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ORIGINAL RESEARCH

Experimental and computational study of the thermal decomposition of 3-buten-1-ol in *m*-xylene solution

Víctor López · Jairo Quijano · Sofía Luna · Pablo Ruiz · Diego Rios · Wilson Parra · Edilma Zapata · Jair Gaviria · Rafael Notario

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Abstract An experimental study of the thermal decomposition of a β-hydroxy alkene, 3-buten-1-ol, in *m*-xylene solution, has been carried out at three different temperatures: 553.15, 573.15, and 593.15 K. The temperature dependence of the rate constants for the decomposition of this compound in the corresponding Arrhenius equation is given by ln k (s^{-1}) = (27.34 ± 1.24)–(19,328 ± 712) (kJ mol^{-1}) T^{-1}. A computational study has been performed at the MP2/6-31+G(*d*) level of theory to calculate the rate constants and the activation parameters by the classical transition state theory. The Arrhenius equation obtained theoretically, ln k (s^{-1}) = (28.252 ± 0.025)–(19,738.0 ± 14.4) (kJ mol^{-1}) T^{-1}, agrees very satisfactorily with the experimental one. The bonding characteristics of reactant, transition state, and products have been investigated by the natural bond orbital analysis which provides the natural atomic charges and the Wiberg bond indices used to follow the progress of the reaction. The enthalpy of the reaction has been calculated using experimental values taken from literature and theoretic calculations. The agreement between both values is satisfactory.

Keywords β-Hydroxy alkenes · 3-Buten-1-ol · Thermal decomposition · Reaction mechanism · Wiberg index

Introduction

The mechanism of the thermal decomposition of β-hydroxy alkenes in the gas phase has been previously studied both experimentally [1–3] and theoretically [4]. They decompose thermally to give a mixture of alkenes and carbonyl compounds, following a first order homogeneous unimolecular reaction [3]:

$$\mathrm{R-CH=CH-CH_2-CR'R''OH} \\ \rightarrow \mathrm{R-CH_2-CH=CH_2+R'R''\ CO} \quad (1)$$

Experimental studies [1] indicate that tertiary alcohols decompose more readily than secondary and primary alcohols. From a study of the products of pyrolysis, Arnold and Smolinsky [2] proposed a mechanism via a six-membered cyclic transition state (TS) (Fig. 1). This cyclic TS is similar to that proposed for the thermal decompositions of the carboxylic esters [5] and β,γ-unsatured acids [6]. Smith and Yates [1] studied the homogeneous gas phase pyrolysis of a β-hydroxy alkene, 3-buten-1-ol, which follows a first order law, and the data could be fitted to the Arrhenius equation:

$$\ln k\left(\mathrm{s}^{-1}\right) = 25.61 - 20547\left(\mathrm{kJ\ mol^{-1}}\right) \cdot T^{-1} \quad (2)$$

A theoretic study of this reaction in the gas phase, at the MP2/6-31G(*d*) and B3LYP/6-31G(*d*) levels, was carried out by us [4] some years ago. We concluded that MP2 method seems to be a better choice than the DFT method to study this reaction.

We have taken up the subject carrying out an experimental study of the thermal decomposition of 3-buten-1-ol

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This article is dedicated to María Victoria Roux on the occasion of her retirement.

V. López (✉) · J. Quijano · S. Luna · P. Ruiz · D. Rios · W. Parra · E. Zapata · J. Gaviria
Laboratorio de Fisicoquímica Orgánica, Facultad de Ciencias, Universidad Nacional de Colombia, Sede Medellín,
AP 3840 Medellín, Colombia
e-mail: valopeza@unal.edu.co

R. Notario
Instituto de Química Física Rocasolano, CSIC, Serrano 119,
28006 Madrid, Spain

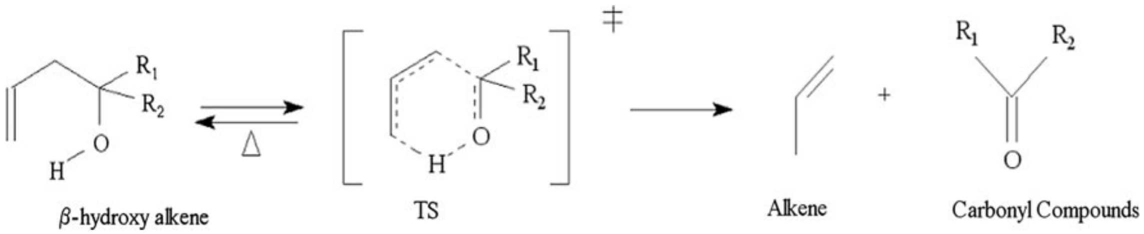

Fig. 1 Mechanism of the thermal decomposition of β-hydroxy alkenes

in *m*-xylene solution within a temperature range of 553.15–593.15 K. *m*-Xylene has been chosen as solvent because it is a low polar solvent adequate for carrying out the thermolysis reaction of this type of compounds, and it has been used previously by us in the experimental study of the thermal decomposition of methyl β-hydroxyesters [7] and 4-hydroxy-2-butanone [8].

