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The mechanism of the homogeneous, unimolecular gas-phase elimination kinetic of 1,1-dimethoxycyclohexane: experimental and theoretical studies

Felix Rosas[a], Rosa M. Domínguez[a], María Tosta[a], José R. Mora[a], Edgar Márquez[a], Tania Córdova[b] and Gabriel Chuchani[a]*
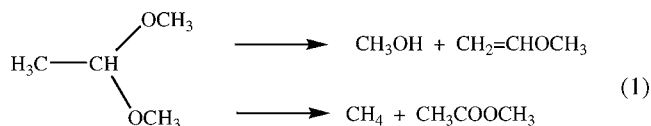
The gas-phase elimination of 1,1-dimethoxycyclohexane yielded 1-methoxy-1-cyclohexene and methanol. The kinetics were determined in a static system, with the vessels deactivated with allyl bromide, and in the presence of the free radical inhibitor cyclohexene. The working temperature was 310–360 °C and the pressure was 25–85 Torr. The reaction was found to be homogeneous, unimolecular, and follows a first-order rate law. The temperature dependence of the rate coefficients is given by the following Arrhenius equation: $\log k(s^{-1}) = [(13.82 \pm 0.07) - (193.9 \pm 1.0)(kJ\,mol^{-1})](2.303RT)^{-1}$; $r = 0.9995$. Theoretical calculations were carried out using density functional theory (DFT) functionals B3LYP, MPW1PW91, and PBE with the basis set 6-31G(d,p) and 6-31G++(d,p). The calculated values for the energy of activation and enthalpy of activation are in reasonably good agreement with the experimental values using the PBE/6-31G (d,p) level of theory. Both experimental results and theoretical calculations suggest a molecular mechanism involving a concerted polar four-membered cyclic transition state. The transition state structure of methanol elimination from 1,1-dimethoxycyclohexane is characterized by a significantly elongated C—O bond, while the C_β—H bond is stretched to a smaller extent, as compared to the reactant. The process can be described as moderately asynchronic with some charge separation in the TS. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this paper.

Keywords: kinetics; unimolecular elimination; 1,1-dimethoxycyclohexane; DFT calculations

INTRODUCTION

The thermal decompositions of ethylal, dimethyl acetal, and diethyl acetal were studied in a static system and in the temperature range of 389–530 °C. These compounds were the first ketals substrates examined in the gas-phase.[1] Thus, ethylal decomposed mainly via a radical mechanism, while dimethyl and diethyl acetals were considered to undergo rearrangement reactions. Conversely, dimethyl acetal decomposed up to 50% reaction, in parallel eliminations. The reactions follow a first-order rate law and the products are described in reaction (1).

$$H_3C-CH \begin{array}{c} OCH_3 \\ \\ OCH_3 \end{array} \quad \begin{array}{c} \longrightarrow CH_3OH + CH_2=CHOCH_3 \\ \\ \longrightarrow CH_4 + CH_3COOCH_3 \end{array} \quad (1)$$

Additional studies by Molera *et al.*[2,3] investigated the gas-phase thermal decompositions of methylal (472–520 °C)[2] and propylene methylal (512–572 °C).[3] According to products' formation, these reactions were thought to proceed through biradical mechanisms. Moreover, the reexamination of methylal pyrolysis in a flow system at 600–732 °C[4,5] was shown to give a complex radical reaction.

Recently, the significance of the hydrogen atom participation present at the C_α—H or C_β—H bond in the transition state mechanism of gas-phase elimination kinetics of ketals, shown in Scheme 1, was examined.[6] Along this line of thought, an electron withdrawing substituent Z at the β-carbon should increase the acidity C_β—H bond for a more facile abstraction of the alkoxy group.

