

Experimental and theoretical studies of the elimination kinetics of 3-hydroxy-3-methyl-2-butanone in the gas phase

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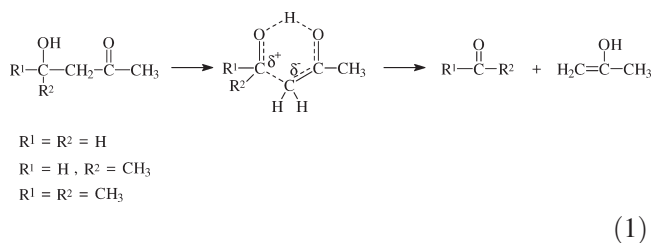
Received 28 June 2004; revised 11 January 2005; accepted 17 January 2005

ABSTRACT: The kinetics of the gas-phase elimination of 3-hydroxy-3-methyl-2-butanone was investigated in a static system, seasoned with allyl bromide, and in the presence of the free chain radical inhibitor toluene. The working temperature and pressure range were 439.6–489.3 °C and 81–201.5 Torr (1 Torr = 133.3 Pa), respectively. The reaction was found to be homogeneous, unimolecular and to follow a first-order rate law. The products of elimination are acetone and acetaldehyde. The temperature dependence of the rate coefficients is expressed by the following equation: $\log [k_1(\text{s}^{-1})] = (13.05 \pm 0.53) - (229.7 \pm 5.3) \text{ kJ mol}^{-1} (2.303RT)^{-1}$. Theoretical estimations of the mechanism of this elimination suggest a molecular mechanism of a concerted non-synchronous four-membered cyclic transition-state process. An analysis of bond order and natural bond orbital charges suggests that the bond polarization of $\text{C}(\text{OH})-\text{C}(=\text{O})-$, in the sense of $\text{C}(\text{OH})^{\delta+} \cdots \text{C}(=\text{O})^{\delta-}$, is rate limiting in the elimination reaction. The rate coefficients obtained experimentally are in reasonably good agreement with the theoretical calculations. The mechanism of 3-hydroxy-3-methyl-2-butanone elimination is described. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: kinetics; elimination; pyrolysis; RHF/6–31G*; MP2/6–31G*; DFT B3LYP/6–31G*; 3-hydroxy-3-methyl-2-butanone

INTRODUCTION

The gas-phase elimination kinetics of primary, secondary and tertiary 2-hydroxy ketones have been examined and reported [reaction (1)].^{1,2} The kinetic data for these retro-Aldol type of decomposition give increased rates from primary to tertiary carbon bearing the hydroxyl substituent. In other words, methyl substitution at the hydroxyl carbon caused a significant increase in rates, which means that bond breaking from primary to tertiary— $\text{C}(\text{OH})-$, in the sense of $\text{R}_2\text{C}(\text{OH})^{\delta+} \cdots \text{CH}_2\text{COCH}_3^{\delta-}$ bond polarization, is a determining factor [reaction (1)].



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It would be obvious that if the hydroxy substituent of hydroxy ketones is at the α -position with respect to the $\text{C}=\text{O}$ bond, a different mechanistic pathway in the elimination process may occur. Therefore, the present work was aimed at examining the kinetics of elimination of primary, secondary and tertiary 1-hydroxy ketones in the gas phase, together with theoretical studies for a reasonable mechanistic interpretation. The theoretical calculations aimed to procure the kinetic parameters and the characterization of the potential energy surface (PES) as a means to understand the nature of the molecular mechanism of this reaction. Consequently, the kinetics for the gas-phase elimination reaction of 3-hydroxy-3-methyl-2-butanone into acetone and acetaldehyde was studied using *ab initio* RHF, MP2 and DFT/B3LYP methods with 6–31G, 6–31G* and 6–31G** basis sets as implemented in Gaussian 98W.³ Calculations with MP2/6–31G** were carried out specifying 6–31G** for the hydrogen being transferred in the reaction; for all other atoms 6–31G* was used. The Berny analytical gradient optimization routines were used for optimization. The nature of stationary points was established by calculating and diagonalizing the force constant matrix to determine the number of imaginary frequencies. Intrinsic reaction coordinate (IRC) calculations were

performed to verify transition-state structures. The transition-state structures were characterized by means of a normal-mode analysis.

