Thermal Decomposition of 4-Hydroxy-2-butanone in *m*-Xylene Solution: Experimental and Computational Study

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Received 30 January 2011; revised 28 April 2011, 20 June 2011; accepted 20 June 2011

DOI 10.1002/kin.20591

ABSTRACT: The mechanism of thermal decomposition of 4-hydroxy-2-butanone in *m*-xylene solution was studied experimentally and theoretically at the M05-2X/6-31G(*d*, *p*) level of theory. It follows first-order kinetics and appears to be homogeneous and unimolecular. The proposed mechanism is via a six-membered cyclic transition state to give a mixture of formaldehyde and acetone. Rate constant values were experimentally determined at three temperatures: 483.15, 493.15, and 503.15 K. Calculated rate constants are of the same order of magnitude than the experimental ones. Calculated Gibbs energies of activation agree very well with the experimental values. Computationally, the progress of the reactions was followed by means of the Wiberg bond index. The results indicate that the transition state has an intermediate character between reactants and products, and the calculated synchronicity shows that the reaction is slightly asynchronous. The bond-breaking processes are more advanced than the bond-forming ones, indicating a bond deficiency in the transition state. © 2012 Wiley Periodicals, Inc. Int J Chem Kinet 44: 407–413, 2012

INTRODUCTION

The mechanism of thermal decomposition of β-hydroxy ketones has been studied in many previous works both in the gas phase and in solution [1–3]. These decompose thermally to give a mixture of aldehydes and/or ketones in a reaction, which is the reverse of the aldol condensation [1]. 4-Hydroxy-4-methyl-2-pentanone was determined in the true

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Contract grant sponsor: Vicerrectoría de Investigación, Universidad Nacional de Colombia.
Tables S1 and S2 with detailed information about the theoretical calculations are available as Supporting Information in the online issue at www.wileyonlinelibrary.com.

homogeneous gas-phase state by Smith and Yates [1]. Additional kinetic studies of two other β-hydroxy ketones, i.e., 4-hydroxy-3-methyl-2-pentanone and 4-hydroxy-2-pentanone, were studied in a xylene solution to examine the influence of the substituted methyl group on the mechanism and velocity [2]. In another work, Chuchani and coworkers [3] probed, under similar conditions, the homogeneous gas-phase pyrolyses of 4-hydroxy-2-butanone, 4-hydroxy-2-pentanone, and 4-hydroxy-4-methyl-2-pentanone, which follow a first-order rate law, and the data were fitted to the Arrhenius equations [3]:

$$\log k\,(\mathrm{s}^{-1}) = (12.18 \pm 0.39) - (150.0 \pm 3.9)\mathrm{kJ}\cdot\mathrm{mol}^{-1}(2.303RT)^{-1} \qquad (1)$$

$$\log k\,(\mathrm{s}^{-1}) = (11.64 \pm 0.28) - (142.1 \pm 2.7)\mathrm{kJ}\cdot\mathrm{mol}^{-1}(2.303RT)^{-1} \qquad (2)$$

$$\log k(\mathrm{s}^{-1}) = (11.36 \pm 0.52) - (133.4 \pm 4.9)\mathrm{kJ}\cdot\mathrm{mol}^{-1}(2.303RT)^{-1} \qquad (3)$$

respectively.

It was proposed that the reaction involves a cyclic six-membered transition state (TS) [4], as shown in Fig. 1, and is similar to that thought to be involved in other thermal decompositions such as the thermolysis of β-hydroxyesters [4–6] ($R_1R_2C(OH)CH_2COOR_3$), β-hydroxyolefins [7,8] ($R_1R_2C(OH)CH_2CH{=}CH_2$), and β-hydroxyacetylenes [9,10] ($R_1R_2C(OH)CH_2C{\equiv}CH$). The experimental results show that these reactions are homogeneous and unimolecular and follow a first-order rate law.