In this respect, the gas-phase elimination kinetics of 2, 2-diethoxyethyl amine and 2, 2-diethoxy-*N*, *N*-diethyl ethylamine, in seasoned reaction vessels, were carried out at 320–380 °C and 40–150 Torr.[6] The reactions proved to be homogeneous, unimolecular and to obey a first-order rate law. These decomposition processes involved two parallel reactions. The first substrate

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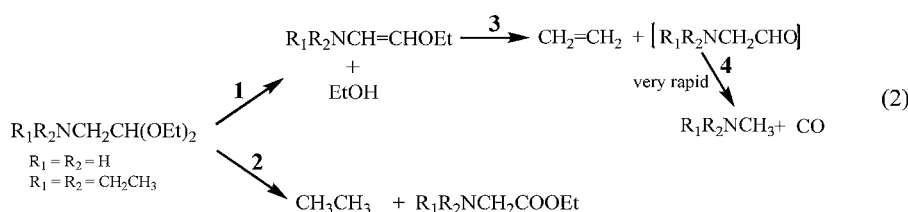
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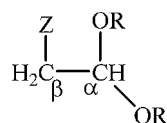
Z = Substituent
R = Alkyl

Scheme 1.

produced ethanol and the corresponding 2-ethoxyethenamine; yet, the latter product further decomposed to ethylene, CO, and the corresponding amine. The second parallel reaction produced, to a lesser amount, ethane and the corresponding ethyl ester of an α-amino acid (reaction (2)). Apparently, the H of the C_β—H bond appears to assist better the elimination of ethanol.

Thermodynamic quantities such as zero point vibrational energy (ZPVE), temperature corrections [$E(T)$] and absolute entropies [$S(T)$] were obtained from frequency calculations. Temperature corrections and absolute entropies were obtained assuming ideal gas behavior from the harmonic frequencies and moments of inertia by standard methods[8] at average temperature and pressure values within the experimental range. Scaling factors for frequencies and zero point energies for the B3LYP method used are taken from the literature.[9] In the case of DFT functionals MPW1PW91 and PBE, the B3LYP scaling factor was used.[9]

The first-order rate coefficient $k(T)$ was calculated using the TST[10] and assuming that the transmission coefficient is equal to 1, as expressed in the following expression:

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

(2)

The scarce information on the homogeneous, molecular decomposition of ketals in the gas-phase led us to examine, both experimentally and theoretically, the gas-phase elimination kinetics of a molecule without an α-hydrogen at the carbon containing the two alkoxy groups. The molecule to investigate is 1,1-dimethoxycyclohexane. Therefore, we want to understand how important is the hydrogen abstraction of the C_β—H bond by the leaving alkoxy groups in this elimination reaction. The objectives of theoretical study at density functional theory (DFT) computational levels consider a reasonable elimination mechanism of this substrate and to compare the kinetic and thermodynamic parameters of activation with the experimental values.

where $\Delta G^{\#}$ is the Gibbs free energy change between the reactant and the transition state and k_B, h are the Boltzmann and Planck 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, $\Delta ZPVE$ 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.

COMPUTATIONAL METHOD AND MODEL

Theoretical calculations on the potential energy surface in the region between 1, 1-dimethoxycyclohexane and products 1-methoxy-1-cyclohexene and methanol were carried out using DFT methods with functionals: B3LYP, MPW1PW91, and PBE with the basis set 6-31G(d,p) and 6-31G++(d,p) implemented in Gaussian 03W.[7] The Berny analytical gradient optimization algorithm was used throughout. The requested convergence on the density matrix was 10^{-9} atomic units, the threshold value for maximum displacement was 0.0018 Å, and that for the maximum force was 0.00045 Hartree Bohr^{-1}. Transition states search was performed using Quadratic Synchronous Transit protocol. The nature of stationary points was recognized by calculating and diagonalizing the Hessian matrix (force constant matrix). TS structures were characterized by means of normal-mode analysis, by having 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.

RESULTS AND DISCUSSION

The gas-phase elimination products of 1, 1-dimethoxycyclohexane, in a static system, seasoned with allyl bromide, and in the presence of the free radical inhibitor cyclohexene, are described in reaction (3).

(3)
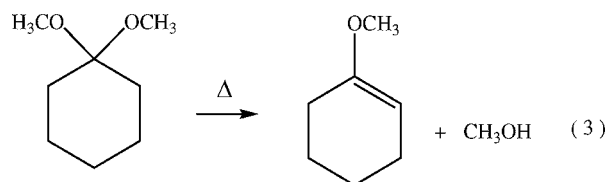
The stoichiometry of reaction (3) indicates that the final pressure P_f should be twice the initial pressure P_o. The average experimental results of P_f/P_o at six different temperatures and ten half-lives gave a mean value of 2.00 (Table 1). Additional examination of stoichiometry represented in reaction (1), up to 80% decomposition, was possible by comparing the amount of

Table 1. Ratio of final (P_f) to initial pressure (P_0)[a]

Substrate	Temp (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Av.
1,1-dimethoxycyclohexane	310.7	18.0	36.0	2.00	2.00 ± 0.01
	320.5	25.0	50.0	2.00	
	329.9	39.0	77.5	1.99	
	339.7	24.5	49.5	2.02	
	349.7	55.0	110.5	2.01	
	360.1	35.5	70.5	1.99	

[a] Seasoned vessel and in the presence of cyclohexene inhibitor.