The unique imaginary frequency associated with the transition vector (*TV*) was characterized. Frequency calculations provided thermodynamic quantities such as zero point vibrational energy (*ZPVE*), temperature corrections and absolute entropies, 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 methods⁴ at average temperature and pressure values within the experimental range (737.15 K and 0.197 atm). Scaling factors for frequencies and zero point energies for the HF, DFT/B3LYP and MP2 methods used were taken from the literature.⁵

The first-order rate coefficient $k(T)$ was calculated using the TST⁶ and assuming that the transmission coefficient is equal to 1, as expressed in the following relation:

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

where $\Delta G^\ddagger$ is the Gibbs free energy change between the reactant and the transition state and K and h are the Boltzmann and Planck constants, respectively.

$\Delta G^\ddagger$ was calculated using the following relations:

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

and

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

where $V^\ddagger$ is the potential energy barrier and $\Delta ZPVE$ and $\Delta E(T)$ are the differences in *ZPVE* and temperature corrections between the transition state (TS) and the reactant, respectively.

RESULTS AND DISCUSSION

Attempts to examine the gas-phase elimination kinetics of hydroxyacetone (acetol, HOCH₂COCH₃) and 3-hydroxy-2-butanone [acetoin, CH₃CH(OH)COCH₃] were difficult owing to the hydroscopic nature of the former (92.4% purity), and crystallization to a dimer of the latter (95.2% purity). For kinetic determinations it is essential to have organic substrates above 97.5% purity.

The pyrolysis products of 3-hydroxy-3-methyl-2-butanone described in reaction (2), a twofold increase in the final pressure, P_f , is required, i.e. $P_f = 2P_0$:



Table 1. Temperature and pressure data for pyrolysis reaction for 3-hydroxy-3-methyl-2-butanone

Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Average
439.6	104.5	217	2.08	2.19
450.2	129	294.5	2.28	
460.2	139	279.5	2.18	
468.2	125	275	2.20	

Table 2. Stoichiometry of the elimination reaction for 3-hydroxy-3-methyl-2-butanone at 460.5 °C

Parameter	Value				
Time (min)	6	10	13	17	24
Reaction (%) (pressure)	16.90	30.15	36.75	45.25	53.85
Acetone (%) (GC)	17.80	31.08	35.72	44.38	51.81

where P_0 is the initial pressure. The average experimental P_f/P_0 values at four temperatures and after 10 half-lives is 2.19 (Table 1). The observed $P_f/P_0 > 2$ was found to be due to a small degree of decomposition of the acetone product. Additional verification of stoichiometry (2) was made by comparing, up to 55% decomposition, the pressure measurements with the results of quantitative analyses of the product acetone (Table 2).

The effect of the addition of different proportions of toluene inhibitor is shown in Table 3. The pyrolysis experiments on hydroxybutanone were always carried out in seasoned vessels and in the presence of at least twice the amount of toluene in order to prevent any possible radical chain reaction. No induction period was observed and the rates were reproducible with a relative standard deviation not greater than 5% at a given temperature.

To examine the effect of the surface on the rate of elimination, several runs in the presence of at least a twofold amount of toluene inhibitor were carried out in a vessel with a surface-to-volume ratio of six times greater than that of the normal vessel. The rate of elimination of the hydroxybutanone was unaffected in a packed and an unpacked seasoned Pyrex vessel, whereas a significant heterogeneous effect was observed in the clean packed and unpacked Pyrex vessels (Table 4).