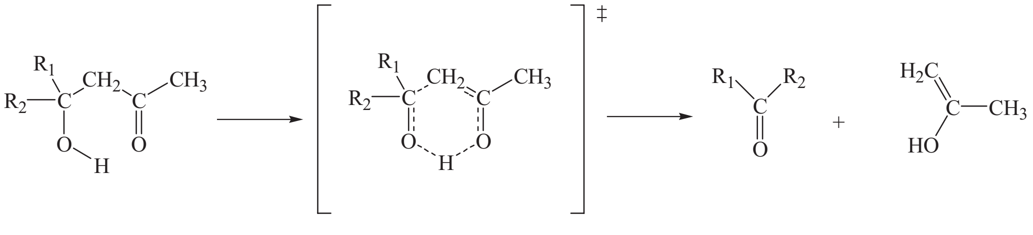
An additional mechanistic study of β-hydroxyketone decomposition was the primary kinetic deuterium effect of 4-deuteroxy-4-methyl-2-pentanone in dilute xylene solutions [11]. The result of the primary isotope effect supported the above mechanism, characterized by partial bonds between the hydroxyl hydrogen and the carbonyl oxygen, and that hydrogen transfer had not a linear path.

This work is another contribution to the kinetic study of β-hydroxy ketones in solution. To our knowledge, kinetic measurements have not been carried out for the thermal decomposition of 4-hydroxy-2-butanone in the m-xylene solution and there are no theoretical studies on this reaction. Also we present an experimental and computational study of the pyrolysis kinetics of this primary β-hydroxy ketone in a temperature range of 483.15–503.15 K.

EXPERIMENTAL PROCEDURE

4-hydroxy-2-butanone was obtained commercially (Aldrich, St. Louis, MO, USA), distilled carefully before use, and its purity was checked by gas chromatography–mass spectrometry (GC-MS) using a DB-WAX column (30 m × 0.25 mm i.d., film thickness 0.25 μm), which is a polyethylene glycol (PEG) column with high polarity.

Thermolysis was carried out in a heated aluminum block, 60 mm length × 60 mm diameter, insulated by glass wool. The block was heated by resistance coil, and its temperature was controlled to ±0.2°C by a Barber–Colman PID (proportional–integral–derivative) temperature controller. The absolute temperature was checked by a chromel–alumel thermocouple. This thermolysis was carried out in a sealed glass ampoule made from carefully washed glass tubes, having 2-mm i.d. and 500-mm length; approximately 50 μL of a solution of β-hydroxyketone (~4% v/v) and toluene as an internal standard (~1% v/v) in m-xylene was injected in the tube. Toluene also served as a free radical inhibitor. The ampoule was then sealed. Twenty capillary tubes were placed in holes drilled in the block, the diameter of holes was such that the tubes fitted precisely, and at determined



R_1, R_2 = H, Me

Figure 1 Mechanism of decomposition of β-hydroxy ketones.

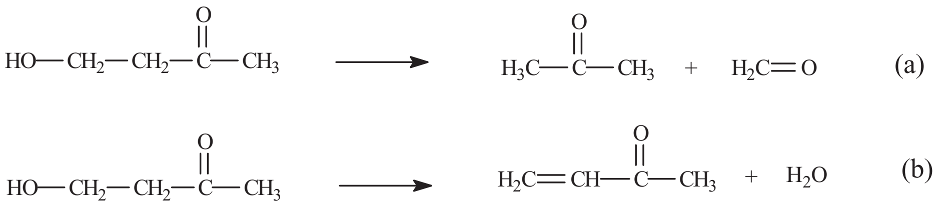


Figure 2 (a) Elimination reaction of 4-hydroxy-2-butanone and (b) dehydration reaction of 4-hydroxy-2-butanone.

intervals the tubes were withdrawn and the amount of acetone produced was determined by gas–liquid chromatography (GLC) as the same of purity check. The rate of decomposition of 4-hydroxy-2-butanone was determined by observing the disappearance rate of 4-hydroxy-2-butanone again by GLC using a DB-WAX column (30 m × 0.25 mm i.d., film thickness 0.25 μm).

COMPUTATIONAL DETAILS

All calculations were carried out using the Gaussian03 computational package [12]. The geometric parameters for all the reactant, TS, and products of the studied reactions were fully optimized using density functional theory [13] with M05-2X [14] functional with the 6-31G(d,p) basis set [15]. A scaling factor [16] of 0.9631 for the zero-point vibrational energies (ZPE) was used. Thermal corrections to enthalpy (TCH) and entropy values were evaluated at the experimental temperatures of 483–503 K. To calculate enthalpy and entropy values at a temperature T, the difference between the values at that temperature and 0 K was evaluated according to standard thermodynamics [17]. M05-2X is a high nonlocally functional with double the amount of nonlocal exchange (2X) that is parameterized only for nonmetals, and it is based on simultaneously optimized exchange and correlation functionals, both including kinetic energy density. It has shown very good performance for applications involving thermochemistry, kinetics, and noncovalent interactions [18], and we have used it with good results in a previous theoretical study [19].