Table 2. Stoichiometry of the reaction[a]

Substrate	Temp (°C)	Time (min)	Reaction (%) (pressure)	MeOH (%) (GLC)
1,1-dimethoxycyclohexane	329.9	1	7.9	6.3
		2	12.1	12.5
		3	18.5	17.4
		5	28.0	27.7
		6.5	36.5	36.0
		8	41.0	40.1
		10	48.1	47.9
		10.2	55.3	54.5
		13.3	60.8	61.0
		16.7	68.2	67.7
		20	78.0	78.2

[a] Seasoned vessel and in the presence of cyclohexene inhibitor.

decomposition of the substrate calculated from measurements with that obtained from gas-liquid chromatographic (GLC) analyses of the reacted amount of substrate (Table 2).

The kinetic runs of 1, 1-dimethoxycyclohexane were carried out in the presence of at least an equal amount of the chain suppressor cyclohexene to inhibit any possible free radical processes. The effect of different proportions of cyclohexene in the reactions is shown in Table 3. The rate coefficient was reproducible with a relative deviation less than 5% at a given temperature.

In order to examine the effect of surface on the rate of elimination, several runs, and in the presence of the chain

inhibitor cyclohexene, were carried out in a vessel with a surface-to-volume ratio of 6.2 relative to that of the normal vessel which is equal to 1. The packed and unpacked clean Pyrex vessels had a marked effect on the rates. However, when the packed and unpacked vessels are seasoned with allyl bromide, no significant effect on the rate coefficient of this ketal was obtained (Table 4)

The rate coefficients calculated from $k_1 = (2.303/t)$ log $[(2P_0 - P_t) - P_0)]$ were found to be invariable with changes of the initial pressure, P_0, of the substrate (Table 5), and the first-order plots of log $(2P_0 - P_t)$ against time t are satisfactorily up to 80% decomposition. The variations of the rate coefficients with temperature are described in Table 6. The results given in Table 6

Table 3. Effect of free radical chain inhibitor cyclohexene on rates[a]

Substrate	Temp (°C)	P_s (Torr)	P_i (Torr)	P_i/P_s	$10^4 k_1$ (s^{-1})
1,1-dimethoxycyclohexane	329.9	70.0	—	—	6.51 ± 0.21
		90.0	49.0	0.5	8.34 ± 0.54
		56.0	54.0	1.0	10.88 ± 0.51
		39.5	76.0	1.9	10.99 ± 0.37
		37.0	125.0	3.4	10.81 ± 0.38
		35.0	85	2.0	10.79 ± 0.32

P_s = pressure substrate. P_i = pressure inhibitor.
[a] Seasoned vessel and in the presence of cyclohexene inhibitor.

Table 4. Homogeneity of the elimination reaction

Substrate	S/V (cm^{-1})[a]	$10^4 k_1$ (s^{-1})[b]	$10^4 k_1$ (s^{-1})[c]
1,1-dimethoxycyclo-hexene at 330.0°C	1	64.20 ± 3.20	10.81 ± 0.44
	6.2	78.86 ± 7.07	10.79 ± 0.48

[a] S = surface area; V = Volume.
[b] Clean Pyrex vessel.
[c] Seasoned vessel and in the presence of cyclohexene inhibitor.

Table 5. Invariability of the rate coefficients with initial pressure[a]

Substrate	Temp (°C)	P_o (Torr)	$10^4 k$ (s^{-1})
1,1-dimethoxy-cyclohexane	329.9	25.0	10.86 ± 0.25
		35.0	10.79 ± 0.32
		39.5	10.92 ± 0.37
		52.0	10.85 ± 0.24
		56.0	10.88 ± 0.51
		63.0	10.84 ± 0.41
		85.0	10.81 ± 0.38

[a] Seasoned vessel and in the presence of cyclohexene inhibitor.