Table 3. Effect of the inhibitor toluene on rates for 3-hydroxy-3-methyl-2-butanone at 469.0 °C^a

P_s (Torr)	P_i (Torr)	P_f/P_s	$10^4 k_1$ (s ⁻¹)
114	—	—	9.43
168.5	90.5	0.5	8.97
106	113	1.1	8.43
123	155	1.3	7.84
121.5	282	2.3	7.25
81	280	3.4	7.43

^a P_s = pressure of the substrate; P_i = pressure of the inhibitor. Vessel seasoned with allyl bromide.

Table 4. Homogeneity of the reaction for 3-hydroxy-3-methyl-2-butanone at 460.5 °C

S/V (cm ⁻¹) ^a	$10^4 k_1$ (s ⁻¹) ^b	$10^4 k_1$ (s ⁻¹) ^c
1	10.12	5.01
6	18.75	5.06

^a S = surface area (cm²); V = volume (cm³).^b Clean Pyrex vessel.^c Vessel seasoned with allyl bromide.**Table 5.** Variation of rate coefficients with initial pressure for 3-hydroxy-3-methyl-2-butanone at 468.2 °C^{a,b}

Parameter	Value				
P_0 (Torr)	81	121.5	131	154.5	201.5
$10^4 k_1$ (s ⁻¹)	7.46	7.25	7.28	7.02	7.42

^a Vessel seasoned with allyl bromide.^b In the presence of the inhibitor toluene.**Table 6.** Temperature dependence of the rate coefficients for 3-hydroxy-3-methyl-2-butanone

Parameter	Value					
Temperature (°C)	439.6	450.2	460.5	468.2	479.0	489.3
$10^4 k_1$ (s ⁻¹)	1.59	3.03	5.01	7.38	12.32	20.60

Rate equation: $\log[k_1 \text{ (s}^{-1}\text{)}] = (13.05 \pm 0.53) - (229.7 \pm 5.3) \text{ kJ mol}^{-1} (2.303 RT)^{-1}$; $r = 0.9996$.

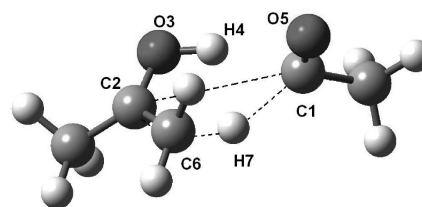
The first-order rate coefficients of this substrate described from $k_1 = (2.303/t) \log P_0/(2P_0 - P_t)$ were independent to initial pressures (Table 5). A plot of $\log(2P_0 - P_t)$ against time t gave a good straight line up to 55% reaction. The variation of the first-order rate coefficient with temperature and the corresponding Arrhenius equation are described in Table 6, which gives rate coefficients at the 90% confidence level obtained from a least-squares procedure.

According to the results in Table 6, and to describe the most probable mechanism for the elimination of 3-hydroxy-3-methyl-2-butanone in the gas phase, a theoretical study was carried out.

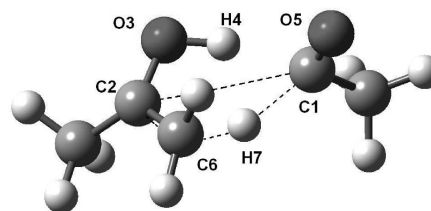
THEORETICAL RESULTS

The substrate 3-hydroxy-3-methyl-2-butanone exists mainly in two conformations; **C-1** and **C-2** (Fig. 1). In conformer **C-1**, the hydroxyl group is *anti* to the carbonyl whereas in conformer **C-2** these groups are eclipsed and an additional stabilization of 11.17 kJ mol⁻¹ (MP2/6-31G*, 737.15 K and 0.197 atm) is obtained owing to an intramolecular hydrogen bond (Fig. 1).