A computational study was carried out at the MP2/6-31+G(*d*) level to calculate the rate constants and the activation parameters by the classical transition state theory (TST) [7, 9, 10].

This work is a contribution to the kinetic study of β-hydroxy alkenes in solution. To our knowledge, kinetic measurements have not been carried out for the thermal decomposition of 3-buten-1-ol in *m*-xylene solution and there are no theoretic studies on this reaction.

Experimental procedure

3-Buten-1-ol 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 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 25 μL of a solution of 3-buten-1-ol (~4 % v/v) and benzene as an internal standard (~1 % v/v) in *m*-xylene was injected in the tube. Benzene also served as a free radical inhibitor. The ampoule was then sealed. Sixteen capillary tubes were placed in holes drilled in the block, the diameter of holes was such that the tubes fitted precisely, and at determined intervals the tubes were withdrawn and the amount of propene produced was determined by gas–liquid chromatography (GLC) as the same of purity check. The rate of decomposition of 3-buten-1-ol was determined by observing the disappearance rate by GLC using a DBWAX column (30 m × 0.25 mm i.d., film thickness 0.25 μm).

Computational details

All computational studies were performed by means of the Gaussian 09 computational package [11] by ab initio methods according to how they are implemented in the computational package. The geometric parameters of the reactant, TS, and products of the studied reaction were fully optimized by ab initio analytical gradients post-Hartree–Fock MP2 method [12] with the 6-31+G(*d*) basis set. Each structure was characterized as a minimum or a saddle point of first order by analytical frequency calculations. A scaling factor [13] of 0.9670 for the zero-point vibrational energies has been used. Thermal corrections to enthalpy and entropy values have been evaluated at the experimental temperatures of 553.15, 573.15 and 593.15 K. To calculate enthalpy and entropy values at a temperature *T*, the difference between the values at that temperature and 0 K has been evaluated according to standard thermodynamics [14].

Vibrational frequency calculations were carried out in order to confirm the stationary states, including TS structure. An IRC calculation [15] has been performed to verify that localized TS structure connects with the corresponding minimum stationary points associated with reactant and products.

Energies and vibrational frequencies in solution were computed using the integral equation formalism variant of the polarizable continuum model (IEFPCM) [16]. To simulate *m*-xylene as the solvent interacting with substrate, a dielectric constant of 2.3478 was used [11, 17].

MP2/6-31+G(*d*)-calculated electronic energies, zero-point vibrational energies, thermal corrections to enthalpies, and entropies, for the reactant, TS, and products, involved in the thermal decomposition reaction of 3-buten-1-ol in *m*-xylene solution, are collected in Table 1.

The bonding characteristics of reactant, TS, and products have been investigated by a population partition

Table 1 MP2/6-31+G(*d*)-calculated electronic energies E_{el}, zero-point vibrational energies *ZPE*, and thermal corrections to enthalpies *TCH*, in Hartrees, and entropies *S*, in cal mol^{-1} K^{-1}, for the reactant, TS, and products, involved in the thermal decomposition reaction of 3-buten-1-ol, at 553.15, 573.15, and 593.15 K, in diluted *m*-xylene solution

Structure	E_{elec}	ZPE
3-Buten-1-ol (R)	−231.668033	0.115564
TS	−231.600935	0.110559
Propene (P1)	−117.463579	0.081038
Formaldehyde (P2)	−114.179792	0.027287

	T = 553.15 *K*		*T* = 573.15 *K*		*T* = 593.15 *K*	
Structure	TCH	*S*	TCH	*S*	TCH	*S*
R	0.134866	94.432	0.136070	95.774	0.137304	97.101
TS	0.128332	88.791	0.129497	90.090	0.130693	91.376
P1	0.094064	75.170	0.094843	76.038	0.095641	76.897
P2	0.034975	58.098	0.035323	58.487	0.035678	58.868

technique, the natural bond orbital (NBO) analysis of Read and Weinhold [18, 19]. The NBO formalism provides the values for the atomic natural total charges and also provides the Wiberg bond indices [20] used to follow the progress of the reaction. The NBO analysis has been performed using the NBO program [21] implemented in the Gaussian 09 package [11] and has been carried out on the MP2 charge densities in order to explicitly include electron correlation effects.