Table 6. Variation of rate coeffcients with temperature[a]

Substrate	Temp (°C)	$10^4 k$ (s^{-1})
1,1-dimethoxycyclohexane	310.7	3.12 ± 0.02
	320.5	5.86 ± 0.03
	329.9	10.85 ± 0.01
	339.7	20.07 ± 0.11
	349.7	37.19 ± 0.12
	360.1	69.60 ± 0.05

$\log k$ (s^{-1}) = [(13.82 ± 0.07) − (193.9 ± 1.0)(kJ mol^{-1})](2.303RT)$^{-1}$; $r = 0.9995$

[a] Seasoned vessel and in the presence of cyclohexene inhibitor.
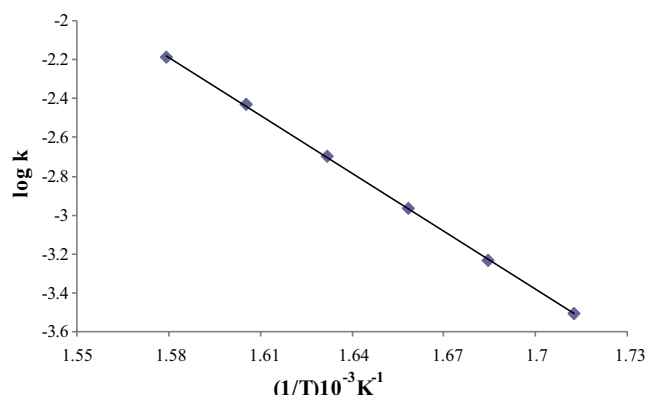
Figure 1. Graphic representation of the Arrhenius plots for the gas-phase elimination of 1,1- dimethoxycyclohexane

lead, by using the least-squares procedure and 90% confidence coefficients, to the shown Arrhenius equation. The Arrhenius plot is depicted in Fig. 1.

Analysis of the experimental results of the kinetic and thermodynamic parameters of activation is given in Table 7; the substrate elimination suggests a concerted polar four-membered cyclic transition state type of mechanism, as shown in reaction (4). To support or change this interpretation, theoretical calculation were undertaken to elucidate a reasonable mechanism of elimination of 1,1-dimethoxycyclohexane.

the region between the reactant and products was explored and the transition state structure was determined to be a four-membered ring, with elongation of the C—O bond. The optimized geometries for reactant, transition state, and products are shown in Fig. 2.

The TS structure was verified by IRC calculations. The IRC calculations demonstrated that the TS structure leads to reactant and products. A description of the TS nature is given by the geometrical parameters and NBO charges shown in the following sections.


(4)
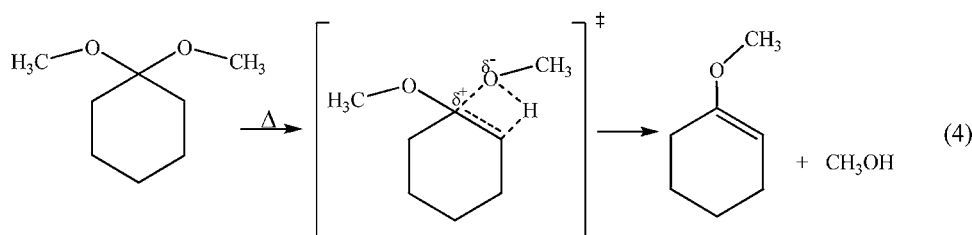
THEORETICAL RESULTS

The gas-phase thermal decomposition of 1,1-dimethoxycyclohexane [reaction (4)] was studied using theoretical calculations so as to provide some possible information regarding the mechanism of this molecular elimination. The PES encompassing

KINETIC AND THERMODYNAMIC PARAMETERS OF ACTIVATION

Results from theoretical calculations using DFT methods B3LYP/6-31G(d,p), B3LYP/6-31G++(d,p), MPW1PW91/6-31G(d,p), MPW1PW91/6-31G++(d,p) and PBE/6-31G (d,p), PBE/6-31G++(d,p) for