Transition-state geometries were obtained using quadratic synchronous transit protocols QST2 and QST3 as



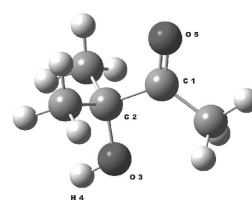
TS- RHF/6-31G*



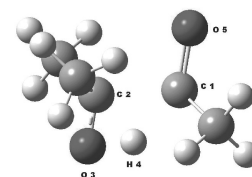
TS-B3LYP/6-31G*

Figure 1. Transition-state structures found by RHF/6-31G* and B3LYP are virtually identical. Product formation involves the transfer of hydrogen from C-6 to C-1, to give acetaldehyde and the enol form of acetone. Activation parameters for RHF deviate from the experimental values (Table 7); B3LYP values are better than RHF but still show some departure from experimental

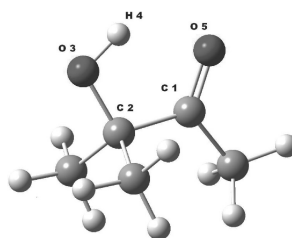
implemented in Gaussian 98W. Calculations at the average experimental temperature and pressure were carried out for both substrate conformers **C-1** and **C-2**. Starting from these two conformers of 3-hydroxy-3-methyl-2-butanone, two possible four-membered ring transition states, **TS-1** and **TS-2**, were obtained from MP2/6-31G* calculations (Fig. 2).



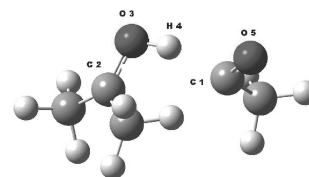
Reactant C-1: anti conformation



TS-1



Reactant C-2: eclipsed conformation



TS-2

Figure 2. Conformations of the reactant 3-hydroxy-3-methyl-2-butanone **C-1** and **C-2** and their corresponding transition-state structures, **TS-1** and **TS-2**, from MP2/6-31G* calculations. Activation parameters for **TS-2** are best when compared with experimental values (Table 7). This TS structure is late in the sense of C-1—C-2 bond breaking

Table 7. Activation parameters calculated at the RHF, B3LYP and MP2 levels of theory for the thermal decomposition of 3-methyl-3-hydroxy-2-butanone at 737.15 K and 0.917 atm

Level	$\Delta H^\ddagger$ (kJ mol ⁻¹)	E_a (kJ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	Log [A (s ⁻¹)]	k_1 (s ⁻¹)
RHF/6-31G*	341.8	347.9	349.7	-10.72	13.06	2.55×10^{-12}
B3LYP/6-31G*	242.8	248.9	250.7	-10.72	13.06	2.64×10^{-5}
MP2/6-31G*TS-1	353.0	359.1	360.9	-10.72	13.06	4.07×10^{-13}
MP2/6-31G*TS-2	226.4	232.5	234.3	-10.72	13.06	7.62×10^{-4}
MP2/6-31G**/TS-2	228.6	234.8	236.6	-10.76	13.07	2.69×10^{-4}
Experimental	223.6	229.7	231.5	-10.77	13.05	5.89×10^{-4}

Even though theoretical calculations of transition-state structures have been a useful tool for reasonable mechanistic interpretations of organic reactions, the results have usually been limited to enthalpy of activation, and consequently to energy of activation. Frequently the entropies of activation are far from experimental. It is our experience in gas-phase reactions that the difference in values between experimental energy of activation (E_a^{exp}) and the free energy of activation ($\Delta G^\ddagger_{\text{exp}}$) gives an idea of the magnitude of the entropy of activation.

In view of the above considerations, entropy values were estimated according to Chuchani-Cordova,⁷ considering a factor C^{exp} . This factor is intended to rationalize the limitations of the theoretical methods since they do not consider the collisional entropy. Therefore,

$$\Delta H^\ddagger_{\text{exp}} \cong \Delta H^\ddagger_{\text{theo}}$$

and consequently

$$E_a^{\text{exp}} \cong E_a^{\text{theo}}$$

We expect that

$$\Delta G^\ddagger_{\text{exp}} \cong \Delta G^\ddagger_{\text{theo}}$$

and therefore

$$\Delta G^\ddagger_{\text{exp}} - E_a^{\text{exp}} = C^{\text{exp}}$$

hence we obtain

$$\Delta G^\ddagger_{\text{theo}} = E_a^{\text{theo}} + C^{\text{exp}}$$

where the superscripts exp and theo refer to experimental and theoretical values, respectively, and the parameter C^{exp} is given by

$$C^{\text{exp}} = nRT - T\Delta S^\ddagger_{\text{exp}} \quad (n = 1 \text{ unimolecular reaction})$$

