A theoretical study of the $\dot{\text{H}}$ - and $\text{HO}\dot{\text{O}}$ -assisted propen-2-ol tautomerizations: reactive systems to evaluate collision efficiency definitions on chemically activated reactions using SS-QRRK theory

E. Grajales-González*, M. Monge-Palacios, S. Mani Sarathy

King Abdullah University of Science and Technology, Clean Combustion Research Center,
Physical Sciences and Engineering Division, Thuwal, Saudi Arabia

* Corresponding author

E-mail address: edwing.grajalesgonzalez@kaust.edu.sa

Abstract. In combustion, enols can undergo keto-enol tautomerizations, which are intermediate steps in the formation of pollutant species. In this work, we performed a theoretical kinetic study of the step-wise propen-2-ol tautomerization catalyzed by hydrogen and hydroperoxyl radicals. Ab initio calculations at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ level were run, and rate constants were calculated using the multistructural torsional variational transition state theory with

small-curvature tunneling corrections. Hydrogen and hydroperoxyl radicals can induce a step-wise mechanism toward keto formation with a lower barrier than that of unimolecular tautomerization. The potential energy surface comprising these reactions is complex, involving different intermediates that are connected by different types of pathways. The hydrogen-assisted tautomerization consists of two steps where the formation of an intermediate radical takes place as a result of the addition of the hydrogen atom to the double bond of propen-2-ol. The high-pressure limit rate constants of the reactions of this intermediate radical toward propen-2-ol and acetone exhibit an Arrhenius behavior, in agreement with previous works. In the hydroperoxyl-assisted tautomerization, the acetone formation has two routes involving an overall of four steps. The route with the highest energy barrier becomes prominent above 800 K due to multistructural anharmonicity effects, which must be included for an accurate kinetic description of the titled reactions. Calculations of pressure-dependent rate constants showed that the original system-specific quantum Rice-Ramsperger-Kassel theory, together with the modified strong collision model (SS-QRRK/MS-C), significantly underpredict the bimolecular stabilization rate constants for the hydrogen-assisted tautomerization above 1200 K by factors of up to three orders of magnitude when compared with the benchmark Rice-Ramsperger-Kassel-Markus/master equation method. To solve this problem, we tested two alternative definitions of the collision efficiency parameter by using an improved implementation of the SS-QRRK/MS-C approach developed by us for chemically activated reactions. One of these definitions, provided by Gilbert et al. (1983), corrected the bimolecular stabilization rate constant behavior and yielded a maximum deviation factor of only 4.5 at 2000 K and 100 atm. For the hydroperoxyl-assisted tautomerization, pressure effects are negligible because the stabilization of the energized adduct cannot compete with the reaction for the production of the final product for most of the physical conditions studied. Our

calculated rate constants can be used to perform more accurate kinetic modeling of alcohols. Besides, the implementation of the SS-QRRK theory with the collision efficiency of Gilbert et al. (1983) proposed in this work is useful for computing pressure-dependent rate constants of chemically activated reactions, including all possible refinements (multi-dimensional tunneling, multistructural anharmonicity, etc.) considered in the calculation of high-pressure limit rate constants.

Keywords: Transition state theory; Keto-enol tautomerization; Chemically activated reactions; System-specific QRRK; RRKM/ME; Collision efficiency.

1. Introduction

Bio-alcohols such as bio-ethanol and bio-butanol are promising alternatives to petroleum-based transportation fuels because of their liquid nature, potential for climate change mitigation [1], and broad range of applications [2]. For this purpose, detailed knowledge of their reaction mechanisms under combustion conditions is necessary.

Although experimental evidence has shown that compression ignition and spark ignition engines can use alcohols as fuels with minor modifications, their combustion chemistry is less understood than that of petroleum-derived transportation fuels [2]. Therefore, efforts have been conducted to unravel dominant routes in alcohol combustion chemistry. Above 1000 K, which are frequent combustion temperatures, vast and diverse radical pools predominantly undergo decomposition to form unsaturated bonds [3]. As a result, saturated alcohols can produce enols by β -scission reactions [4], and the pioneering work of Taatjes et al. [5] detected these species in appreciable concentrations in flames of not only alcohols but also hydrocarbons. Ever since (after 2005), these

unsaturated alcohols represent an essential part of many gas-phase reactive systems that range from atmospheric [6] to the interstellar environments [7]. Among all possible reactive routes of enols, of especial interest are the keto-enol tautomerizations that lead to carbonyl compounds, such as acetone and formaldehyde, since they represent environmental and health problems due to their toxicity and propensity to form urban smog [2,3].

Several interesting theoretical studies have been performed on gas-phase keto-enol tautomerization, such as that of da Silva et al. [8]. They found that the unimolecular tautomerization of vinyl alcohol has a considerable energy barrier of $233.9 \text{ kJ mol}^{-1}$, which is possible to overcome at combustion conditions. In subsequent works, da Silva et al. [9,10] studied the stepwise mechanism of hydroperoxyl-assisted vinyl alcohol tautomerization to produce acetaldehyde. The authors found a lower energy barrier (29.3 kJ mol^{-1}) with catalytic effects present only at high concentrations of the hydroperoxyl radical. Zádor et al. [11] explored the potential energy surface (PES) of the propene plus hydroxyl radical reactive system finding the path of propen-2-ol to acetone in a process assisted by the hydrogen radical, a reaction that displays in a first step a barrier height of $12.13 \text{ kJ mol}^{-1}$. Hansen et al. [12] highlighted the importance of $\dot{\text{H}}$ -atom catalyzed keto-enol tautomerization reactions.

Because many kinetic models use vinyl alcohol reactions as an analogue to those of larger enols, and due to the relevance of the keto-enol species in combustion applications [5], some of our previous theoretical works focused on the keto-enol tautomerizations of propen-2-ol, 1-propenol, and vinyl alcohol to their respective ketones. We have investigated unimolecular tautomerization [13], formic acid assisted tautomerization [14], and a novel concerted pathway assisted by hydroperoxyl radical via a double hydrogen atom transfer [15]. Concentration profile simulations of relevant species showed marked differences when our calculated rate constants for those

tautomerizations are implemented, indicating the necessity for such studies in reducing uncertainties in chemical kinetic models of alcohols.

