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Theoretical Study of the Thermolysis Reaction of β -Hydroxynitriles in the Gas Phase

EDUARDO CHAMORRO,^{1*} JAIRO QUIJANO,² RAFAEL NOTARIO,³ CLAUDIA SÁNCHEZ,² LUIS A. LEÓN,² GABRIEL CHUCHANI⁴

¹*Departamento de Física, Facultad de Ciencias, Universidad de Chile, Santiago, Chile*

²*Laboratorio de Fisicoquímica Orgánica, Escuela de Química, Universidad Nacional de Colombia, Sede Medellín, Apartado Aéreo 3840, Medellín, Colombia*

³*Instituto de Química Física "Rocasolano," C.S.I.C., Serrano 119, 28006 Madrid, Spain*

⁴*Centro de Química, Instituto Venezolano de Investigaciones Científicas (I.V.I.C.), Caracas, Venezuela*

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ABSTRACT: The gas-phase thermal decomposition of 3-hydroxypropionitrile, 3-hydroxybutyronitrile, and 3-hydroxy-3-methylbutyronitrile has been studied at the MP2/6-31G(d) level of theory at 683.15 K and 0.06 atm. Results based both in energy and structure data seem to indicate a favorable route of decomposition via a six-membered cyclic transition state (similar to those suggested for thermal decomposition of other related compounds, such as β -hydroxyketones, β -hydroxyalkenes, and β -hydroxyalkynes) rather than a four-membered cyclic transition state or even a quasiheterolytic pathway. © 2002 Wiley Periodicals, Inc. *Int J Quantum Chem* 91: 618–625, 2003

Key words: transition-state structures; ab initio computational methods; thermolysis reactions; β -hydroxynitriles; reaction mechanisms

Introduction

It has been recently reported [1] that β -hydroxynitriles decompose thermally to give a mixture of aldehydes or ketones and nitriles as

Correspondence to: E. Chamorro; E-mail: echamorro@abello.unab.cl

*Current address: Departamento de Química, Facultad de Ecología y Recursos Naturales, Universidad Nacional Andrés Bello (UNAB), Avenida República 217.

depicted in Figure 1. This reaction seems to be similar to that thought to be involved in related thermal decompositions such as for β -hydroxyketones [2–6], β -hydroxyolefins [7–10], β -hydroxyesters [4, 11–14], and β -hydroxyalkynes [15–18]. In these reactions, calculated activation energies ($E_a \approx 150$ – 180 kJ mol^{-1}) and activation entropies ($\Delta S^\ddagger \approx -19$ to $-60 \text{ J mol}^{-1} \text{ K}^{-1}$) have been used in support of reaction mechanisms via a six-membered cyclic transition state (Fig. 1) [19, 20].

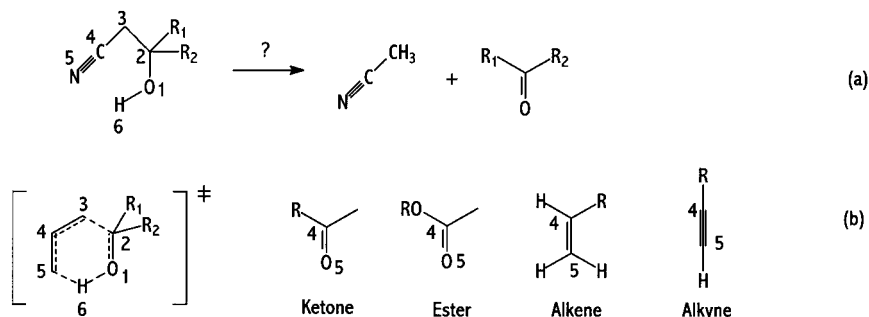


FIGURE 1. (a) Schematic representation for thermal decomposition of β -hydroxynitriles in the gas phase. (b) Six-membered cyclic transition structure currently accepted for thermal decomposition of related β -hydroxy compounds (ketones, esters, alkenes, and alkynes).