C^{exp} includes the contribution of collisional entropy, which has not been considered in frequency calculations (isolated molecules).

Using

$$\Delta G^\ddagger_{\text{theo}} = \Delta H^\ddagger_{\text{theo}} - T\Delta S^\ddagger_{\text{theo}}$$

$\Delta S^\ddagger_{\text{theo}}$ was obtained. From $\Delta S^\ddagger_{\text{theo}}$ and E_a^{theo} , logA and the rate coefficients can be calculated.

Transition states from RHF and B3LYP/6-31G* are very similar in structure (Fig. 1), being very late with regard to C-1—C-2 bond breaking. Polarization of the C-1—C-2 bond in both TS structures occurs in the sense $\text{C}(\text{OH})^{\delta+} \cdots \text{C}(=\text{O})^{\delta-}$, that is, C-2 becomes more positive and C-1 less positive in charge. The TS is a twisted four-membered ring structure including atoms C-1, C-2, C-6 and H-7. There is a hydrogen transfer from C-6 (one of the methyl groups in C2) to C-1, whereas C-2—C-6 has double bond character in the transition state (1.407 Å, Table 8), leading to the formation of acetaldehyde and the enol form of acetone. Activation parameters for RHF/6-31G* (Table 7) are too high compared with the experimental values, whereas the B3LYP/6-31G* values are better but still show some departure from the experimental data.

MP2 results vary depending on the conformation of the substrate. For conformer **C-1** transition state **TS-1** was found and for conformation **C-2** **TS-2** (Fig. 2). Activation parameters for **TS-2** are in good agreement with the experimental values, whereas for **TS-1** they are too high (Table 7). This result suggest that **TS-2** is the most likely transition-state structure for this reaction. The structure of the transition state **TS-2** is a twisted four-membered ring, compressing atoms C-1, C-2, O-3 and H-4, where a hydrogen atom is being transferred from the hydroxyl group to C-1 to give acetaldehyde and acetone. **TS-2** is late in the sense of C-1—C-2 bond breaking and there is some double bond character in the C-2—C-6 bond in the transition state (Table 9). NBO charges reveal a strong polarization for the C-1—C-2 bond in the sense $\text{C}(\text{OH})^{\delta+} \cdots \text{C}(=\text{O})^{\delta-}$, as found in the previous calculations (RHF and B3LYP described above).

Electronic structure calculation results suggest that the thermal decomposition of 3-methyl-3-hydroxy-2-butanone may occur through **TS-2** (MP2/6-31G* from conformation **C-2**), leading to acetaldehyde and acetone. An alternative pathway is possible through **TS-1** (B3LYP/6-31G*) to give acetaldehyde and the enol form of acetone.

Table 8. Structural parameters for reactant and transition states for RHF/6–31G* and B3LYP/6–31G* calculations^a

Structure	C-1—C-2	C-2—O-3	O-3—H-4	C-1—O-5	H-7—C-1	C-2—C-6
Reactant RHF	1.550	1.410	0.940	1.210	2.710	1.536
TS RHF	3.200	1.280	1.012	1.200	1.690	1.407
Reactant B3LYP	1.544	1.410	0.970	1.220	2.730	1.544
TS B3LYP	3.157	1.310	1.070	1.210	1.600	1.413
	C-2—O-3—H-4	C-1—C-2—O-3	C-2—C-1—O-5	O-3—C-2—C-1—O-5		
TS RHF	107.14	61.58	104.59	95.11		
TS B3LYP	104.89	61.250	129.973	76.260		