Energies and vibrational frequencies in solution were computed using the integral equation formalism variant of the polarizable continuum model. [20] To simulate *m*-xylene as the solvent interacting with the substrate, a dielectric constant of 2.3478 was used [21].

Full geometry optimizations were followed by analytical calculation of frequencies to determine the nature of the stationary point, i.e. each structure was characterized as a minimum or a saddle point of first order by these calculations.

The bonding characteristics of the reactant, TS, and products were investigated using a population partition technique, the natural bond orbital (NBO) analysis of Reed and Weinhold [22,23]. The analysis was performed using the NBO program [24] implemented in the Gaussian03 package that also provides values for the atomic natural total charges and the Wiberg bond index [25] used to follow the progress of the reaction. We have selected the classical TS theory) [26,27] to calculate the kinetic parameters.

RESULTS AND DISCUSSION

Experimental

The elimination products of 4-hydroxy-2-butanone (Fig. 2a) in *m*-xylene solution were mainly (∼95%) acetone and formaldehyde. The side reaction (∼5%) (Fig. 2b) was not studied in this work. For this reason, and to follow only the main reaction, the amount of acetone as a function of time was obtained by chromatographic analysis.

Good first-order kinetics was observed for the thermolysis of 4-hydroxy-2-butanone, the reaction being followed both by the rate of appearance of the ketone as by the rate of disappearance of the β-hydroxyketone.

The plot of $\log_{10} C/C_0$ was found to be linear to at least three half-lives. No rate constant variation was obtained by using different concentrations of 4-hydroxy-2-butanone in *m*-xylene (in the range of 1%–10% of ester by volume); the reaction was shown to be homogeneous by increasing the surface area of the reaction vessel. Thus, in the case of 4-hydroxy-2-butanone, a rate constant of 0.54×10^{-4} s^{-1} was obtained at 483.15 K in capillary tubes packed with glass wool, with surface area increased by a factor of 4, compared with 0.51×10^{-4} s^{-1} in unpacked tubes.

The Arrhenius plot showed excellent linearity, and the equation is

$$\log k\ (\mathrm{s}^{-1}) = (13.3 \pm 0.01) \\ - (162.3 \pm 0.1)\,\mathrm{kJ \cdot mol^{-1}}\,(2.303RT)^{-1}$$

The rate constants obtained at 483, 493, and 503 K are (0.54 ± 0.02) × 10^{-4}, (1.23 ± 0.01) × 10^{-4}, and (2.70 ± 0.01) × 10^{-4} s^{-1}, respectively.

The differences between the Arrhenius equations obtained in the gas phase and in solution can be observed as increments of both the activation entropy and the activation energy when the system is in the solution; the former is due to the fact that the solvated TS is more rigid than the gas-phase TS because of the solvent interaction, and the latter because the reactant is stabilized or the TS is destabilized due to the interaction with the solvent molecules.

Computational

Electronic energies, E_{el}, zero-point vibrational energies, TCHs, and entropies (S), at three temperatures (483, 493, and 503 K), for the reactant, TS, and products involved in the reaction were studied (see Fig. 3) and were calculated at the M05-2X/6-31G(d,p) level of theory; the results are presented in Table S1 in the Supporting Information. The Cartesian coordinates for all the structures, optimized at the M05-2X/6-31G(d,p) level, are collected in Table S2 in the Supporting Information.

Calculated values of the activation parameters and experimental and calculated rate constants for the thermal decomposition of 4-hydroxy-2-butanone are collected in Table I.

As can be observed from Table I, the calculated rate constants using M05-2X functional are of the same order of magnitude than the experimental ones. With increasing the temperature by 10 K, the rate constant doubles; this fact is in agreement with the Arrhenius equation linearity. The current study confirms the good performance of the M05-2X functional to determinate rate constants. The activation entropy is compatible with a semipolar six-membered cyclic TS postulated for other β-hydroxy compounds; it is negative in all cases, indicating that the TS has less degrees of freedom. Calculated Gibbs energies of activation agree very well with the experimental values.