Although high-pressure limit (HPL) rate constants help reduce uncertainties in kinetic modeling, pressure effects also play a significant role in combustion [16,17]. Rice-Ramsperger-Kassel-Markus/master equation (RRKM/ME) simulations are the state-of-the-art for estimating pressure effects; however, the recently developed system-specific quantum Rice-Ramsperger-Kassel (SS-QRRK) theory [18,19] - together with the modified strong collision (MSC) model – is also a convenient tool in many circumstances. The SS-QRRK/MSC methodology is not as rigorous as RRKM/ME, but is computationally inexpensive (suitable for a fast initial screening before performing more sophisticated calculations, such as RRKM/ME), does not require information of the saddle point, and readily incorporates variational effects, multidimensional tunneling, and multistructural torsional anharmonicity from the pre-computed HPL rate constants [20].

Despite the advantages of the SS-QRRK/MSC method, its original formulation underpredicts the values of pressure-dependent rate constants for reactive systems involving large molecules and at high temperatures. In our previous work [21], we reduced these underestimations of pressure effects when dealing with thermally activated reactions (reaction type $A \rightarrow B$) by implementing two alternative definitions for the collision efficiency, which refer to the work of Gilbert et al. [22] and Dean et al. [23,24]. However, chemically activated reactions (reaction type $A+B \rightarrow AB^* \rightarrow P$) were not addressed.

In this work, we conducted a theoretical kinetic study of the propen-2-ol tautomerization to acetone in gas-phase assisted by hydrogen and hydroperoxyl radicals (hereafter $\dot{H}$ -assisted and $HO\dot{O}$ -assisted, respectively) in stepwise mechanisms. To our knowledge, the latter has not been studied previously. Since the first step of each tautomerization entails a bimolecular reaction, they

offered a suitable scenario to also address the underestimation of chemically activated rate constants derived from the original SS-QRRK/MSM formulation. To achieve this goal, we tested the same collision efficiency definitions that were successfully implemented for thermally activated reactions in our previous work [21].

2. Theoretical methodology

2.1. Potential energy surface and high-pressure limit rate constants

Electronic structure calculations were performed at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ level of theory using the Gaussian09 package [25] to explore the PESs of the following overall reactions:

where $\text{CH}_2=\text{C}(\text{OH})\text{CH}_3$ and CH_3COCH_3 are, respectively, propen-2-ol and acetone. The elementary steps for the $\dot{\text{H}}$ -assisted tautomerization (R1) are:

and those for the $\text{HO}\dot{\text{O}}$ -assisted tautomerization (R2), displaying the two different routes found for the production of acetone, are:

For the sake of clarity, each species is assigned a label which is associated with the species shown in Fig. S1 (global minimum structures) of the Supplementary Material (SM); the labels over the arrows belong to saddle point species. The PESs of these reactions are shown in Fig. 1. R1. 1 is the hydrogen addition to the primary carbon of the double bond of propen-2-ol. R1. 2 refers to the hydrogen elimination from the hydroxyl group of the species formed in R1. 1 to form acetone. R2. 1 is a concerted step where the hydroperoxyl radical is added simultaneously to the two unsaturated carbon atoms of the reactant propen-2-ol. R2. 2 corresponds to the elimination of hydroperoxyl radical of the intermediate species formed in R2. 1 to produce acetone. R2. 3 is the addition of the hydroperoxyl radical to the carbon attached to the hydroxyl group in propen-2-ol. Finally, R2. 4 exemplifies an internal hydrogen shift to form the same intermediate as that produced in R2. 1 but from the intermediate formed in R2. 3.

Geometry optimizations and frequencies calculations used the M06-2X method [26] and the cc-pVTZ basis set [27]; the energy was refined using the CCSD(T) coupled-cluster method [28] with the aug-cc-pVTZ basis set [27].

The minimum energy paths and variational transition state rate constants (CVT) were calculated with the Gausrate-2016 [29] and Polyrate 2016-A [30] codes, respectively. The effect of the multiple conformers (multistructural anharmonicity) was included by using multistructural rovibrational partition functions with a coupled torsional potential and torsional anharmonicity corrections, MS-T(C) [31,32], using the MSTor program [33] with scaled frequencies [34]. Within this scheme, the term “conformers” refers to distinguishable structures that can be converted into each other by internal rotations. Tunneling effect was estimated with the small-curvature tunneling (SCT) approach. Further details on these calculations are provided in Section 1 of the SM.

2.2. Pressure-dependent rate constants computations using the original SS-QRRK/MSCF formulation

The reaction paths illustrated by Fig. 1(a) and the first route of Fig. 1(b) (marked with the green dashed line) embody a chemically activated mechanism of two-step reactions, which have the following scheme:

Scheme 1. Chemically activated mechanism of two-step reactions.

In Scheme 1, AB^* is the energized adduct formed by the association of the reactants A and B in the entrance channel, AB is the stabilized adduct generated by the collisions between AB^* and the bath gas M , and P is the product of the reaction of AB^* . k_{add} is the rate constant of formation of the energized adduct, which is pressure independent and corresponds to the HPL rate constant of the bimolecular reaction, k_{diss} stands for the rate constant of dissociation of the energized adduct back to the reactants, k_{deac} holds for the de-activation collisional rate constant of AB^* , and k_{con} is the rate constant for the formation of the products from AB^* . Henceforth, k_p , k_{stab} , and k_{rev} denote the rate constants of formation of the product from the reactants ($A + B \rightarrow P$), the bimolecular stabilization rate constant ($A + B \rightarrow AB$), and the overall rate constant of dissociation back to the reactants (partial flux of k_{add} that does not lead to new species), respectively.