^a Atom distances are in Å and dihedral angles in degrees.*Mülliken atomic charges for reactant and transition states from RHF/6–31G* and B3LYP/6–31G* levels of theory*

Structure	C-1	C-2	O-3	H-4	O-5	H-7	C-6
Reactant RHF	0.516	0.238	−0.773	0.473	−0.551	0.178	−0.488
TS RHF	0.115	0.533	−0.664	0.488	−0.520	0.216	−0.680
Reactant B3LYP	0.438	0.250	−0.658	0.407	−0.460	0.157	−0.453
TS B3LYP	0.120	0.422	−0.555	0.383	−0.372	0.147	−0.537

Table 9. Structural parameters for reactant conformations **C-1** and **C-2** and transition states **TS-1** and **TS-2**

Structures	C-1—C-2	C-2—O-3	O-3—H-4	C-1—O-5	C-1—H-4	C-2—C-6
C-1	1.545	1.430	0.960	1.210	4.300	1.530
TS-1	2.911	1.330	0.990	1.220	1.082	1.430
C-2	1.550	1.410	0.940	1.210	2.229	1.530
TS-2	3.020	1.300	1.030	1.210	1.100	1.430
Products	3.320	1.220	2.379	1.220	1.100	1.510
	C-2—O-3—H-4	C-1—C-2—O-3	C-2—C-1—O-5	O-3—C-2—C-1—O-5		
TS-1	102.11	77.090	67.834	−178.922		
TS-2	104.89	61.250	129.973	76.260		

^a Atom distances are in Å and dihedral angles in degrees (MP2/6–31G*).*Atomic charges from NBO analysis for C-2, TS-2 and products (MP2/6–31G* level of theory)*

Structure	C-1	C-2	O-3	H-4	O-5	C-6
C-2	0.626	0.226	−0.790	0.493	−0.614	−0.486
TS-2	0.157	0.715	−0.702	0.477	−0.640	−0.654
Products	0.454	0.661	−0.655	0.200	−0.627	−0.592

Both transition-state structures are twisted four-membered rings. This is in accord to the experimental pre-exponential factor *A* as suggested by Benson and O'Neal.⁸ This means that the experimental $\log A = 13.05$ suggests a four-membered cyclic transition state rather than a radical process. The latter type of decomposition commonly gives $\log A = 8$ –10.

Rate coefficients and Arrhenius pre-exponential factors were determined and compared with experimental values. The results show very good agreement for **TS-2** for MP2/6–31G* and MP2/6–31G** calculations (Table 7), within 1.25, 1.22, 1.21 and 0.46% error for $\Delta H^\ddagger$, E_a , $\Delta G^\ddagger$ and $\Delta S^\ddagger$, respectively, MP2/6–31G* and 2.23, 2.22, 2.20

and 0.09% for MP2/6–31G**. The first-order rate coefficient for **TS-2** is of the same order of magnitude as the experimental value (29% error). Values for **TS-1** are far from the experimental data, therefore **TS-2** is the most reasonable transition state for the reaction path of the gas-phase elimination reaction of 3-hydroxy-3-methyl-2-butanone.

Bond order analysis

To investigate further the nature of the TS along the reaction pathway, bond order calculations were

performed^{9–11} using the **TS-2** structure. Wiberg bond indexes¹² were computed using the natural bond orbital (NBO) program¹³ 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.*,¹⁴ defined by the expression

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

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

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

where the superscripts R, TS and 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

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

Bonds indexes were calculated for those bonds suffering major modifications during the reaction, i.e. C-1—C-2 (*B*₁₂), C-2—O-3 (*B*₂₃), O-3—H-4 (*B*₃₄) and H-4—C-1 (*B*₄₁). The results are given in Table 10. The greatest progress in the reaction coordinate is the breaking of the C-1—C-2 bond.

