxetan-2-one (β -butyrolactone) is shown in reaction (3), where the R group is hydrogen or methyl, respectively.



Calculated parameters for oxetan-2-one and 4-methyl-oxetan-2-one elimination reactions are reported in Tables 1 and 2, respectively. When comparing the estimated parameters with experimental values, for oxetan-2-one, best results were obtained when using MPW1PW91/6-31G(d), MPW1PW91/6-31G(d,p), PBE1PBE /6-31G(d), PBE1PBE /6-31G(d,p) methods. Diffuse functions did not improve the results with these methods.

B3LYP results with all basis sets employed in this study resulted in lower enthalpy of activation and energy of activation – over 17 kJ/mol –, when compared to the experimental values. The long range correlated method CAMB3LYP /6-31G(d,p) gave enthalpy of activation and energy of activation about 7 kJ/mol higher than experimental; calculated parameters improved with CAMB3LYP /6-31G++(d,p), however, increasing the basis set size resulted in lower experimental parameters. Perturbation methods MP2 results are comparable with CAMB3LYP.

Analysis of calculated parameters versus experimental for 4-methyl-oxetan-2-one, gave similar conclusions regarding the methods used. Best calculated parameters were obtained when using MPW1PW91/6-31G(d), MPW1PW91/6-31G(d,p). As observed for oxetan-2-one, the B3LYP functional gave very low calculated parameters; over 15 kJ/mol when compared to experimental. For all methods used the entropy of activation was underestimated, due to the contribution of low frequency modes and the use of the harmonic approximation.

The presence of the methyl group substituent reduces the energy of activation in - 17 kJ/mol-, which is consistent with the proposed transition state, in reaction (3). The effect of this substitution is further discussed in the following section reporting geometrical parameters, NBO charges and bond orders at MPW1PW91/6-31G-(d,p) level of theory. Reaction profiles are shown in Figs. 1 and 2, for oxetan-2-one and 4-methyl-oxetan-2-one, respectively.

TABLE 1 MECHANISM A, THERMODYNAMIC AND ARRHENIUS PARAMETERS CALCULATED FOR GAS-PHASE DECOMPOSITION OF OXETAN-2-ONE AT 260.0 °C (533,15 K)

Method	Ea (kJ/mol)	log A (s ⁻¹)	ΔH [*] (kJ/mol)	ΔS [*] (J/molK)	ΔG [*] (kJ/mol)
Experimental	180.46	14.86	176.0	26.5	161.9
B3LYP /6-31G(d)	163.2	13.82	158.8	6.45	155.3
B3LYP /6-31G(d,p)	162.3	13.82	157.9	6.43	154.4
B3LYP /6-31G++(d,p)	156.4	13.83	152.0	6.75	148.4
B3LYP /6-311G(d,p)	151.5	13.77	147.1	5.46	144.2
B3LYP /6-311G++(d,p)	149.4	13.79	144.9	5.85	141.8
B3PW91/6-31G(d)	173.1	13.84	168.7	6.83	165.1
B3PW91/6-31G(d,p)	172.3	13.84	167.8	6.82	164.2
B3PW91/6-31G++(d,p)	168.0	13.85	163.5	7.16	159.7
B3PW91/6-311G(d,p)	163.0	13.79	158.5	5.87	155.4
B3PW91/6-311G++(d,p)	161.4	13.81	157.0	6.26	153.7
MPW1PW91/6-31G(d)	180.6	13.84	176.2	6.94	172.5
MPW1PW91/6-31G(d,p)	179.7	13.84	175.3	6.91	171.6
MPW1PW91/6-31G++(d,p)	175.2	13.86	170.8	7.27	166.9
MPW1PW91/6-311G(d,p)	170.8	13.79	166.3	6.02	163.1
MPW1PW91/6-311G++(d,p)	168.9	13.81	164.5	6.39	161.1
PBEPBE /6-31G(d)	148.4	13.83	144.0	6.78	140.4
PBEPBE /6-31G(d,p)	147.5	13.83	143.1	6.79	139.5
PBEPBE /6-31G++(d,p)	143.0	13.85	138.6	7.10	134.8
PBEPBE /6-311G(d,p)	138.2	13.78	133.8	5.81	130.7
PBEPBE /6-311G++(d,p)	137.0	13.81	132.6	6.29	129.2
PBE1PBE /6-31G(d)	182.2	13.85	177.8	7.06	174.0
PBE1PBE /6-31G(d,p)	181.4	13.85	176.9	7.05	173.2
PBE1PBE /6-31G++(d,p)	176.7	13.86	172.2	7.37	168.3
PBE1PBE /6-311G(d,p)	172.5	13.80	168.0	6.12	164.8
PBE1PBE /6-311G++(d,p)	170.9	13.82	166.5	6.54	163.0
CAMB3LYP /6-31G(d)	188.4	13.84	183.9	6.95	180.2
CAMB3LYP /6-31G(d,p)	187.5	13.84	183.0	6.88	179.4
CAMB3LYP /6-31G++(d,p)	181.3	13.86	176.9	7.31	173.0
CAMB3LYP /6-311G(d,p)	175.6	13.79	171.2	5.86	168.1