Table 7. Kinetic and thermodynamic parameters of activation at 340 °C

Substrate	E_a (kJ mol^{-1})	log A (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K)	$\Delta G^{\neq}$ (kJ mol^{-1})
1,1-dimethoxycyclohexane	193.9 ± 1.0	13.82 ± 0.11	188.3	4.6	185.2
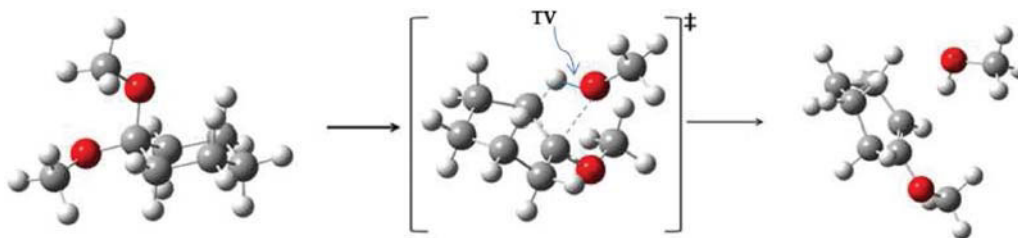
Figure 2. Structures of reactant (left) and transition state TS (right) optimized at PBE/6-31G(d,p) level of theory.

1,1-dimethoxycycloohexane decomposition to 1-methoxy-1-cyclohexene and methanol are described in Table 8. The PBE/6-31G (d,p) level of theory provides good agreement with the experimental values for enthalpy and energy of activations. The use of a bigger basis set including diffuse functions did not improve the calculated parameters, resulting in lower energy of activation. We observed that energy barriers are well estimated using the PBE functional. However, deviations in the entropy of activation and consequently the free energy of activation and Log A values are observed, regardless of the method used. The deviation from the experimental value observed in entropies of activation is the consequence of the use of the harmonic approximation. The harmonic approximation fails because of the existence of low frequency modes in the reactant and TS that contribute to the entropy. Frequently when the TS is very symmetric in a unimolecular process, reasonably good values of entropies of activation are obtained due to similar contribution of the low frequency modes in both the reactant and the TS. The performance of different electronic structure methods varies, depending on the nature of the transition state for unimolecular reaction.[11,12] In the present study, we have found that values of enthalpy and energies of activations are best reproduced with PBEPBE/6-31G(d,p) calculations compared to other DFT functionals. Calculated values for entropies of activation are similar for all DFT methods used, but deviate from the experimental value as described above.

TRANSITION STATE AND MECHANISM

From the previous section, it is clear that the calculated energy of activation from PBE/6-31G(d,p) is in accord with the experimental value; thus we expect that the description of the TS geometry in terms of bond formation and bond breaking can be obtained from the PBE/6-31G(d,p) calculations. We have selected this method 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 transition state structure is a four-membered ring comprising the atoms C_1, C_2, O_3, and H_4. The unique imaginary frequency describing the TS is obtained and the corresponding TV is associated with the hydrogen H_4 migration from the carbon C_1 to O_3 to produce methanol (Scheme 2, Fig. 2). Structural parameters and charges for the reactant 1, 1- dimethoxycyclohexane (R), the transition state (TS), and products methanol and 1-methoxy-1-cyclohexene (P) are given in Table 9.

Geometrical parameters show important elongation of C_2—O_3 bond from 1.44 to 2.27 Å. Also, the distance O_3—H_4 is shortened in significant amount from 2.76 to 1.44 Å, illustrating the migration of the hydrogen from the carbon at the cyclohexane ring to the oxygen to produce methanol. Comparatively, other distances show less change, i.e., C_1—C_2 and H_4—C_1. Dihedral angles are small indicating a distorted-planar geometry in the TS.

Table 8. Calculated kinetic and thermodynamic parameters of activation for 1,1-dimethoxy cyclohexane elimination at 340.0 °C

	E_a (kJ mol^{-1})	log A (sec^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
Experimental	**193.9 ± 1.0**	**13.8**	**188.3**	**185.2**	**4.6**
B3LYP/6-31G(d,p)	219.7	14.8	214.1	199.0	22.4
B3LYP/6-31G++(d,p)	206.7	15.0	201.1	182.8	27.2
MPW1PW91/6-31G(d,p)	225.1	14.8	219.5	203.7	23.5
MPW1PW91/6-31G++(d,p)	222.8	15.0	217.2	198.8	27.4
PBE/6-31G(d,p)	**195.2**	**14.7**	**189.6**	**175.2**	**21.4**
PBE/6-31G++(d,p)	184.4	15.0	178.8	161.1	26.3
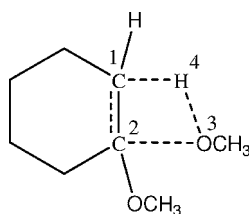
Scheme 2.