The chemically activated rate constants for the $\dot{\text{H}}$ -assisted tautomerization were computed initially using the SS-QRRK theory with the MSC model suggested for its application [18,19]. This original implementation is denoted hereafter as the SS-QRRK/MSC approach and was executed in this work by a bespoke Python [35] code. We used the Lennard-Jones parameters of n-propanol, $\sigma = 4.549 \text{ \AA}$ and $\varepsilon/k_b = 576.7 \text{ K}$, for the intermediate radical formed after the addition of the $\dot{\text{H}}$ atom (species C in Fig. 1). Nitrogen was the bath gas with Lennard-Jones parameters $\sigma = 3.798 \text{ \AA}$ and $\varepsilon/k_b = 71.4 \text{ K}$ [36]. The averaged de-activation energy transferred was estimated by the expression $\alpha = \Theta(T/300)^n$, where $\Theta = 200 \text{ cm}^{-1}$ and $n = 0.85$. The energy parameters just presented and scaled frequencies were used in all subsequent pressure-dependent calculations, including those of the RRKM/ME method.

2.3. *Alternative collision efficiency definitions*

Initial calculations for the chemically activated $\dot{\text{H}}$ -assisted tautomerization using the original SS-QRRK/MSC approach [18,19] displayed an underestimation of the bimolecular stabilization rate constant k_{stab} , similar to the underestimation of pressure-dependent rate constants of thermally activated reactions previously corrected [21]. The following paragraphs provide a brief description of such correction; for a more detailed discussion of the topic, the reader is referred to the original publication [21].

Our solution to the underestimation of thermally activated rate constants was to implement two alternative definitions of collision efficiency, a parameter that pertains to the MSC model. Shortly, the collision efficiency definition used in the original SS-QRRK/MSC approach is:

$$\beta_c = \left(\frac{\alpha}{\alpha + F_E k_B T} \right)^2 \quad (1)$$

where α is the average energy transferred during the de-activation process, F_E stands for the normalized number of unimolecular states above the threshold energy in the energized adduct, k_B is the Boltzmann constant, and T corresponds to the temperature. The two alternative definitions of the collision efficiency take the following general form:

$$\beta_{c,\Delta} = \left(\frac{\alpha}{\alpha + F_E k_B T} \right)^2 \frac{1}{\Delta} \quad (2)$$

where Δ denotes a correction factor, which defines the new collision efficiency $\beta_{c,\Delta}$. One collision efficiency definition – namely, a correction factor - belongs to the work of Gilbert et al. [22]:

$$\Delta = \int_0^{E_0} f(E) \left[1 - \frac{F_E k_B T}{\alpha + F_E k_B T} \exp\left(-\frac{E_0 - E}{F_E k_B T}\right) \right] dE \quad (3)$$

with E_0 as the Tolman activation energy or energy threshold that under the framework of the SS-QRRK theory is temperature-dependent, and $f(E)$ is the collision model. The second collision efficiency definition tested was explicitly proposed by Dean et al. [23,24]:

$$\Delta = \Delta_1 - \left(\frac{F_E k_B T}{\alpha + F_E k_B T} \right) \Delta_2 \quad (4)$$

Because of the usefulness of the collision efficiency definition given by Eqs. (3) and (4) when estimating pressure effects for thermally activated reactions [21,37], we tested in this work the same relations to alleviate the underestimation of pressure-dependent rate constants in chemically activated processes. Two methods were tested, which resulted from the SS-QRRK theory [18,19] combined with the MSC model adopting the collision efficiency definitions of Eqs. (3) and (4); hereafter, the two methods are denoted as the SS-QRRK/MSC-GCA and SS-QRRK/MSC-DCA approaches, respectively. A new Python [35] code implements these two approaches to tackle chemically activated processes and it is provided with the SM.

As indicated in Section 2.4, two sets of results were obtained for the $\dot{\text{H}}$ - and $\text{HO}\dot{\text{O}}$ -assisted tautomerizations. One set includes HPL rate constants with all the refinements mentioned in Section 2.1 (variational effects, SCT corrections, and multistructural torsional anharmonicity), and the other set includes HPL rate constants considering only TST, which were necessary to compare with RRKM/ME results.

The second route of the $\text{HO}\dot{\text{O}}$ -assisted propen-2-ol tautomerization (depicted with the purple dashed line in Fig. 1(b)) entails thermally activated processes. Therefore, their low pressure rate constants were computed following the indications given in our previous work [21], that is, with the implementation of a modified version of the original SS-QRRK/MS approach, referred to as SS-QRRK/MS-Dean, where the collision efficiency definition of Dean et al. [23,24] (Eq. (4)) is used.

2.4. Comparison with the benchmark RRKM/ME pressure-dependent calculations

To evaluate the accuracy of the original and proposed SS-QRRK/MS approaches, we compared their results with the more sophisticated RRKM/ME computations performed for the $\dot{\text{H}}$ -assisted and $\text{HO}\dot{\text{O}}$ -assisted propen-2-ol tautomerizations. The pressure-dependent computations carried out for comparison purposes consider only TST rate constants, that is, excluding variational effects, tunneling and multistructural torsional anharmonicity (improvements described in Section 2.1). Including these effects in RRKM/ME calculations requires considerable extra effort [20], and are not pursued in the current work.

RRKM/ME calculations were performed with MultiWell software [38,39] running $5 \cdot 10^7$ stochastic trajectories for each physical condition and adopting the exponential collision model. The number of states of each adduct (species C and H in Fig. 1) and saddle point (species B, D, G,

and I, also shown in Fig. 1) was obtained with the complete sum option. Energy and rotational data were obtained from quantum computations using Gaussian09 software [25], as described in Section 2.1.

3. Results and discussion

3.1. Stationary points

All conformers of the reactants, saddle points, and products of the studied reactions were optimized and characterized at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ level. The Cartesian coordinate matrix, potential energy, and zero point energy (ZPE) of all the optimized structures are given in Section 2 of the SM; the global minima of each species, with their corresponding number of distinguishable conformers and the imaginary frequency of the saddle points indicated in parenthesis, are also provided in the SM (Fig. S1).

3.2. Potential energy profiles

The adiabatic (harmonic ZPE corrected) potential energy profiles of reactions R1 and R2 are plotted, respectively, in Fig. 1(a) and Fig. 1(b) displaying the global minimum of each species, whose energy is defined with respect to that of the reactants.