Over the temperature range 360–450°C and pressure range 47–167 torr, reaction decompositions of β -hydroxynitriles have been found to be homogenous and to follow a first-order law. The rate coefficients for 3-hydroxypropionitrile (1), 3-hydroxybutyronitrile (2), and 3-hydroxy-3-methylbutyronitrile (3) are given by the following Arrhenius equations: $\log k_1 = (14.29 \pm 0.47) - (234.9 \pm 6.3) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}$, $\log k_1 = (13.76 \pm 0.10) - (222.6 \pm 0.7) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}$, and $\log k_1 = (13.68 \pm 0.68) - (212.5 \pm 8.7) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}$, respectively. Further, the decomposition rates of β -hydroxynitriles, as is the case for the above-mentioned β -hydroxy-related compounds, increase from primary to tertiary carbon containing the hydroxyl group. Indeed, relative rates of decomposition for the β -hydroxynitriles were found to be slower than those for the corresponding β -hydroxyalkyne analogs [7–9, 15], i.e., 1:178, 1:87, and 1:26 for the primary (1), secondary (2), and tertiary (3) compounds, respectively, at 683.15 K and 0.06 atm. However, for β -hydroxynitriles experimental values of $\log A$ in the range of 13.7–14.4 seems to point out a reaction pathway that does not involve a cyclic six-membered transition state. Therefore, it has been suggested [1] on the basis of available activation parameters that a quasiheterolytic transition state, TSII, or a four-membered cyclic transition state, TSIII, are the most probable decomposition routes, as depicted in Figure 2.

It must be noted, however, that based on the available activation entropies ΔS^\ddagger and their associated standard deviation errors we cannot neglect completely the six-membered transition state route as was suggested before [1]. It must be noted, for instance, that at 683.15 K ΔS^\ddagger ranges (in $\text{J mol}^{-1} \text{ K}^{-1}$) from +4.1 to +25.9 for (1), from +1.4 to +5.2 for (2), and from –11.3 to +14.8 for (3). It is clear

that more specific experimental studies are needed, mainly being devoted to the complete identification of all reaction intermediates and products for the thermal decomposition of β -hydroxynitriles.

In the absence of other types of theoretical treatments of such reactions and with the aim to get some insights about the reaction mechanism and obtain further characterization concerning the detailed nature of transition states, we examined from ab initio calculations the three pathways schematized in Figure 2 for 3-hydroxypropionitrile (1), 3-hydroxybutyronitrile (2), and 3-hydroxy-3-methylbutyronitrile (3) compounds. Transition structures have been located and activation parameters calculated and compared with the corresponding experimental data. These results have been discussed in the light of theoretical and experimental data for the reaction decomposition of related β -hydroxyalkenes [15–18] and β -hydroxyalkynes [7–9, 15] species.

Computational Details

All calculations were carried out using the Gaussian 98 software package [21]. Optimized stationary points for both the four-membered (TSII) as well as the six-membered (TSI) cyclic transition states were obtained and fully characterized at the MP2/6-31G(d) level of theory. The search for the quasiheterolytic transition structures (TSII) failed at this level of theory. Higher-level calculations at either MP2/6-311++G(d, p) or B3LYP/6-311++G(d, p) also failed to locate such a type of transition structure. We therefore calculated the bond dissociation energy ($C_\alpha \dots C_\beta$) for a radical pathway. Optimized transition structures for pathways via the TSI and TSIII were found with only one imag-