CAMB3LYP /6-311G++(d,p)	173.7	13.65	167.6	3.25	165.9
MP2/6-31G(d)	186.5	13.80	182.0	6.15	178.8
MP2/6-31G(d,p)	186.8	13.80	182.3	6.14	179.1
MP2/6-31G++(d,p)	178.4	13.85	174.0	6.99	170.2
MP2/6-311G(d,p)	178.6	13.72	174.1	4.52	171.7
MP2/6-311G++(d,p)	174.7	13.74	170.2	5.06	167.5

TABLE 2 THERMODYNAMIC AND ARRHENIUS PARAMETERS CALCULATED FOR GAS-PHASE DECOMPOSITION OF 4-METHYL-OXETAN-2-ONE AT 260.0 °C (533.15 K)

Method	Ea (kJ/mol)	log A (s ⁻¹)	ΔH‡ (kJ/mol)	ΔS‡ (J/molK)	ΔG‡ (kJ/mol)
Experimental	163.40	14.39	159.0	17.5	149.7
B3LYP /6-31G(d)	148.4	13.89	144.0	7.78	139.9
B3LYP /6-31G(d,p)	147.7	13.89	143.2	7.88	139.0
B3LYP /6-31G++(d,p)	140.4	13.94	136.0	8.82	131.3
B3LYP /6-311G(d,p)	136.9	13.83	132.5	6.67	128.9
B3LYP /6-311G++(d,p)	127.2	14.05	122.8	10.97	116.9
B3PW91/6-31G(d)	158.1	13.91	153.6	8.29	149.2
B3PW91/6-31G(d,p)	157.3	13.91	152.8	8.18	148.5
B3PW91/6-31G++(d,p)	151.6	13.97	147.2	9.37	142.2
B3PW91/6-311G(d,p)	147.6	13.85	143.2	7.02	139.4
B3PW91/6-311G++(d,p)	145.1	13.90	140.6	8.00	136.4
MPW1PW91/6-31G(d)	165.4	13.91	160.9	8.27	156.5
MPW1PW91/6-31G(d,p)	164.5	13.92	160.1	8.40	155.6
MPW1PW91/6-31G++(d,p)	158.7	13.97	154.3	9.34	149.3
MPW1PW91/6-311G(d,p)	155.2	13.85	150.8	7.01	147.0
MPW1PW91/6-311G++(d,p)	152.4	13.90	148.0	8.03	143.7
PBEPBE /6-31G(d)	134.2	13.92	129.8	8.37	125.3
PBEPBE /6-31G(d,p)	133.5	13.93	129.0	8.61	124.4
PBEPBE /6-31G++(d,p)	127.6	13.98	123.1	9.53	118.1
PBEPBE /6-311G(d,p)	123.9	13.85	119.4	7.10	115.7
PBEPBE /6-311G++(d,p)	121.4	13.91	117.0	8.14	112.6
PBE1PBE /6-31G(d)	167.0	13.92	162.6	8.47	158.1
PBE1PBE /6-31G(d,p)	166.2	13.93	161.8	8.61	157.2
PBE1PBE /6-31G++(d,p)	160.3	13.98	155.9	9.59	150.8
PBE1PBE /6-311G(d,p)	157.0	13.85	152.6	7.17	148.8
PBE1PBE /6-311G++(d,p)	154.5	13.91	150.0	8.17	145.7
CAMB3LYP /6-31G(d)	174.1	13.91	169.7	8.16	165.3
CAMB3LYP /6-31G(d,p)	173.3	13.91	168.9	8.29	164.4
CAMB3LYP /6-31G++(d,p)	165.7	13.98	161.3	9.52	156.2
CAMB3LYP /6-311G(d,p)	161.3	13.83	156.9	6.76	153.3
CAMB3LYP /6-311G++(d,p)	158.2	13.73	152.1	4.85	149.5
MP2/6-31G(d)	177.6	13.78	173.1	5.79	170.0
MP2/6-31G(d,p)	178.3	13.78	173.8	5.77	170.8
MP2/6-31G++(d,p)	169.9	13.85	165.4	7.06	161.7
MP2/6-311G(d,p)	170.7	13.69	166.2	3.99	164.1
MP2/6-311G++(d,p)	166.3	13.73	161.8	4.88	159.2