The $\dot{\text{H}}$ -assisted tautomerization globally consists of an exothermic process with an enthalpy of reaction of $-50.12 \text{ kJ mol}^{-1}$. The first step, reaction R1. 1, is very exothermic with an enthalpy of reaction of $-143.95 \text{ kJ mol}^{-1}$ and a saddle point displaying a relatively low barrier with 6.04 kJ mol^{-1} . There are minor differences with the work of Zádor et al. [11], who reported a barrier height for R1. 1 of $12.13 \text{ kJ mol}^{-1}$ using the RQCISD(T)/cc-pV ∞ Z//B3LYP/6-311++G(d,p) level of theory. The adiabatic energies for the rest of the stationary points are similar with reported values of -

141.84, -7.11, and -48.95 kJ mol⁻¹ [11] for the intermediate radical (C), second saddle point (D), and acetone plus hydrogen radical (E + $\dot{\text{H}}$), respectively.

The second step (R1. 2) presents a barrier height of 136.83 kJ mol⁻¹ for the forward processes which is endothermic with a heat of reaction of 93.83 kJ mol⁻¹. This barrier height computed for the $\dot{\text{H}}$ -assisted tautomerization is in relatively good agreement with those reported by Huynh et al. [40], who calculated forward and reverse barrier heights of 124.26 kJ mol⁻¹ and 52.3 kJ mol⁻¹, respectively, at the CCSD(T)/cc-pVDZ//B3LYP//cc-pVTZ level of theory.

The overall HO $\dot{\text{O}}$ -assisted tautomerization is also exothermic with the same value of enthalpy of reaction than that of the $\dot{\text{H}}$ -assisted process. Besides the double hydrogen atom transfer concerted mechanism previously described [15], there are two possible stepwise routes for this reaction.

Fig. 1. CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ adiabatic potential energy profile of the reactions R1 (a) and R2 (b) defined with the global minimum structures of each stationary point.

Blue: minimum species, Red: saddle point species. Green and purple dashed lines in (b) are different routes to the same products. Species F and J are intermediate complexes.

The first route (R2. 1, dashed green line) implies the formation of a non-bonded intermediate complex propen-2-ol $\cdots$ HO $\dot{O}$ (species F) stabilized by $-23.55\text{ kJ mol}^{-1}$. The saddle point G, with a barrier height of 22.10 kJ mol^{-1} , is the bottleneck of this route and leads to the intermediate radical species H which lies at $-107.39\text{ kJ mol}^{-1}$. This radical species H is also formed by the second route (dashed purple line). It should be also noted that the intermediate complex labeled in this work as F is the same OH $\cdots\pi$ hydrogen bond complex characterized in [15], which lies in the entry channel of the double hydrogen atom transfer concerted mechanism we described in that work; this indicates the complex network of reactions and routes that the HO $\dot{O}$ -assisted tautomerization of propen-2-ol can go through.

In the first step of the second route (R2. 3) a first bottleneck of 39.91 kJ mol^{-1} (species K), which is 17.8 kJ mol^{-1} higher than the energy of the saddle point of the first route (species G), has to be overcome. However, species K has twenty-two conformers (species G only has four), and therefore more pathways through this saddle point may become accessible; this fact may make the second route competitive with respect to the first one even though it is not energetically favored, as will be discussed later. The second step of the second route (R2. 4) can be rate limiting since the corresponding saddle point (species M with only four conformers) lies at 46.68 kJ mol^{-1} , with a barrier height of 79.01 kJ mol^{-1} with respect to the intermediate L. In addition, the species L has thirty-two conformers, which may favor the availability of reactant-like states thereby decreasing reactivity. After passing the saddle point represented by the species I (R2. 2), with a barrier height of 46.82 kJ mol^{-1} with respect to the intermediate H, an acetone $\cdots$ HO $\dot{O}$ non-bonded intermediate

complex (species J) is formed, which leads finally to the acetone and HO $\dot{\text{O}}$ products (E+ HO $\dot{\text{O}}$) through an endothermic process with a heat of reaction of 57.27 kJ mol⁻¹.

We did not find references in the literature for the PES of reaction R2; similar works, albeit describing the paths of the reaction between vinyl alcohol and HO $\dot{\text{O}}$ are available [9,10], and therefore are commonly used as an analogy to reaction R2. However, the energy profiles of both reactions are remarkably different. For instance, the equivalent saddle point G for vinyl alcohol and HO $\dot{\text{O}}$ reaction is 17.23 kJ mol⁻¹ [9] higher in energy. Similarly, for the equivalent second route of the vinyl alcohol and HO $\dot{\text{O}}$ PES, saddle points that are 17.83 and 18.67 kJ mol⁻¹ [9] less stabilized than those reported in this work were found. Furthermore, the overall enthalpy of reaction for the referenced study is 19.58 kJ mol⁻¹ less exothermic. These differences may result in an underestimation of the role of the propen-2-ol + HO $\dot{\text{O}}$ tautomerization if the analogy of vinyl alcohol + HO $\dot{\text{O}}$ is employed in kinetic modelling.

To explain the observed differences, we took as reference the reaction R2. 3 and recomputed its energy barrier with the composite method G3B3 [9]. In this calculation, we use the global minimum of the saddle point K and a conformation similar to that reported for the corresponding reaction of the vinyl alcohol [9]. The new energy barriers were 38.47 and 51.36 kJ mol⁻¹, which are 1.44 kJ mol⁻¹ lower and 11.45 kJ mol⁻¹ higher, respectively than that shown in Fig. 1(b). In this case, the different levels of theory have a slight influence on the energy profile. On the other hand, the conformational space strongly influences the PESs of the HO $\dot{\text{O}}$ -assisted tautomerizations of propen-2-ol and vinyl alcohol. Because for vinyl alcohol, we did not find an “equivalent” structure to the minimum of the saddle point K, we hypothesize that the methyl group allows propen-2-ol to adopt different and more relaxed conformations, which reduces the energy barrier of the associated reactions. However, further calculations would be necessary to validate this

observation. With the G3B3 computations considering the alternative conformer (not the minima of the species K), the differences with respect to vinyl alcohol reaction reduced from 17.83 to 6.18 kJ mol⁻¹ (equivalently reduced by 11.45 kJ mol⁻¹), a remaining gap that could be associated with more specific stabilizing roles of the methyl group.