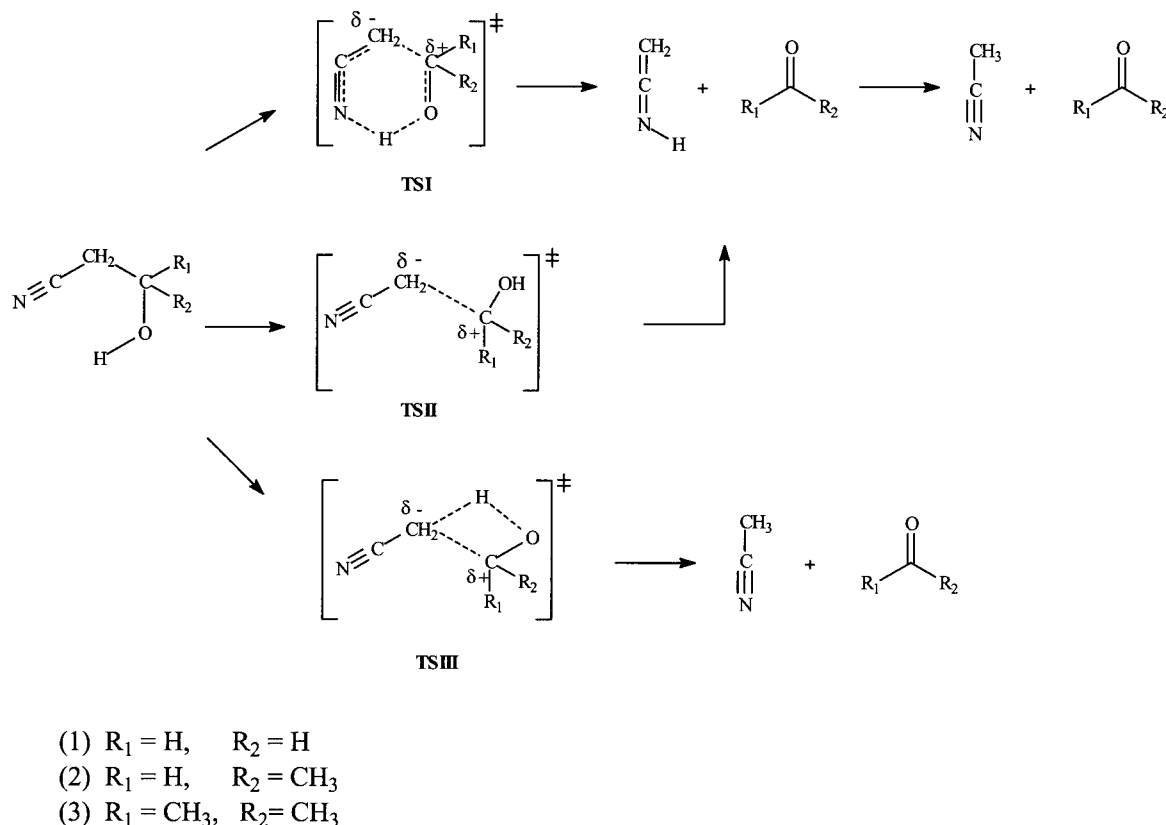


FIGURE 2. Schematic representation for three mechanistic routes for the thermal decomposition of β -hydroxynitriles in the gas phase.

inary frequency, which corresponds to the expected vibrational mode. Intrinsic reaction coordinate (IRC) [22–24] calculations were performed to verify that the located transition structures connect in effect with the correct conformations of reactants and products.

Results and Discussion

Table I summarizes the main activation parameters available both experimentally and theoretically for β -hydroxyolefins, β -hydroxyacetylenes, and β -hydroxynitriles at 683.15 K and 0.06 atm.

A careful examination of these data reveals that for the β -hydroxynitriles the decomposition through a six-membered cyclic transition structure (TSI) is predicted, at the present level of calculation, as the best pathway. Activation parameters are predicted through this path in close agreement (within ca. 5% relative error) with the experimental available evidence for reactions corresponding to 3-hydroxypropionitrile (1), 3-hydroxybutyronitrile (2),

and 3-hydroxy-3-methylbutyronitrile (3) compounds.