We have selected the classical TST [9, 10] to calculate the kinetic parameters. The rate constant, *k*(*T*), of the kinetic scheme (see Fig. 2) was computed by this theory assuming that the transmission coefficient is equal to unity, as expressed by the following relation, known as Eyring-Polanyi equation:

$$k(T) = \frac{k_{\mathrm{B}}T}{h} e^{\frac{-\Delta G^{\neq}(T)}{\mathrm{RT}}} \qquad (3)$$

where k_{B}, *h*, and *R* are the Boltzmann constant, the Planck constant, and the universal gas constant, respectively. $\Delta G^{\neq}(T)$ is the standard-state Gibbs energy of activation, at the absolute temperature *T*.

The activation energy, E_{a}, and the Arrhenius *A* factor have been calculated by Eqs. 4 and 5, respectively, derived from the TST theory:

$$E_{\mathrm{a}} = \Delta H^{\neq}(T) + \mathrm{RT} \qquad (4)$$

$$A = \frac{e k_{\mathrm{B}} T}{h} e^{\frac{\Delta S^{\neq}(T)}{R}} \qquad (5)$$

Results and discussion

Determinations of the rate of decomposition of 3-buten-1-ol in *m*-xylene solution were made at three different temperatures: 553.15, 573.15, and 593.15 K. The reaction was essentially homogeneous and of first order. The measured rate constants at the three temperatures are collected in Table 1. The Arrhenius plot was linear (see Fig. 3), and treating the data by the method of least squares gave E_{a} = (160.7 ± 5.9) kJ mol^{-1} and ln *A* = (27.34 ± 1.24). The enthalpies and entropies of activation calculated from experimental data by Eqs. 4 and 5 are collected in Table 2.

Theoretical calculations at the MP2/6-31+G(*d*) level of theory have been carried out to explore the nature of the mechanism of the thermal decomposition of 3-buten-1-ol, in *m*-xylene solution, the products of the reaction being propene and formaldehyde. The mechanism proposed is a one-step process proceeding through a six-membered cyclic TS (Fig. 2).

The kinetic parameters for the reaction studied have been calculated at the same temperatures used in the experiments, 553.15, 573.15, and 593.15 K. Calculated values of the activation parameters and the rate constants are collected in Table 2, and compared with the experimental ones. There is a very good agreement between the experimental and the calculated values. The Arrhenius plot obtained from theoretic data is drawn in Fig. 3, compared with the experimental plot. As it can be observed, both lines are almost parallel. Values of E_{a} = (164.11 ± 0.12) kJ mol^{-1} and ln *A* = (28.252 ± 0.025) have been calculated in very good agreement with the experimental ones.

The optimized geometry for the TS in the postulated mechanism is shown in Fig. 4. The structure consists in a near planar six-membered ring, in which the hydrogen

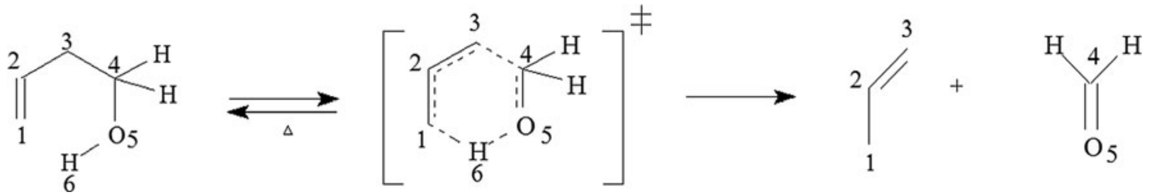

Fig. 2 Proposed mechanism for the thermal decomposition of 3-buten-1-ol

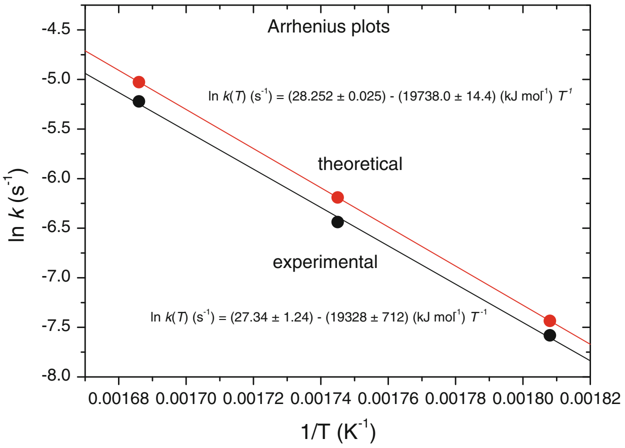

Fig. 3 Arrhenius plots obtained from experimental and calculated data

transfer is approaching to linear angles ($C_1H_6O_5$ angle of 152.0°). There is one and only one imaginary vibrational frequency in the TS, 1133.3i, in *m*-xylene solution, evaluated at the MP2/6-31+G(*d*) level of theory.