3.3. Multistructural anharmonicity

The multistructural anharmonicity factors ($F^{MS-T(C)}$), as defined in Section 1 of the SM, of some of the steps of the HO $\ddot{O}$ -assisted tautomerization are shown in Fig. 2. Those for the $\dot{H}$ -assisted tautomerization are not discussed as the conformational space of its stationary points is reduced. All the $F^{MS-T(C)}$ factors are tabulated in the SM, together with a discussion of the torsional anharmonicity effects (Section 3).

Of special interest is the step R2. 3f, whose $F^{MS-T(C)}$ factor reaches a maximum value of around 9.6 and thereby increases the rate constant by almost one order of magnitude at around 800 K due to the large number of conformers of its saddle point (species K). For the step R2. 4f we got $F^{MS-T(C)}$ values that go from 0.2 to 0.1 (secondary y-axis) approximately, hindering reactivity significantly as the result of the large number of conformers of its reactant (species L). Step R2. 2r has $F^{MS-T(C)}$ values of one at any temperature due to the single conformer of the reactant (acetone) and saddle point (species I). Step R2. 1f, which competes with the others as an alternative route yielding acetone, is also favored by multistructural anharmonicity, but not to the same extent as R2. 3f. Therefore, multistructural anharmonicity is expected to play an important role in determining the prominence of these two routes we described for reaction R2, as will be discussed in the next section.

Fig. 2. Multistructural anharmonicity factors $F^{MS-T(C)}$ for some of the steps of the HO $\dot{O}$ -assisted tautomerizations. Those for the step R2. 4f are represented in the secondary y-axis.

3.4. High-pressure limit rate constants

The calculated high-pressure limit (HPL) rate constants include variational effects, tunneling, and multistructural torsional anharmonicity; they are usually labeled as $k_{MS-T(C)}^{CVT/SCT}$, but hereafter we will refer to them as k . Values of the rate constants and SCT coefficients of all the investigated reactions are tabulated in Section 4 of the SM.

Fig. 3 shows the computed HPL rate constants for the $\dot{H}$ -assisted tautomerization. Rate constants for the step R1. 1f (secondary y-axis) show large values with minor temperature dependence, as expected for a reaction with a low energy barrier, while those for the step R1. 2r (secondary y-axis) show a larger variation with temperature. Steps R1. 1r and R1. 2f (primary y-axis) are slow at low temperatures but become notably faster as temperature increases.

Fig. 3. HPL rate constants for the different steps described for reaction R1, including variational effects, tunneling, and multistructural torsional anharmonicity. Solid lines: this work, dashed lines: Zádor and Miller [41]. Primary y-axis: R1. 1r and R1. 2f, secondary y-axis: R1. 2r and R1. 1f.

Rate constants computed by Zádor and Miller [41] for steps R1. 1r and R1. 2f using RRKM/ME methodology are also plotted in Fig. 3. There are slight deviations especially at low temperatures which vanish for R1. 1r and remain for R1. 2f as temperature increases. These differences can be attributed to the different levels of theory (for instance, for R1. 1r these authors predicted a barrier that is 3.98 kJ mol⁻¹ higher than that determined in this work), kinetics theories, and multistructural anharmonicity.

Fig. 4 presents the calculated HPL rate constants for the HO $\dot{O}$ -assisted tautomerization; to the best of our knowledge, no rate constants have been previously reported for this reactive system. Fig. 4(a) displays a relevant characteristic related to the relative importance of the steps R2. 1f and R2. 3f (primary y-axis with the green and purple colors of the routes illustrated in Fig. 1(b), correspondingly), which may control the relative prominence of the two routes described for reaction R2. The barrier height of R2. 1f is 17.81 kJ mol⁻¹ lower than that of R2. 3f, and the rate constants of the former are higher at low temperatures, accordingly. However, as temperature

increases, multistructural anharmonicity exerts an enhancement in R2. 3f which results in larger rate constants than those of R2. 1f. As a result, the second route overcomes the first one above 800 K despite being energetically unfavorable. These findings demonstrate the importance of considering multistructural anharmonicity in certain reactive systems for accurate kinetic modeling.

Of special interest are also the rate constants of the step R2. 2r (Fig. 4(b), secondary y-axis), which present a non-Arrhenius behavior with a minimum at 800 K attributed to the presence of a submerged barrier [42,43] corresponding to the acetone $\cdots$ HO $\dot{O}$ complex.

Fig. 4. HPL rate constants for the different steps described for reaction R2, including variational effects, tunneling, and multistructural torsional anharmonicity. Primary y-axis: R2. 1f, R2. 3f and R2. 2r, secondary y-axis: R2. 1r, R2. 4r, R2. 2f, R2. 3r and R2. 4f.

These rate constants were used for the calculation of the equilibrium constants, which are plotted and tabulated in Section 4 of the SM.

3.5. Pressure-dependent rate constants

3.5.1. Pressure-dependent rate constant of the $\dot{H}$ -assisted tautomerization computed with the original SS-QRRK/MS approach. Comparison to the RRKM/ME method

Fig. 5 shows the pressure-dependent rate constants computed using the original SS-QRRK/MS approach and the RRKM/ME method for the chemically activated $\dot{H}$ -assisted tautomerization following the indications presented in Sections 2.2 and 2.4, respectively. As highlighted in Section 2.4, these calculations omit SCT and multistructural torsional anharmonicity since they may interfere with our goal of comparing the performance of both methodologies in estimating pressure effects.

Fig. 5(a) corresponds to the bimolecular stabilization rate constants k_{stab} , whose values computed with the titled methods strongly agree until 1200 K, with deviation factor values below 1.6. The opposite scenario takes place above 1400 K, where pronounced deviations appear, resulting in a maximum underestimation by the SS-QRRK/MS approach of three orders of magnitude at 2800 K for all pressures studied.