On the other hand, it must be noted that activation barriers are strongly overestimated by the consideration of four-membered cyclic transition structures (TSII). Because the TSII has not been found, we considered the bond dissociation energies as the “activation energies” via the quasiheterolytic (radical) path. Calculated values (from ΔG) are 258.9, 255.5, and 253.4 kJ mol⁻¹ for decompositions of β -hydroxynitriles (1), (2), and (3), respectively. Again, these values do not agree with the range of experimental determinations. Moreover, from comparisons between theoretical values of activation parameters for the case of β -hydroxyalkenes [10] and β -hydroxyalkynes [18], with β -hydroxynitriles, we can observe that while concerned with a six-membered cyclic transition structure for decomposition the predicted reactivity order (i.e., alkenes < alkynes < nitriles) agrees with experimental observations. The stronger argument against a six-membered cyclic transition structure was before based on the small positive values for activation entropies

TABLE I

Summary for experimental and theoretical (in brackets) activation parameters corresponding to thermal decomposition of β-hydroxyalkenes, β-hydroxyalkynes, and β-hydroxynitriles at 683.15 K and 0.06 atm.

Systems	E_a (kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
β-hydroxyalkenes ^a				
(1) HO—CH ₂ —CH ₂ —CH=CH ₂	170.3 [150.2]	164.6 [144.5]	-47.7 [-58.9]	197.2 [184.7]
(2) HO—CH(CH ₃)—CH ₂ —CH=CH ₂	168.2 [156.5]	162.5 [148.9]	-43.9 [-41.2]	192.5 [177.0]
(3) HO—C(CH ₃) ₂ —CH ₂ —CH=CH ₂	169.5 [155.9]	163.8 [150.0]	-36.0 [-35.2]	188.4 [174.0]
β-hydroxyalkynes ^b				
(1) HO—CH ₂ CH ₂ —C≡CH	166.9 [175.6]	161.2 [169.9]	-44.8 [-19.2]	191.8 [183.0]
(2) HO—CH(CH ₃)—CH ₂ —C≡CH	164.8 [171.0]	159.1 [165.3]	-42.3 [-35.6]	188.0 [189.6]
(3) HO—C(CH ₃) ₂ —CH ₂ —C≡CH	166.9 [172.7]	161.2 [167.0]	-37.7 [-19.7]	187.0 [180.5]
β-hydroxynitriles ^c				
(1) HO—CH ₂ CH ₂ —C≡N	237.7 [228.1] ^d [405.4] ^e	232.0 [222.4] ^d [399.7] ^e	15.1; 7.7 ^f [-3.9] ^d [3.0] ^e	221.7 [225.1] ^d [391.0] ^e
(2) HO—CH(CH ₃)—CH ₂ —C≡N	222.6 [221.9] ^d [364.5] ^e	216.9 [216.2] ^d [358.8] ^e	3.3; 2.8 ^f [-6.9] ^d [2.4] ^e	214.6 [220.9] ^d [351.9] ^e
(3) HO—C(CH ₃) ₂ —CH ₂ —C≡N	212.5 [221.7] ^d [361.4] ^e	206.8 [216.0] ^d [355.7] ^e	1.9; 1.8 ^f [-0.6] ^d [3.5] ^e	205.5 [216.4] ^d [345.6] ^e

^a Experimental data from Ref. [7]. Theoretical data from Ref. [10].

^b Experimental data from Ref. [15]. Theoretical data from Ref. [18].

^c Experimental data from Ref. [1].

^d MP2/6-31G(d) values determined in the present work at 683.15 K and 0.06 atm on the basis of a six-membered transition structure pathway.

^e MP2/6-31G(d) values determined in the present work at 683.15 K and 0.06 atm on the basis of a four-membered transition structure pathway.

^f Experimental value recalculated from Table 8 of Ref. [1].