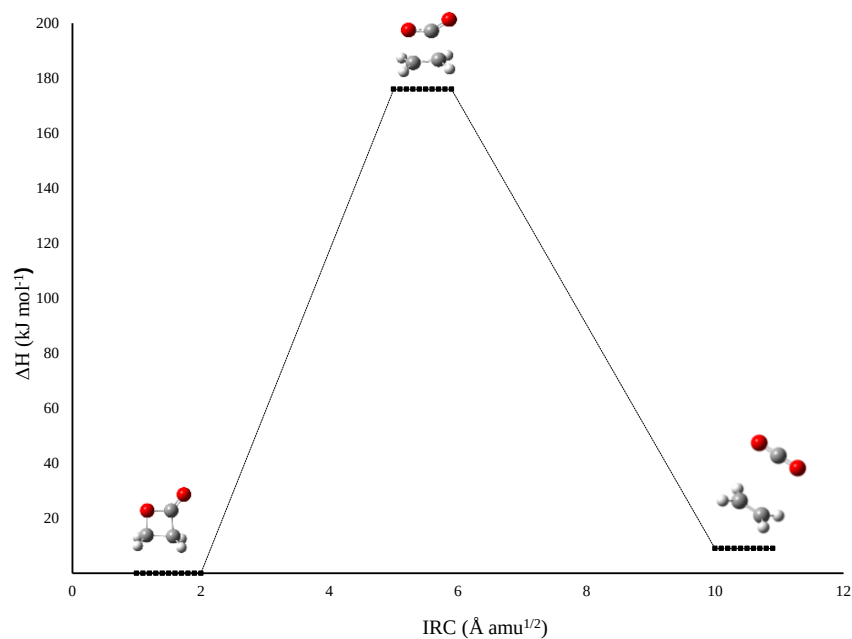


Fig. 1 Reaction profile for the thermal decomposition of oxetan-2-one at the MPW1PW91/6-31G(d,p) level of theory

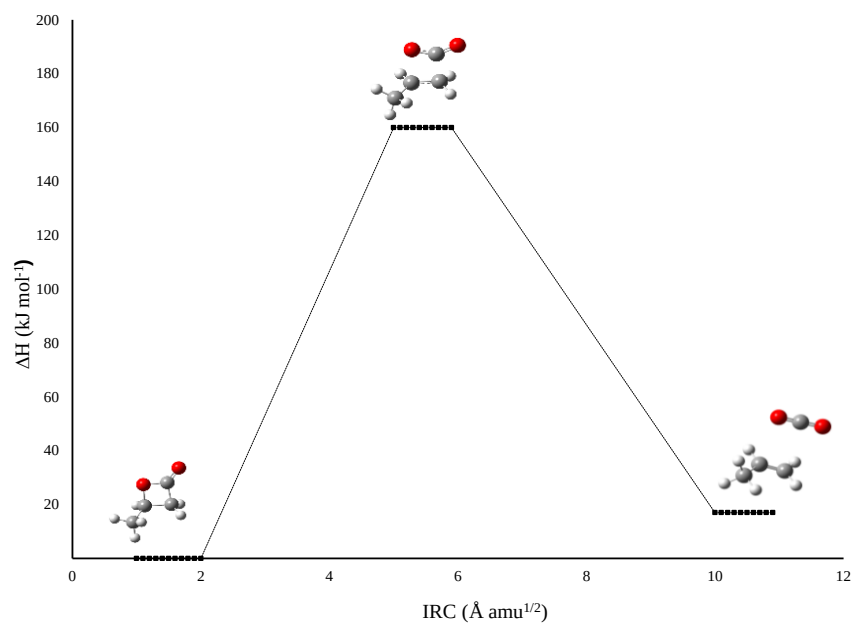
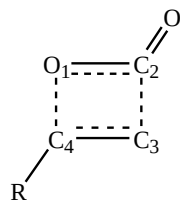


Fig. 2 Reaction profile for the thermal decomposition of 4-methyl-oxetan-2-one at the MPW1PW91/6-31G(d,p) level of theory

B. Transition State and Mechanism

The structures of reactant, TS and products of oxetan-2-one (β -propiolactone) and 4-methyl-oxetan-2-one (β -butyrolactone) in the gas phase elimination, optimized at MPW1PW91/6-31G(d,p) level of theory are shown in Figs. 3 and 4, respectively. Geometrical parameters are presented in Table 3. Atoms numbers are shown in Scheme 1.