By comparing the experimental results with the calculated ones, it can be seen that an increment in the calculated rate constant is related to lower activation enthalpies. The differences in these results could be due to the theoretical method applied; probably the continuum model used is not as adequate as other methods like the Multiple Minimum Hypersurface methodology used by some authors to study chemical organic reactions [28,29]. Furthermore, it should be noted that the product obtained from TS is the ketone, both in enol and keto forms. It is known that the keto form

Table I Experimental and Calculated Rate Constants and Activation Parameters of the Thermolysis of 4-Hydroxy-2-butanone in the *m*-Xylene Solution

	k ($\times 10^4 s^{-1}$)		$\Delta S^{\neq}$ ($J \cdot mol^{-1} K^{-1}$)		$\Delta H^{\neq}$ ($kJ \cdot mol^{-1}$)		$\Delta G^{\neq}$ ($kJ \cdot mol^{-1}$)		
T (K)	Experimental	Calculated[a]	Experimental	Calculated[a]	Experimental	Calculated[a]	Experimental	Calculated[a]	Difference (%)
483.15	0.54 ± 0.02	0.3	−2.3	−54.1	166.3	135.9	167.4	162.1	3.2
493.15	1.23 ± 0.01	0.6	−2.5	−54.2	166.4	136.0	167.6	162.8	2.9
503.15	2.70 ± 0.01	1.1	−2.6	−54.4	166.4	136.1	167.8	163.5	2.1

[a] In solution, at level M05-2X/6-31G(d,p).

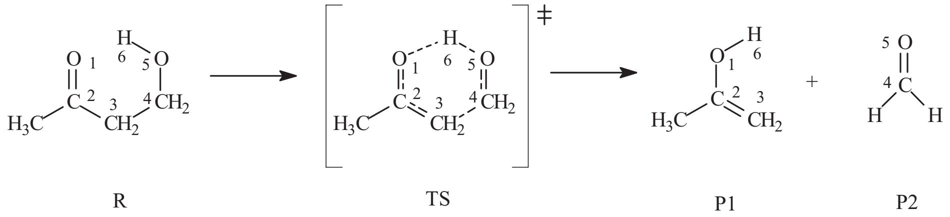


Figure 3 Proposed mechanism of decomposition of 4-hydroxy-2-butanone.

is more stable than the enol form, and therefore it is the experimentally observed. Andrés et al. [30] have suggested that the interconversion of the two forms involves the movement of a proton and the shifting of bonding electrons through a four-membered ring transition structure. The 1,3-intramolecular hydrogen migration is much more advanced than the hybridization changes on donor and acceptor centers at the transition structure. The corresponding barrier heights can be related to the change in bond orders and acid/base properties of these centers. A comparison of the results obtained with different methods made by the authors renders that the nature of the transition structure seems to be a rather robust entity. This may be the reason why the rate constants do not fit quite well.

Because NBO is a powerful tool for understanding and interpreting results from mechanistic studies, the progress of the reaction has been followed, like in other theoretical studies on reaction mechanisms carried out by us [31–34] by means of the Wiberg bond indices [21], B_i. The bond index between two atoms is a measure or the bond order, and hence of the bond strength between these two atoms; thus if the evolution of the bond index corresponding to the bonds being made or broken in a chemical reaction is analyzed along the reaction path, a very precise image of the timing and extent of the bond-breaking and bond-forming processes at every point can be achieved [35].

The Wiberg bond indices corresponding to the bonds involved in the reaction center of the mechanism proposed are collected in Table II.

As it can be seen in Table II, the transformation of the O_1—C_2 double bond into a single one (64.7%) is the most advanced process, followed by the breaking of bonds O_5—H_6 (61.6%) and C_3—C_4 (54.6%), and the formation of the H_6—O_1 single bond (51.3%). The least advanced processes are the formation of double bonds C_2—C_3 (44.2%) and C_4—O_5 (38.5%). The $\delta B_{av} = 0.52$ value indicates that the TS has a character intermediate between reactants and products. Synchronicities