($\Delta S^\ddagger > 0$), which were determined in Ref. [1]. However, on the basis of the standard deviation errors associated with these determinations it is not completely clear that such a reaction pathway can be discarded. Here, we obtained at the MP2/6-31G(d) level of calculation small negative values for the activation entropy: -3.9, -6.9, and -0.6 Jmol⁻¹ K⁻¹ for (1), (2), and (3), respectively. These values can be compared with the corresponding recalculated data from Table 8 of Ref. [1], which gives small positive values: +7.7, +2.8, and +1.8 Jmol⁻¹ K⁻¹ for (1), (2), and (3), respectively. It is evident that additional experimental studies concerning the precise identification of the intermediates of reactions are required. Of particular importance here will be to determine the existence of the intermediate H₂C=C=N—H that will be formed from the six-membered cyclic transition structure TSI.

Figures 3 and 4 depict the main geometric parameters for the fully optimized structures corresponding to the six-membered cyclic transition states (TSI) and the four-membered transition structures (TSII). It will be remarked that the six-membered cyclic transition structures are completely planar in the center of the reaction, while the cyclic

four-membered transition structures show a small deviation of the planarity in the range of 18–30° involving the hydroxylic hydrogen transfer from the oxygen to the alpha carbon center. It must be remarked that the complete characterization of the intimate nature of dominant orbital interactions, i.e., pericyclic or pseudopericyclic bonding at the transition structures [25], remains to be further established for these reaction processes.

It is clear from data in Table I that, although a route via the six-membered cyclic transition structure seems to be favored, there is a marked difference between the activation entropies for the β-hydroxy-alkenes and -alkynes, and the -nitriles. Such a difference can be rationalized directly resorting to the standard statistical thermodynamics formalism from which entropies are being calculated in terms of partition functions, where there is an important contribution from the normal modes of vibration [26]. We can note from the normal-mode analysis of reactants and transition states that the rise of contributions of lower frequencies, going from -alkenes to -alkynes (i.e., double bonds CC, triple bond CC, and triple bond CN, and associated bonds with hydrogen atoms) will carry to less negative values

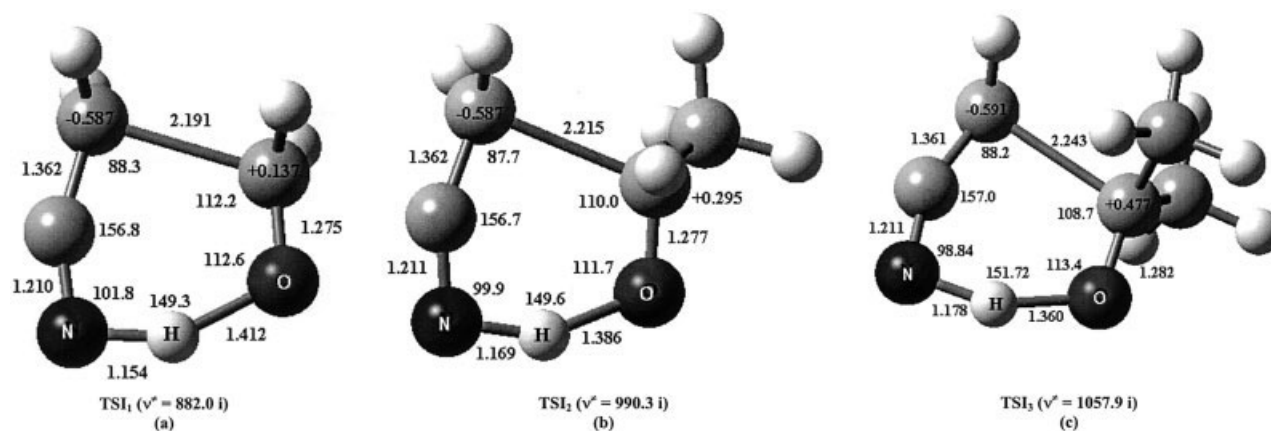


FIGURE 3. Some MP2/6-31G(d)-optimized geometric parameters corresponding to the six-membered cyclic transition structure for the thermal decomposition of β -hydroxynitriles in the gas phase. Distances in Å, angles in degrees. Mulliken charges for the alpha and beta centers are also indicated. Frequencies for the imaginary mode are expressed in cm^{-1} .

for ΔS^{\ddagger} , as can be noted from theoretical values in Table I.