NBO calculations were used to study the electron density redistribution in the reaction path of 1, 1-dimethoxycyclohexane decomposition. NBO charges are shown in Table 10 for the reactant (R), transition state (TS), and products (P).

Charges of the atoms involved in the elimination reaction illustrate an increase in electron density at the oxygen atom O_3 from the reactant to the TS, from -0.574 to -0.750. The hydrogen H_4 is already deficient in electron density in the reactant, i.e., acidic, and becomes more positively charged in the TS, increasing its positive charge from 0.255 to 0.397. In the products, the atoms O_3 and H_4 show much less charge separation as methanol is formed. Smaller changes in NBO charges are observed for carbons C_2 and C_1. These observations are in reasonable agreement with the reported atom distances, and imply that the elongation of C_2—O_3 bond with charge separation in the sense $C_\alpha^{\delta+}\ldots O^{\delta-}$ is significant in the TS, while the C_1—H_4 bond which polarizes in the TS in the sense $C_\beta^{\delta-}\ldots H^{\delta+}$ is only slightly stretched, as compared to the reactant.

BOND ORDER ANALYSIS

The reaction progress along the reaction pathway was also investigated by means of NBO bond order calculations.[13–15] Wiberg bond indexes[16] were computed using the natural bond orbital NBO program[17] as implemented in Gaussian 03W. These indexes can be used to estimate bond orders from population analysis. Bond breaking and bond making process involved in the reaction mechanism are monitored by means of the Synchronicity (Sy)

Table 10. NBO Charges of the atoms involved in 1,1-dimethoxycyclohexane thermal decomposition from PBE/ 6-31G(d) calculations

	1,1-dimethoxycyclohexane		
	R	TS	P
C_1	-0.549	-0.621	-0.391
C_2	0.571	0.533	0.304
O_3	-0.574	-0.750	-0.352
H_4	0.255	0.397	0.193

concept proposed by Moyano *et al.*[18] defined by the expression:

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

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

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

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

The evolution in bond change is calculated as:

$$\%Ev = \delta Bi * 100$$

The average value is calculated from:

$$\delta Bave = 1/n \sum_{i=1}^{n} \delta Bi$$

In this analysis, the B_i values indicate bond order and δB_i is the change in bond order as the reaction progresses from 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 considered. The synchronicity parameter Sy varies between 0 and 1, with a value of Sy $= 0$ for asynchronic processes and Sy $= 1$ for a concerted synchronic.

Table 9. Structural parameters for optimized reactant (R), transition state (TS) and products (P) from 1,1-dimethylcyclohexane elimination with PBE/6-31G(d,p) method. atom distances in Å and dihedral angles in degrees

	Atom distances (Å)			
	C_1—C_2	C_2—O_3	O_3—H_4	H_4—C_1
R	1.544	1.438	2.758	1.104
TS	1.447	2.273	1.444	1.221
P	1.345	3.494	0.966	2.368
	Dihedrals			
	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	-5.017	7.793	-10.344	5.003
	Imaginary frequency (cm^{-1})			
TS				-599.1

Table 11. NBO Analysis for 1, 1-dimethoxycyclohexane thermal decomposition from PBE/6-31G(d) calculations. Wiberg bond indexes (B_i), % evolution through the reaction coordinate (%E_v), are shown for R, TS, and P. Average bond index variation (δB_{av}) and synchronicity parameter (Sy) are also reported

	Methanol formation				
	C_1—C_2	C_2—O_3	O_3—H_4	H_4—C_1	Sy
B_i^R	0.9815	0.8886	0.0023	0.9010	0.809
B_i^{ET}	1.2081	0.3090	0.2356	0.5538	
B_i^P	1.7474	0.0051	0.7253	0.0166	
%E_v	29.6	65.6	32.3	39.3	

The Wiberg indexes B_i have been used to illustrate the reaction changes in the reaction coordinate as bonds are being formed and broken. The indexes were calculated for those bonds involved in the reaction changes, i.e., C_1—C_2, C_2—O_3, O_3—H_4, and H_4—C_1 (Scheme 1, Table 11). All other bonds remain practically unaffected during the process.