Fig. 5. Comparison between the pressure-dependent rate constants computed with the original SS-QRRK/MS approach (solid lines) and the RRKM/ME method (dots) for the chemically activated $\dot{\text{H}}$ -assisted propen-2-ol tautomerization. (a) Bimolecular stabilization rate constants, k_{stab} , (b) rate constants for the formation of products, k_p , and (c) overall rate constants for the dissociation of the energized adduct back to the reactants, k_{rev} . See text of Scheme 1 for explanation of the rate constants labels.

The underestimations of k_{stab} (Fig. 5(a)) resembles the underestimation of pressure-dependent rate constants for thermally activated reactions when implementing the original SS-QRRK/MS approach. In our previous study using the unimolecular propen-2-ol tautomerization as a reactive system [21], the explanation given to the mentioned underestimation relies on the high values of

the variable that described the number of unimolecular states above the threshold energy (parameter F_E in Eq. (1)) for large molecules and high temperatures [23,24,44]. High values of F_E lead to underestimations of the collision efficiency B_c (Eq. (1)), which eventually leads to an overestimation of pressure effects. The same explanation applies to the chemically activated reactions addressed in the present work, being the species AB^* (Scheme 1) the adduct in this case. For more details about the behavior of F_E and its influence in the computations, refer to Section 3.5.3.

Deviations of k_{stab} at high temperatures with respect to the RRKM/ME values imply that the MSC model used by the original SS-QRRK/MSC approach lacks of a good description of the collision efficiency. To overcome this problem, for the chemically activated reactions studied in this work we tested two alternative collision efficiency definitions (Eqs. (3) and (4)) as we did for the unimolecular case [21]. Results are discussed in Sections 3.5.2 and 3.5.4.

Contrary to the k_{stab} picture, Fig. 5(b) shows that the rate constants for the formation of products k_p computed by the original SS-QRRK/MSC and RRKM/ME approaches are in good agreement, presenting a maximum deviation factor of 1.9 at 600 K and 100 atm. The results of both approaches also have a good agreement for the overall rate constant of dissociation of the energized adduct back to the reactants k_{rev} (Fig. 5(c)), which has a maximum deviation of 4.0 times at 600 K and 10.0 atm. For most of the other conditions evaluated, the discrepancies keep factors lower than 2.0.

The computed k_p and k_{rev} values suggest that the protocol of the SS-QRRK theory [18,19] to determine the microcanonical rate constants is suitable for the system under investigation because of their agreement with those rate constants obtained with the most rigorous RRKM/ME approach. Although k_p and k_{rev} depend on k_{stab} , this dependence is marginal in the high-temperature regime

due to the gap between the rate constants values ($k_p, k_{rev} \gg k_{stab}$). The data plotted in Fig. 5 is provided in Sections 5.1 (RRKM/ME) and 6.2 (SS-QRRK/MS) of the SM.

3.5.2. Benchmark of the SS-QRRK/MS-GCA and SS-QRRK/MS-DCA approaches against the RRKM/ME method for the $\dot{H}$ -assisted propen-2-ol tautomerization

Fig. 6 displays the pressure-dependent rate constants k_{stab} (panels a and b), k_p (panels c and d), and k_{rev} (panels e and f) of the chemically activated $\dot{H}$ -assisted propen-2-ol tautomerization computed with the SS-QRRK/MS-GCA (panels a, c, and e) and SS-QRRK/MS-DCA (panels b, d, and f) approaches. In all cases, the RRKM/ME results are also included for comparison purposes.

The SS-QRRK/MS-GCA approach agrees with the RRKM/ME results for the bimolecular stabilization rate constant k_{stab} (Fig. 6(a)), which were poorly predicted by the original SS-QRRK/MS approach (Fig. 5(a)). Similar to the data presented in Fig. 5(a), below 1200 K the deviation factors are lower than 1.6 and at higher temperatures the deviation factors raise as the pressure increases to a maximum value of 4.5 at 2000 K and 100 atm, which is almost two thousand times lower than the maximum deviation obtained with the original SS-QRRK/MS approach (8950.9 at 2800 K and 100 atm). In general, the maximum deviations lie between 1600 K and 2000 K – except at 0.001 atm, where the maximum underestimation is observed at 2800 K.

Fig. 6. Comparison between the pressure-dependent rate constants of the chemically activated $\dot{\text{H}}$ -assisted propen-2-ol tautomerization computed with the SS-QRRK/SCG (lines) and RRKM/ME (dots) methods. For the SS-QRRK/SCG approach, two collision efficiency definitions are used: Gilbert et al. [22] (panels a, c, and e) and Dean et al. [23,24] (panels b, d, and f). Bimolecular

stabilization rate constants k_{stab} : panels a and b; rate constants for the formation of products k_p : panels c and d; rate constants for the dissociation of the energized adduct back to the reactants k_{rev} : panels e and f. See text of Scheme 1 for explanation of the rate constants labels.

The values of k_{stab} computed with the SS-QRRK/MS-C-DCA approach (Fig. 6(b)) have a maximum deviation factor of 39.5 at 2800 K and 0.1 atm, which is around 230 times smaller than the maximum deviation obtained with the original SS-QRRK/MS-C approach. However, the SS-QRRK/MS-C-DCA approach presents, on average, larger discrepancies than the SS-QRRK/MS-C-GCA approach (Fig. 6(a)), especially at the low pressures and high temperatures tested.

These findings contrast with the results previously obtained for thermally activated processes [21], where the SS-QRRK/MS-C-GCA approach reproduced well the RRKM/ME results but with an overall better performance of the SS-QRRK/MS-C-DCA approach.

As explained in Section 3.5.1, the rate constants for the formation of products k_p and the rate constants for the dissociation of the energized adduct back to the reactants k_{rev} are insensitive, in this case, to the collision efficiency definition selected. As a result, SS-QRRK/MS-C-GCA and QRRK/MS-C-DCA approaches yield similar values, which are also comparable to those of the original SS-QRRK/MS-C approach. Therefore, Fig. 5(b) mirrors Fig. 6(c) and Fig. 6(d), and Fig. 5(c) mirrors Fig. 6(e) and Fig. 6(f). One can expect the selected energy transfer model plays a more prominent role when the population of the stabilized adduct becomes relevant compared with the population of reactants and products, making the collision efficiency definition critical to achieve reasonable predictions. Sections 5.1 and 6.2 of the SM provide the rate constants values displayed in Fig. 6.