To further examine the progress of the reactions and the details of synchronicity of bond breaking and bond formation, we calculated the Wiberg bond indices, B_i [27], which can be used to measure the evolution of bond order between pairs of atoms along a selected reaction pathway [28]. The relative variation of the bond index at the transition position, δB_i , for each bond i , and the percent of evolution, % Ev, of the corresponding bond order through the path can be obtained from the reactant (R), the transition state (TS), and the corresponding products (P),

$$\delta B_i = \frac{B_i^{TS} - B_i^R}{B_i^P - B_i^R}; \quad \% \text{ Ev} = 100 \delta B_i.$$

Hence, the average value, δB_{av} , the absolute asynchronicity, A , and the synchronicity, Sy , indices are straightforward calculated for the n bonds involved in the center of reaction [28]:

$$\delta B_{\text{av}} = \frac{1}{n} \sum \delta B_i; \quad A = \frac{1}{2n-2} \sum \frac{|\delta B_i - \delta B_{\text{av}}|}{\delta B_{\text{av}}};$$

$$Sy = 1 - A.$$

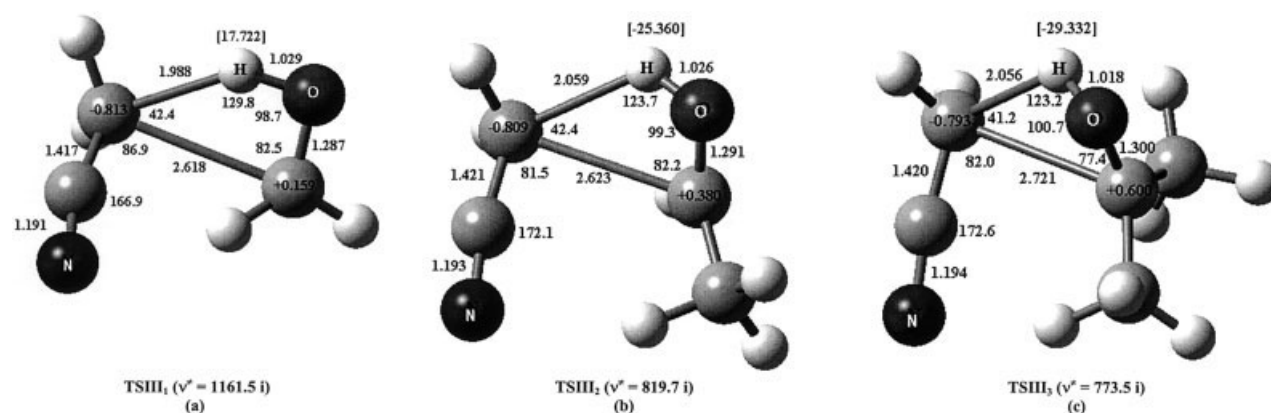


FIGURE 4. Some MP2/6-31G(d)-optimized geometric parameters corresponding to the four-membered cyclic transition structure for the thermal decomposition of β -hydroxynitriles in the gas phase. Distances in Å, angles in degrees. Mulliken charges for the alpha and beta centers are also indicated. Within brackets are the dihedral angles for $\text{H}-\text{O}-\text{C}_{\beta}-\text{C}_{\alpha}$. Frequencies for the imaginary mode are expressed in cm^{-1} .

TABLE II

Wiberg bond indices, B , the percent of evolution, % Ev, the average value, δB_{av} , and the synchronicity index (Sy) for the evolution of the bond indices at the center of reaction for the thermal decomposition of primary, secondary, and tertiary β -hydroxyalkenes through a six-membered cyclic transition state.