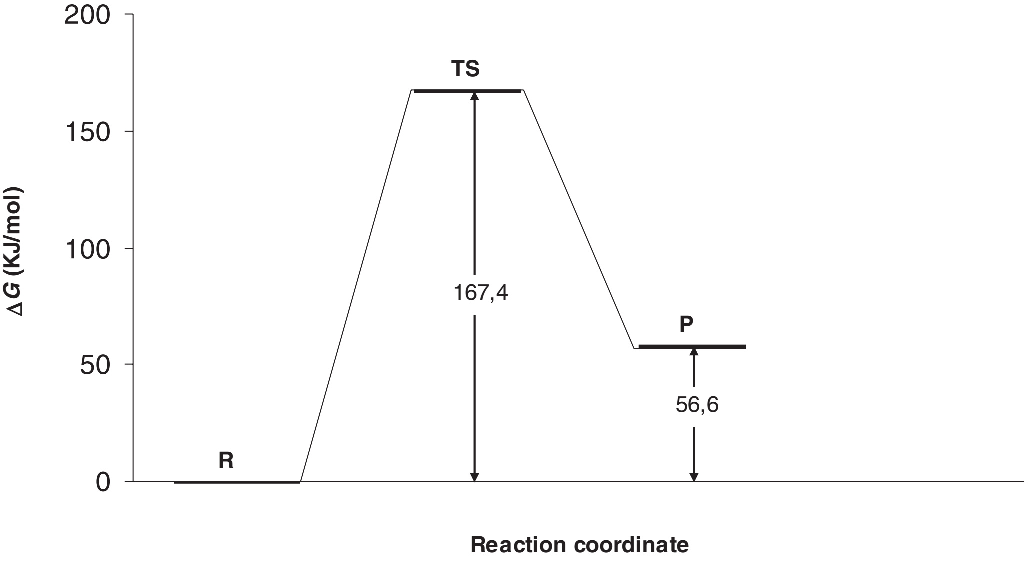


Figure 4 Gibbs energy profile at 483.15 K, evaluated at the M05-2X/6-31G(d,p) level, for the thermal decomposition of 4-hydroxy-2-butanone (first step).

Table II Wiberg bond indices, B_i, of reactant (R), transition state (TS), and products (P)

	O_1—C_2	C_2—C_3	C_3—C_4	C_4—O_5	O_5—H_6	H_6—O_1
B_i^{R}	1.744	0.996	0.980	0.904	0.710	0.015
B_i^{TS}	1.249	1.380	0.445	1.245	0.273	0.376
B_i^{P}	0.979	1.866	0.000	1.789	0.000	0.720
%EV[a]	64.73	44.19	54.62	38.48	61.55	51.28
		δB_{av}^{b}	0.52	Sy^{c}	0.91	

Values are calculated at the M05-2X/6-31G(d,p) level. See Fig. 3 for atom labeling.

[a] Percentage of evolution through the chemical process of the bond rates at the TS, $\%EV = [(B^{TS} - B^{R})/(B^{P} - B^{R})] \times 100$.

[b] Degree of advancement of the TS, $\delta\ B_{av} = ((1/n) \times \%EV)/100$, where n is the number of bonds involved in the reaction.

[c] Absolute synchronicity for the thermolysis of 4-hydroxy-2-butanone in the m-xylene solution (first step), $S_y = 1 - [1/(2n-2) \times \sum(\delta B_{av} - \%EV/100)/\delta B_{av}]$, where n is the number of bonds involved in the reaction.

vary between 0 and 1, which is the case when all of the bonds implicated in the reaction center have broken or formed at exactly the same extent in the TS. The S_y value obtained in this way is, in principle, independent of the degree of advancement of the TS. The synchronicity value is 0.91, indicating that the mechanism corresponds to slightly asynchronous.

The Gibbs energy profile for the thermal decomposition process of 4-hydroxy-2-butanone at 483.15 K is presented in Fig. 4.

CONCLUSIONS

Experimental results on the thermal decomposition in the m-xylene solution of 4-hydroxy-2-butanone show that the reaction is homogeneous, unimolecular, and has first-order kinetics. The theoretical and experimental results indicate that the reaction takes place via a six-membered cyclic TS with a small negative activation entropy. M05-2X/6–31G(d,p)-calculated rate constants are of the same order of magnitude than the experimental ones. Calculated Gibbs energies of activation agree very well with the experimental values.

SUPPORTING INFORMATION

Tables S1 with the M05-2X/6-31G(d,p)-calculated electronic energies, ZPE, TCHs, and entropies, for the reactant, TS, and products involved in all the reaction studied; and Table S2 with the M05-2X/6-31G(d,p)-optimized Cartesian coordinates for all the studied compounds are available in the online issue at www.wileyonlinelibrary.com.

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