Bond indexes are used to illustrate the changes in the TS of the reaction under study. In the TS of this unimolecular elimination reaction, the C_2—O_3 and C_1—H_4 bonds break, while there is a change of hybridization in C_1 and C_2 as C_1—C_2 double bond forms. Also, a new single bond O_3—H_4 is formed. According to these changes, the C_1—C_2 bond order increases from 0.98 to 1.21 in the TS; O_3—H_4 bond order increases from 0.00 to 0.23, while C_2—O_3 and C_1—H_4 bond orders decrease from 0.88 to 0.31 in the TS, and 0.90 to 0.55 I the TS, respectively. When compared to the bond indexes in the products, analysis of Wiberg bond indexes shows that the greatest progress in the reaction coordinate is the breaking of C_2—O_3 bond (65.6%). The breaking of H_4—C_1 shows less progress (39.3%). Bond order changes from sp^3 to sp^2 in C_1—C_2 and bond formation O_3—H_4 are early in the reaction coordinate as seen in the % evolution. These changes in bond order as the reaction progresses illustrate that the process is dominated by the elongation of $C^{\delta+}...O^{\delta-}$ bond while the breaking of $C^{\delta-}...H^{\delta+}$ is of secondary importance. The TS structure appears to be asymmetric with important advance in the breaking of C_2—O_3 compared to other reaction coordinates. In other words, the elongation of the C—O bond dominates in the reaction, and it is accompanied to less extent by the abstraction of hydrogen by the same ketal oxygen. These results suggest that the hydrogen abstraction of the C_β—H bond by the leaving alkoxy groups is less important as the elongation of C_α—O bond in the TS. Bond order indexes and % evolution show that the former process is advanced in the reaction coordinate, while other changes are intermediate or early, that is, the different reaction coordinates progress asymmetrically. This is reflected in the synchronicity value of 0.81 which reveals a process that is concerted, but not fully synchronic.

CONCLUSIONS

The thermal elimination kinetics of 1,1-dimethoxycyclohexane to give 1-methoxycyclohexene and methanol is unimolecular,

homogeneous, and obeys a first-order rate law. The variation of the rate coefficient with temperature gives the Arrhenius expression: log k (s^{-1}) = [(13.82 ± 0.07) − (193.9 ± 1.0) (kJ mol^{-1})](2.303RT)$^{-1}$; r = 0.9995. The reaction path was also studied using theoretical calculations using DFT functionals: B3LYP, MPW1PW91, and PBE with the basis set 6-31G (d,p) and 6-31G++(d,p), We have found that the DFT functional PBE gave reasonable E_a-value when compared with the experimental E_a-value. By increasing the basis set from 6-31G(d,p) to 6-31G++(d,p) the energy of activation tends to diminish. Other DFT methods used produced overestimation of the reaction barrier. The better performance of PBE functional was reported previously in other ketal gas-phase elimination reactions,[6] suggesting that the contribution of local varying density in the TS is important in the thermal decomposition of these substrates because of the analytical form of PBE.[19] Calculated values for entropies of activation are similar for all DFT methods used, but deviate from the experimental value as a consequence of the use of the harmonic approximation. The harmonic approximation fails because of the existence of low frequency modes in the reactant and TS that contribute to the entropy. The elimination process of 1,1-dimethoxycyclohexane is determined by the elongation of the C—O bond, in the sense of $C^{\delta+}...O^{\delta-}$, accompanied to less extent by the polarization of the C_β—H bond. In this sense, the hydrogen acidity does not appear to be decisive in this elimination reaction. Synchronicity parameter Sy = 0.809 suggests a moderately polar asynchronic mechanism.

EXPERIMENTAL

1, 1-Dimethoxycyclohexane (Aldrich) of 99% purity was employed (GC-MS Saturn 2000, Varian, with a DB-5MS capillary column 30 m × 0.53 mm. i.d., 0.53 μm film thickness). The products 1-methoxy-1-cyclohexene and methanol were identified in a GC–MS: Saturn 2000, Varian with a DB-5MS capillary column 30 m × 0.25 mm. i.d., 0.25 μm. The quantitative analysis of the product methanol (Fisher) was carried out by using a Varian 3700 Gas Chromatograph with a Porapak R (80-100 mesh) column.

Kinetics

The kinetic determinations were carried out in a static reaction system as previously reported.[20–22] At each temperature, 6–9 runs are carried out in our experiments. The rate coefficients were calculated from the pressure increase measured manometrically. The temperature was maintained within ±0.2° 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.

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