	O ₁ —H ₆	O ₁ —C ₂	C ₂ —C ₃	C ₃ —C ₄	C ₄ —C ₅	C ₅ —H ₆	δB_{av}	Sy
(1)								
<i>R</i>	0.740	0.919	0.998	1.025	1.980	0.006	0.53	0.87
<i>TS</i>	0.245	1.290	0.544	1.413	1.310	0.529		
<i>P</i>	0.000	1.871	0.000	1.985	1.039	0.939		
% Ev	66.9	39.0	45.5	40.4	71.2	56.1		
(2)								
<i>R</i>	0.737	0.902	0.987	1.026	1.979	0.006	0.53	0.88
<i>TS</i>	0.256	1.271	0.529	1.413	1.319	0.514		
<i>P</i>	0.000	1.822	0.000	1.985	1.039	0.939		
% Ev	65.3	40.1	46.4	40.4	70.2	54.4		
(3)								
<i>R</i>	0.737	0.891	0.973	1.024	1.978	0.007	0.54	0.89
<i>TS</i>	0.256	1.263	0.502	1.426	1.316	0.509		
<i>P</i>	0.000	1.785	0.000	1.985	1.039	0.939		
% Ev	65.3	41.6	48.4	41.8	70.5	53.9		

The Wiberg bond indices corresponding to the bonds being made and broken in the center of reaction for the case of primary, secondary, and tertiary β -hydroxy-alkenes, -alkynes, and -nitriles are reported in Tables II, III, and IV, respectively. It is evident from the percent of evolution data that the decomposition of β -hydroxynitriles via a six-membered cyclic transition state is in better agreement with the Hammond postulated for

these types of thermal decompositions than the pathway via the four-membered cyclic transition state. We can note that the TSI will be "late" on the reaction coordinate while the TSIII will be "earlier" [29]. The synchronicity (Sy) at the center of reaction is lower for the β -hydroxy-alkenes and -alkynes ($Sy = 0.87$ – 0.89 and 0.91 – 0.92 , respectively) than for the -nitriles ($Sy = 0.94$). This correlates well with the relative reactivity order,

TABLE III

Wiberg bond indices, B , the percent of evolution, % Ev, the average value, δB_{av} , and the synchronicity index (Sy) for the evolution of the bond indices at the center of reaction for the thermal decomposition of primary, secondary, and tertiary β -hydroxyalkynes through a six-membered cyclic transition state.

	O ₁ —H ₆	O ₁ —C ₂	C ₂ —C ₃	C ₃ —C ₄	C ₄ —C ₅	C ₅ —H ₆	δB_{av}	Sy
(1)								
<i>R</i>	0.741	0.923	0.992	1.038	2.911	0.002	0.59	0.91
<i>TS</i>	0.243	1.348	0.452	1.484	2.240	0.526		
<i>P</i>	0.000	1.871	0.000	1.616	1.616	0.877		
% Ev	67.2	44.8	54.4	77.2	51.8	59.9		
(2)								
<i>R</i>	0.737	0.906	0.981	1.039	2.910	0.002	0.59	0.92
<i>TS</i>	0.247	1.328	0.436	1.486	2.238	0.519		
<i>P</i>	0.000	1.822	0.000	1.616	1.616	0.877		
% Ev	66.5	46.1	55.6	77.5	51.9	59.1		
(3)								
<i>R</i>	0.739	0.894	0.968	1.038	2.909	0.002	0.60	0.91
<i>TS</i>	0.249	1.312	0.413	1.496	2.238	0.510		
<i>P</i>	0.000	1.785	0.000	1.616	1.616	0.877		
% Ev	66.3	46.9	57.3	79.2	51.9	58.1		

TABLE IV

Wiberg bond indices, B_i , the percent of evolution, % Ev, the average value, δB_{av} , and the synchronicity index (Sy) for the evolution of the bond indices at the center of reaction for the thermal decomposition of primary, secondary, and tertiary β -hydroxynitriles through ^aa six-membered cyclic transition state and ^ba four-membered cyclic transition state.