The synchronicity parameter *Sy* = 0.65 reveals a concerted non-completely synchronic mechanism, where the polarization of the C-1—C-2 bond plays an important role. This is supported by the changes in charges at the C-1 and C-2 atoms as the reaction progress from the reactant to the transition state as described above. Transition state **TS-2** gives the observed products showing more progress in the C-1—C-2 bond breaking than in the transfer of the hydrogen from the hydroxyl to C-1,

Table 10. NBO analysis for MP2/6–31G* calculations^a

	C-1—C-2	C-2—O-3	O-3—H-4	H-4—C-1
<i>B</i> ₁ ^R	0.964	0.671	0.496	0.005
<i>B</i> ₁ ^{TS}	−0.051	0.927	0.293	0.178
<i>%Ev</i>	105.1	38.6	40.9	22.0
<i>dB</i> _{av}		0.517		
<i>Sy</i>		0.655		

^a Wiberg bond indexes (*B*_{*i*}), % evolution through the reaction coordinate (*%Ev*), average bond index variation (*dB*_{av}) and synchronicity parameter (*Sy*) for reaction mechanism (2) are shown.

resulting in a polarized TS. The partial charge on the hydrogen being transferred is positive in the TS. The TS can be described as late in the sense of C-1—C-2 bond breaking but early in the sense of hydrogen transfer. The polarization of the transition state in which C-1—C-2 is almost broken supports a polar molecular mechanism instead of a free radical pathway. These estimations are in accord with the experimental values since this reaction is not affected by radical inhibitors (Table 3).

CONCLUSIONS

Theoretical calculations suggest that the reaction proceeds by a concerted non-synchronous mechanism, through a twisted four-membered transition-state structure. Calculations gave the best results at the MP2/6–31G* and MP2/6–31G** levels of theory. The activation parameters are in agreement with experimental values for the MP2/6–31G* and MP2/6–31G** levels of theory and the first-order reaction rate coefficient is of the same order of magnitude. The suggested transition state, **TS-2**, is late in the sense of C-1—C-2 bond breaking. Structural parameters, natural charges and NBO analysis of the proposed TS suggest that the polarization of the C-1—C-2 bond in the sense CO^{δ−}...C_α(OH)^{δ+} is the determining factor in the decomposition process. The synchronicity parameter *Sy* = 0.65 is in accord with a molecular concerted polar non-synchronic mechanism.

It was demonstrated experimentally that this reaction is molecular in nature, therefore restricted wavefunctions were used for all calculations (RHF, RB3LYP, RMP2). Consequently, calculation problems may arise in this approach if radicals are involved. This was not observed. Moreover, it is known that MP2 tends to stabilize radicals. Even though the best results for activation parameters were obtained with MP2, an alternative mechanism suggested from B3LYP results cannot be ignored.

EXPERIMENTAL

3-Hydroxy-3-methyl-2-butanone. This substrate (Aldrich) of 98.1% purity as determined by GLC (dinonyl phthalate–5% Chromosorb G AW DMCS, 80–100 mesh). The product acetone (Merck) was quantitatively analyzed in the same column. The verification of the identities of substrate and products was carried out by GC–MS (Saturn 2000, Varian) using a DB-5MS capillary column (30 × 0.25 mm i.d., 0.25 μm film thickness).

Kinetic studies. The kinetic experiments were carried out in a static reaction system reported previously^{15–17} with an Omega DP41-TC/DP41-RTD high-temperature performance digital temperature indicator. The reaction vessels were seasoned at all times with allyl bromide and the

process of decomposition was carried out in the presence of the free radical inhibitor toluene. The rate coefficients were determined by quantitative chromatographic analysis of the product acetone. The temperature was controlled by a Shinko DC-PS resistance thermometer controller and an Omega Model SSR280A55 solid-state relay maintained within $\pm 0.2^\circ\text{C}$ and measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was detected along the reaction vessel. The substrate was injected (0.05–0.1 ml) directly into the reaction vessel with a syringe through a silicone-rubber septum.

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