The Gibbs energy profile for the thermal decomposition process of 3-buten-1-ol, at 573.15 K, is presented in Fig. 5.

To avoid the subjective aspects associated with the geometrical analysis of the TS, the progress of the reaction has been followed by means of the Wiberg bond indices B_i [20]. The bond index between two atoms is a measure of the bond order, and hence, of the bond strength between these two atoms; thus, if the evolution of the bond indices 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.

The Wiberg bond indices, corresponding to the bonds involved in the reaction center of the mechanism for all the reactant, TS, and products, are shown in Table 3.

Moyano et al. [22] have defined a relative variation of the bond index at the TS, δB_i, for every bond i, involved in a chemical reaction as

$$\delta B_i = \frac{(B_i^{TS} - B_i^{R})}{(B_i^{P} - B_i^{R})} \tag{6}$$

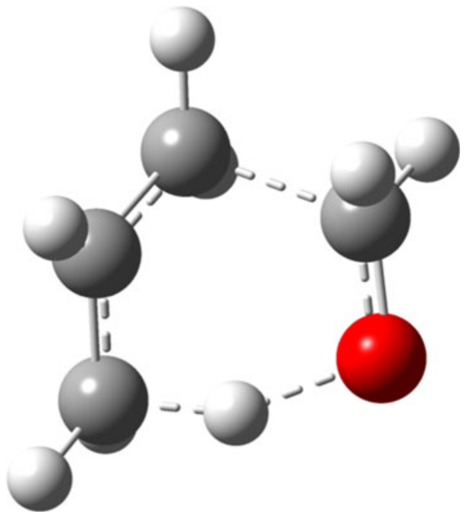

Fig. 4 MP2/6-31+G(*d*)-optimized structure of the TS of the mechanism proposed in Fig. 2

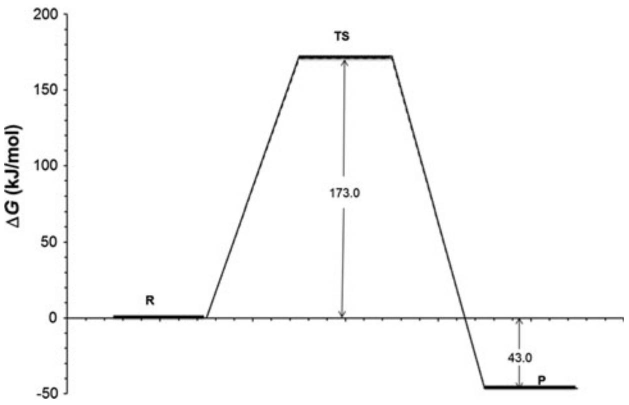

Fig. 5 Gibbs energy profile at 573.15 K, evaluated at the MP2/6-31+G(*d*) level, for the thermal decomposition of 3-buten-1-ol

where the superscripts R, TS, and P refer to reactant, TS, and product, respectively. The calculated percentages of evolution (%EV = 100 δB_i) of the bonds involved in the reaction center are shown in Table 2. As it can be seen, the breaking of the C_1–C_2 double bond (72.7 %) is the most advanced process and the H_6 displacement from O_5 to C_1 is very advanced, the O_5–H_6 bond is almost broken (69.3 %), while the H_6–C_1 bond is less advanced (58.5 %).

Table 2 Experimental and calculated[a] rate constants and activation parameters of the thermolysis of 3-buten-1-ol in *m*-xylene solution

T (K)	10^3 k (s^{-1})		$\Delta S^{\neq}$ (J mol^{-1} K^{-1})		$\Delta H^{\neq}$ (kJ mol^{-1})		$\Delta G^{\neq}$ (kJ mol^{-1})	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
553.15	0.51	0.59	−31.06	−23.60	156.10	159.44	173.28	172.50
573.15	1.60	2.05	−31.36	−23.78	155.93	159.34	173.90	172.97
593.15	5.40	6.56	−31.64	−25.95	155.77	159.24	174.54	173.45