3.5.3. Comparison between the analytical and numerical solutions of F_E and their influence on energy transfer parameters and pressure-dependent rate constants

As explained above, the underestimation in the bimolecular stabilization rate constants arises from the overestimation of the parameter F_E , which is defined by Eq. (5).

$$F_E = \int_{E_0}^{\infty} \frac{\rho(E)}{\rho(E_0)} \exp[-(E - E_0)/(k_B T)] \frac{dE}{k_B T} \quad (5)$$

The computation of the density of states is a difficult task, but in pressure-dependent calculations, modelers frequently use the Whitten-Ravinovitch approximation given by Eq. (6).

$$\rho_v(E) = \frac{[E + a(E)E_Z]^{s-1}}{(s-1)! \prod_{i=1}^s (h\nu_i)} \quad (6)$$

By inserting the equation for the density of states (Eq. (6)) in the equation for F_E (Eq. (5)), one obtains an integral that does not have an analytical solution. To make this integral analytical, Troe considered the function $a(E)$ as energy independent, that is, as a constant. This assumption leads to the commonly used algebraic expression for F_E :

$$F_E = \sum_{i=0}^{s-1} \frac{(s-1)!}{(s-1-i)!} \left(\frac{k_B T}{E_0 + a(E_0)E_Z} \right)^i \quad (7)$$

By the time of the development of these collisional energy transfer theories, analytical approximations were useful for the purpose of efficiency in the calculations. However, current advances in computational infrastructure allow many program languages such as Python [35] or Matlab [45] to solve numerical problems in a fast way. In consequence, Bao and Truhlar [46] recently tested the accuracy of the analytical approximation for F_E by comparing final rate constants $k(T, p)$ computed using Eq. (7) and those obtained by numerical integration of Eq. (5). Their study concluded that for reactions with an energy threshold below 125.25 kJ mol⁻¹, pressure

effects could be underestimated by a factor of 2.0 – 5.8 at high temperatures (≈ 2400 K) when using the analytical approximation for F_E (Eq. (7)). This conclusion turns out to be relevant to our investigation since the first energy barrier for the $\dot{H}$ -assisted tautomerization has a value of 6.04 kJ mol⁻¹.

Given that in reactions with low energy barriers the analytical approximation for F_E implemented in the original SS-QRRK/MS approach introduces additional errors into pressure-dependent rate constants, we preferred to use the numerical integration of Eq. (5). Fig. 7 shows the influence of this modification on several parameters of the energy transfer model and the rate constants of the $\dot{H}$ -assisted tautomerization at 0.001 atm. First, Fig. 7(a) displays the values of F_E calculated numerically ($F_{E,num}$ green line) and approximately ($F_{E,app}$ blue line). As mentioned by Bao and Truhlar [46], the numerical integration gives higher values of F_E at high temperatures than those of the analytical approximation, presenting a particular maximum deviation of three at 2500 K in this case. Discrepancies are a consequence of the increase of the function $a(E)$ in comparison with its initial value $a(E_0)$, which subsequently raises the value of the density of states (Eq. (6)).

Because the relationship between the correction factor Δ of Gilbert et al. [22] and F_E is reciprocal, Fig. 7(b) illustrates the higher values of Δ when calculated using the analytical approximation for F_E ($F_{E,app}$). However, it is pertinent to highlight that the order of magnitude of the correction factor is between minus two and minus three, which is much higher than the maximum deviation factor of three between $F_{E,app}$ and $F_{E,num}$ encountered at high temperatures - as shown in Fig. 7(a). As a result, one would expect then a slight influence of F_E when implementing the collision efficiency (β_c) including Δ (Eq. 2), and a moderate influence when using the initial definition which omits Δ (Eq. 1). In other words, variations in β_c should be

attributed to a larger extent to the inclusion of the correction factor Δ than to the integration scheme used for F_E .

Fig. 7. (a) Normalized number of unimolecular states above the threshold energy, F_E , computed with numerical integration ($F_{E,num}$, green line) and the Troe approximation ($F_{E,app}$, blue line). (b) Correction factor Δ of Gilbert et al. computed considering the parameters $F_{E,num}$ (green line) and $F_{E,app}$ (blue line). (c) Collision efficiency β_c calculated with the definition of Gilbert et al. [22] and using $F_{E,num}$ (solid green line) and $F_{E,app}$ (solid blue line), and collision efficiencies calculated with the original formulation of SS-QRRK/MS (without the correction factor Δ) using $F_{E,num}$ (dashed green line) and $F_{E,app}$ (dashed blue line). (d) Rate constants for H-assisted tautomerization at 0.001 atm considering the collision efficiencies of Gilbert et al. [22] using $F_{E,num}$ (solid green

line) and $F_{E,app}$ (solid blue line), and rate constants computed with the original SS-QRRK/MS formulation for collision efficiency using $F_{E,num}$ (dashed green line) and $F_{E,app}$ (dashed blue line).

To demonstrate this assessment, we computed the collision efficiency with (solid lines in Fig. 7(c)) and without (dashed lines in Fig. 7(c)) the correction factor Δ (Eq. 2 and Eq. 1, respectively) using $F_{E,app}$ and $F_{E,num}$. The results effectively show that neglecting the correction factor Δ decreases the collision efficiency around one order of magnitude (at 2800 K) when replacing $F_{E,app}$ by $F_{E,num}$ (comparing the dashed lines in Fig. 7(c)). Nonetheless, including Δ strongly diminishes the influence of this replacement to a factor of 1.7 (at 1400 K, comparing the solid lines in Fig. 7(c)). On the other hand, the values of the collision efficiency significantly change from two (blue lines in Fig. 7(c)) to three (green lines in Fig. 7(c)) orders of magnitude after considering Δ in the calculation with $F_{E,app}$ and $F_{E,num}$, respectively. In summary, the replacement of $F_{E,app}$ by $F_{E,num}$ alters the collision efficiency around one order of magnitude when omitting the correction factor Δ ; however, considering it, the numerical integration of F_E has negligible influence due to the more pronounced change that Δ exerts by itself, which goes from two to three orders of magnitude.