R = H, CH₃

Scheme 1

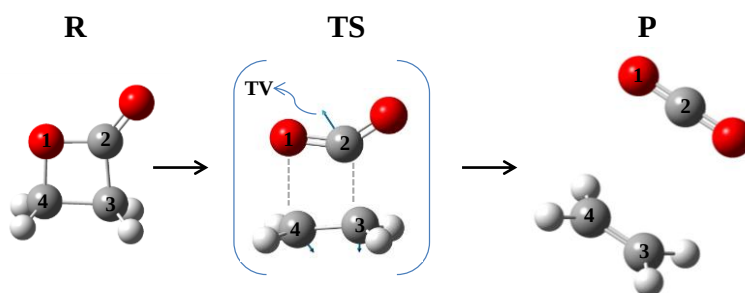


Fig. 3 Optimized structures for reactant, R, transition state, TS, and Products, P, in the gas phase elimination reaction of oxetan-2-one at MPW1PW91/6-31G(d,p) level of theory

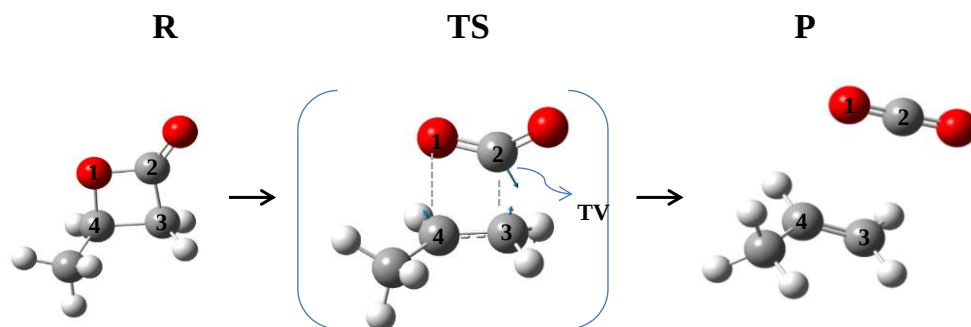


Fig. 4 Optimized structures for reactant, R, transition state, TS, and Products, P, in gas phase elimination reaction of 4-methyl-oxetan-2-one at MPW1PW91/6-31G(d,p) level of theory

TABLE 3 STRUCTURAL PARAMETERS OF REACTANT, R, TRANSITION STATE, TS, AND PRODUCTS, P, FOR GAS-PHASE DECOMPOSITION OF OXETAN-2-ONE AND 4-METHYL-OXETAN-2-ONE AT MPW1PW91/6-31G(D,P) LEVEL OF THEORY

oxetan-2-one				
Interatomic Lengths (Å)				
	O ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₄ -O ₁
R	1.36727	1.52188	1.52879	1.45645
TS	1.24468	1.84438	1.39458	2.06023
P	1.16481	3.44655	1.32863	3.85376
Dihedral angles (degrees)				
	O ₁ -C ₂ -C ₃ -C ₄	C ₂ -C ₃ -C ₄ -O ₁	C ₃ -C ₄ -O ₁ -C ₂	C ₄ -O ₁ -C ₂ -C ₃
TS	-0.38650	0.22425	-0.33661	0.26502
Imaginary frequency (cm ⁻¹)				
-884.65				
4-methyl-oxetan-2-one				
Interatomic Lengths (Å)				
	O ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₄ -O ₁
R	1.36482	1.51963	1.53343	1.46741
TS	1.24441	1.79347	1.40353	2.13639
P	1.16531	3.42933	1.33158	3.40605
Dihedral angles (degrees)				
	O ₁ -C ₂ -C ₃ -C ₄	C ₂ -C ₃ -C ₄ -O ₁	C ₃ -C ₄ -O ₁ -C ₂	C ₄ -O ₁ -C ₂ -C ₃
TS	-1.65097	0.91795	-1.35138	1.10779
Imaginary frequency (cm ⁻¹)				
-810.77				

The most significant change in atom distances is the elongation of C₄-O₁ bond, from 1.46 Å to 2.06 Å and 2.13 Å, for oxetan-2-one and 4-methyl-oxetan-2-one, respectively. This result indicates that this bond is significantly broken as an ion-pair nature in the TS. The elongation of C₄-O₁ bond is greater for 4-methyl-oxetan-2-one, due to the presence of a methyl group substituent at C₄. The C₂-C₃ is also stretched in the TS, to form carbon dioxide, while O₁-C₂ and C₃-C₄ is shortened, indicating the formation of double bonds in the products formation.