[a] At the MP2/6-31+G(*d*) level of theory

Table 3 Wiberg bond indices (B_i), of reactant (R), transition state (TS) and products (P)

	C_1–C_2	C_2–C_3	C_3–C_4	C_4–O_5	O_5–H_6	C_1–H_6
β_i^R	1.985	1.026	1.003	0.912	0.723	0.004
β_i^{TS}	1.299	1.395	0.569	1.263	0.222	0.549
β_i^P	1.042	1.987	0.000	1.834	0.000	0.936
%EV	72.7	38.4	43.3	38.1	69.3	58.5
		$\delta\beta_{av} = 0.53$		Sy = 0.85		

The lengthening of the C_1–C_2 bond with the initial migration of the H_6 atom from O_5 to C_1 can be seen as the driving force for the studied reaction.

The average value, δB_{av}, is calculated as [22]

$$\delta B_{av} = \frac{1}{n}\sum \delta B_i \tag{7}$$

with n being the number of bonds involved in the reaction and it measures the degree of advancement of the TS along the reaction path. Calculated δB_{av} value for the mechanism of the studied reaction is shown in Table 2. The δB_{av} values calculated, 0.53, shows that the TS is slightly "advanced," nearer to the products than to the reactants.

The synchronicity, Sy, of a chemical reaction can be calculated as

$$\mathrm{Sy} = 1 - A \tag{8}$$

A being the asynchronicity calculated by the expression proposed by Moyano et al. [22]:

$$A = \frac{1}{(2n-2)}\sum \frac{|\delta B_i - \delta B_{av}|}{\delta B_{av}} \tag{9}$$

Synchronicities 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 Sy values obtained in this way are, in principle, independent of the degree of advancement of the TS. The Sy value calculated for the reaction studied is shown in Table 2. Calculated synchronicity value (0.85) is not very high, indicating that the mechanism does not correspond to a concerted and highly synchronous process.

Another aspect to be taken into account is the relative asynchronicity of the bond-breaking and bond-forming processes that measures the bond deficiency along the reaction path. In the studied reaction, the bond-breaking processes are more advanced (an average value of ca. 62 %) than the bond-forming processes (an average value of ca. 45 %), indicating a bond deficiency in the TS.

The trend in the degree of bond lengthening is mirrored in the NBO atomic charges. In Table 4, we have collected the natural atomic charges (the nuclear charges minus the summed natural populations of the natural atomic orbitals on the atoms) of the atoms involved in the reaction center of the postulated mechanism for the reaction (see Fig. 2). There is an important positive charge developed on H_6 (+0.507 in the reactant, and +0.406 in the TS), whereas the electronic excess is supported by the O atom and the C_1 and C_3 carbon atoms. The strong negative character of C_1 atom (−0.441 in the reactant, and −0.771 in the TS) allows it to attract the H_6 atom in the TS.

Table 4 NBO charges, calculated at the MP2/6-31+G(*d*) level, at the atoms involved in the reaction

	C_1	C_2	C_3	C_4	O_5	H_6
R	−0.441	−0.224	−0.501	−0.047	−0.837	0.507
TS	−0.771	0.043	−0.581	0.105	−0.838	0.406

Some years ago, we measured [23] the enthalpy of formation in the gas phase of 3-buten-1-ol. Using this value, −(147.3 ± 1.8) kJ mol^{-1}, and the experimental enthalpies of formation of propene and formaldehyde, taken from literature [24], (20.0 ± 0.7) and −(108.6 ± 0.5) kJ mol^{-1}, respectively, a value of (58.7 ± 2.0) kJ mol^{-1} is calculated for the enthalpy of decomposition reaction of 3-buten-1-ol in the gas phase. By means of the theoretical calculations at the MP2/6-31+G(*d*) level a value of 52.0 kJ mol^{-1} is obtained in a reasonable agreement with the experimental one.

Summary

The thermal decomposition of 3-buten-1-ol has been theoretically studied at the MP2/6-31+G(*d*) level of theory. The mechanism proposed is a one-step process proceeding through a six-membered cyclic TS. The agreement between experimental and calculated kinetic parameters is reasonable.

The progress of the reactions has been followed by means of the Wiberg bond indices. The lengthening of the C_1–C_2 bond with the initial migration of the H_6 atom from O_5 to C_1 can be seen as the driving force for the studied reaction. Calculated synchronicity value indicates that the mechanism does not correspond to a concerted and highly synchronous process. The TS is slightly "advanced," nearer to the products than to the reactants.

The enthalpy of the reaction studied has been calculated using experimental values taken from literature and theoretical calculations. The agreement between both values is satisfactory.

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