	O ₁ —H ₆	O ₁ —C ₂	C ₂ —C ₃	C ₃ —C ₄	C ₄ —N ₅	N ₅ —H ₆	δB_{av}	Sy
(1) ^a								
<i>R</i>	0.741	0.928	0.987	1.045	2.9119	0.001	0.65	0.94
<i>TS</i>	0.193	1.429	0.332	1.523	2.277	0.516		
<i>P</i>	0.000	1.871	0.000	1.870	2.021	0.801		
% Ev	74.0	53.1	66.4	57.9	71.5	64.4		
(2) ^a								
<i>R</i>	0.743	0.914	0.975	1.044	2.917	0.001	0.64	0.94
<i>TS</i>	0.207	1.403	0.312	1.525	2.281	0.498		
<i>P</i>	0.000	1.822	0.000	1.870	2.021	0.801		
% Ev	72.1	53.9	68.0	58.2	71.0	62.1		
(3) ^a								
<i>R</i>	0.741	0.898	0.962	1.046	2.916	0.001	0.64	0.94
<i>TS</i>	0.215	1.379	0.294	1.527	2.284	0.484		
<i>P</i>	0.000	1.785	0.000	1.870	2.021	0.801		
% Ev	71.0	54.2	69.4	58.4	70.6	60.4		
(1) ^b								
<i>R</i>	0.741	0.928	0.987	—	—	0.000 ^c	0.42	0.65
<i>TS</i>	0.539	1.357	0.168	—	—	0.1096 ^c		
<i>P</i>	0.000	1.871	0.000	—	—	0.907 ^c		
% Ev	27.3	45.5	83.0	—	—	12.0 ^c		
(2) ^b								
<i>R</i>	0.743	0.914	0.975	—	—	0.000 ^c	0.41	0.62
<i>TS</i>	0.557	1.282	0.130	—	—	0.092 ^c		
<i>P</i>	0.000	1.822	0.000	—	—	0.907 ^c		
% Ev	25.0	40.5	86.7	—	—	10.1 ^c		
(3) ^b								
<i>R</i>	0.741	0.898	0.962	—	—	0.001 ^c	0.40	0.59
<i>TS</i>	0.561	1.237	0.096	—	—	0.083 ^c		
<i>P</i>	0.000	1.785	0.000	—	—	0.907 ^c		
% Ev	24.3	38.2	90.0	—	—	9.1 ^c		

^c For the C₃—H₆ bond.

which is predicted in good qualitative agreement with experiments in all three cases (i.e., primary < secondary < tertiary). For instance, we can see that a greater charge separation (even by examination of the Mlliken populations in Figs. 3 and 4) is involved from the primary to tertiary β -hydroxynitriles transition structures either through TSI or TSIII. This observation agrees with the synchronicity orders reported in Tables II–IV corresponding to a different degree of advance for the bond separation between the alpha and beta centers and the transference of the hydroxylic hydrogen along the reaction coordinate. This trend is also clearly shown along the

series of primary, secondary, and tertiary compounds.

Conclusions

The thermal decomposition of β -hydroxynitriles in the gas phase has been studied at the MP2/6-31G(*d*) level of theory. Results on primary, secondary, and tertiary substrates show that a decomposition route through a six-membered cyclic transition structure (TSI) is more favorable—both from energy and structural considerations—than that corresponding to a four-membered cyclic tran-

sition structure (TSIII) or a quasiheterolytic pathway. Based on the actual available kinetic evidence and also on the comparison of experimental and theoretical activation parameters for these and related compounds (i.e., β -hydroxyalkenes and β -hydroxyalkynes), it can be remarked that a six-membered cyclic transition structure cannot be neglected as a real mechanistic possibility. More complete experimental and theoretical studies are necessary to further elucidate models for the thermal reaction mechanism of decomposition for these types of compounds in the gas phase.

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