C. NBO Changes

Electron distribution changes are illustrated by atomic NBO charges, in the reactant, TS and products, for the elimination reactions of oxetan-2-one and 4-methyl-oxetan-2-one. NBO charges are shown in Table 4. The authors observe an important difference in the charge at C₄ when comparing the two substrates, due to the methyl group substitution. For both oxetan-2-one and 4-methyl-oxetan-2-one there is an increase in electron density at O₁ in the TS, while carbon C₂ becomes more positive in TS. The charges at C₃ are similar for both compounds.

TABLE 4 NBO CHARGES FOR (R) REACTANT, TRANSITION STATE (TS), AND PRODUCTS (P) FOR DECOMPOSITION OF OXETAN-2-ONE AND 4-METHYL-OXETAN-2-ONE AT MPW1PW91/6-31G(D,P) THEORETICAL LEVEL

oxetan-2-one				
	O ₁	C ₂	C ₃	C ₄
R	-0.544	0.832	-0.626	-0.129
TS	-0.647	0.939	-0.699	-0.149
P	-0.519	1.037	-0.456	-0.456
4-methyl-oxetan-2-one				
	O ₁	C ₂	C ₃	C ₄
R	-0.552	0.832	-0.618	0.077
TS	-0.670	0.919	-0.689	0.082
P	-0.523	1.038	-0.474	-0.226

D. Bond Order Analysis

NBO bond orders were used to study the reaction progress along the reaction coordinate for the proposed mechanism [19-21]. Bond orders were estimated with Wiberg bond indexes [22]. They were estimated using the natural bond orbital NBO program implemented in Gaussian 09 [14]. These indexes allow estimating bond orders from population analysis. Bond breaking and making processes involved in the reaction mechanism are followed using the Synchronicity (Sy) concept proposed by Moyano et al. [6] as defined by the expression:

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

The number of bonds directly involved in the reaction is “n”.

The calculated bond index is B_i , and the relative variation of the bond index is obtained from:

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

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

The average value is calculated from:

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

The four bonds involved in the elimination reaction of oxetan-2-one and 4-methyl-oxetan-2-one were followed using Wiberg indexes B_i : O₁-C₂, C₂-C₃, C₃-C₄, and C₄-O₁, values are ported in Table 5.

TABLE 5 WIBERG BOND INDEX OF REACTANT (R), TRANSITION STATE (TS) AND PRODUCTS (P) FOR DECOMPOSITION OF OXETAN-2-ONE AND 4-METHYL-OXETAN-2-ONE AT MPW1PW91/6-31G(D,P) LEVEL OF THEORY

oxetan-2-one					
Bond	O ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₄ -O ₁	S _y
B_i^R	1.0057	0.9646	1.0102	0.8741	0.86
B_i^{TS}	1.4441	0.4933	1.3576	0.2403	
B_i^P	1.8846	0.0025	2.0344	0.0026	
%E _v	49.9	49.0	33.9	72.7	
4-methyl-oxetan-2-one					
Bond	O ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₄ -O ₁	S _y
B_i^R	1.0107	0.9651	0.9931	0.8492	0.83
B_i^{TS}	1.4519	0.5450	1.3050	0.1939	
B_i^P	1.8800	0.0028	1.9725	0.0009	
%E _v	50.8	43.7	31.9	77.3	

The bond orders O_1-C_2 and C_3-C_4 of oxetan-2-one and 4-methyl-oxetan-2-one change from single to double. The former O_1-C_2 is more advanced in the reaction coordinate at around 50 %. Breaking the C_2-C_3 bond shows more progress in the TS for oxetan-2-one (49 %) compared to 4-methyl-oxetan-2-one (44 %). The reaction is dominated by the breaking C_4-O_1 bond for both compounds. The advanced breaking of C_4-O_1 confers the TS an ion pair character. The process can be described as concerted non-synchronous mechanism. This is more evident in the case of 4-methyl-oxetan-2-one, as seen in the S_y parameter.

IV. CONCLUSIONS

The present work reports theoretical calculations using a number of electronic structure methods, including several DFT functionals, to describe the elimination mechanism of oxetan-2-one and 4-methyl-oxetan-2-one. As reported previously for other reaction types [9] the B3LYP method underestimated the calculated thermodynamic parameters when compared with the experimental values. The best agreement between experimental and calculated values was obtained when using MPW1PW91/6-31G(d,p) level of theory. The reactions can be described as unimolecular concerted non-synchronous processes, and the rate determining factor is the elongation of the C-O bond leading to the formation of carbon dioxide. The transition state TS is polar conferring the structure ion pair character. The 4-methyl substitution in 4-methyl-oxetan-2-one favors the reaction, lowering the activation energy by stabilization of the transition state.

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