Bimolecular stabilization rate constants at 0.001 atm for the H-assisted tautomerization present a similar behavior to that of the collision efficiency, and Fig. 7(d) shows the comparable trends. It is relevant to point out that without implementing the correction factor Δ in the collision efficiency definition, the replacement of $F_{E,app}$ by $F_{E,num}$ would worsen the underestimation in the pressure-dependent rate constants described in Section 3.5.1. This does not suggest that it would be preferable to use the analytical approximation over the numerical integration as an alternative to alleviate the mentioned problem. The numerical integration is indeed a more rigorous calculation,

and together with the modified collision efficiency definition implemented in this work, one counts with an approach to calculate more accurate pressure-dependent rate constants. Tabulated data for the energy transfer parameters of Fig. 7 are presented in Section 7 of the SM.

3.5.4. Benchmark of the SS-QRRK/MS-CGCA and SS-QRRK/MS-CDA approaches against the RRKM/ME method for the first route of the HO $\dot{O}$ -assisted propen-2-ol tautomerization

The first route of the HO $\dot{O}$ -assisted tautomerization (Fig. 1(b), dashed green line) exemplifies a particular case of reactions chemically activated. The intermediate adduct H lies in a deep well located at -107.39 kJ mol⁻¹ in the PES with respect to the reactants (A + HO $\dot{O}$), which reacts toward the final products (E + HO $\dot{O}$) through the saddle point I. Even if the saddle point I is above the intermediate adduct H by 46.82 kJ mol⁻¹, it is still -60.57 kJ mol⁻¹ more stable than the reactants. Since both, the intermediate adduct (species H) and the saddle point (species I) populate regions with considerable lower energy than that of the reactants (A + HO $\dot{O}$), the chemically activated species H (H*) is expected to have sufficient energy once formed to react and form the final product quickly. As a result, the species H* is not expected to be collisionally stabilized (H* + M $\rightarrow$ H + M) in the relatively short time frame at which the reaction to the final product proceeds. In other words, the rate constant of bimolecular stabilization k_{stab} is negligible in comparison with the rate constant for the formation of products k_p . This observation stems from the stochastic simulations of MultiWell software [38,39], which output zero for the fractions of stabilized adducts (H) for most of the temperatures and pressures studied. Only at 100 atm and 200-1800 K, a fraction of H is obtained as a consequence of the substantial amount of collisions promoted at this pressure.

Conversely to RRKM/ME-MultiWell [38,39] calculations, which output zero for the majority of k_{stab} results, the SS-QRRK/MS-C approaches always return finite values for this rate constant.

The finite values are below of k_p from two to nine orders of magnitude at the conditions studied, nonetheless, suggesting negligible practical differences between the results of the two methods.

Fig. 8 shows k_p (Fig. 8(a)) and k_{rev} (Fig. 8(b)) rate constants computed with the SS-QRRK/MS-CGCA and SS-QRRK/MS-CDCA approaches (solid lines), including RRKM/ME results (dots) for comparison purposes. Results below 10.0 atm are not presented because the three tested approaches predict similar results, and the bimolecular stabilization rate constants k_{stab} is almost zero in this system for most of the conditions studied.

Fig. 8. Comparison between the pressure-dependent rate constants of the chemically activated HOO-assisted propen-2-ol tautomerization computed with the proposed SS-QRRK/MS-CGCA approaches (lines) and the RRKM/ME method (dots). (a) Rate constants for the formation of products k_p , and (b) rate constants for the dissociation of the energized adduct back to the reactants k_{rev} . The rate constants computed with the proposed SS-QRRK/MS-CGCA and SS-QRRK/MS-CDCA approaches overlap and the lines represent the result of both methods. Results are presented until 10.0 atm because below this pressure rate constants values also overlap.

The negligible value of k_{stab} has a notable consequence: the pressure dependency on k_p and k_{rev} vanishes. Pressure affects the frequency of the collisions, which rule the thermalization of the

energized adduct. However, if thermalization does not compete with the rate of the chemical reaction, pressures effects disappear.

For k_p , as shown in Fig. 8(a), one only distinguishes values between 100 atm and 10 atm in the 400 K – 800 K temperature range, and for all other conditions of temperature and pressure, the rate constants overlap with the curve of 10 atm. The maximum deviation factor is 2.2 at 400 K and 100 atm with underestimations below 1.5 for all other temperatures and pressures. The values of the rate constant k_{rev} (Fig. 8(b)) virtually overlap for all pressures, and the maximum deviation factor is 5.9 at 500 K and 100 atm taking values in the 2.3-4.5 range for most of the remaining conditions of temperature and pressure. Numerical values of Fig. 8 are presented in Sections 5.2 and 6.4 of the SM. Notwithstanding, the rate constants discussed in this section do not include variational effects, tunneling, and multistructural torsional anharmonicity; in Sections 6.1 and 6.3 of the SM are provided the set of $k(T, p)$ that take into account all these improvements from the HPL rate constants and computed with the SS-QRRK/MS-C approaches proposed in this work.

To sum up, the SS-QRRK/MS-C-GCA approach performs better overall than the SS-QRRK/MS-C-DCA and SS-QRRK/MS-C approaches to predict the pressure-dependent rate constants of chemically activated reactions - especially to predict the bimolecular stabilization rate constant k_{stab} - based on comparison with RRKM/ME results. The deviation factor peaks at 2000 K and 100 atm with a value of 4.5 for the $\dot{H}$ -assisted tautomerization, and it is below 4.0 in the high-temperature regime, making the SS-QRRK/MS-C-GCA approach a convenient tool across a wide range of temperatures and pressures. Although we tested in this work the proposed approaches for only two reactive systems, the authors would expect accurate predictions for other systems comprising species with around the same number of degrees of freedom than those of C and H (Fig. 1) with, respectively, 27 and 33.

An approach such as SS-QRRK/MS-CGCA has the advantages of requiring only the information of the reactant species; including all the refinements incorporated into the HPL rate constants: SCT, variational effects, and multistructural torsional anharmonicity; and the lower computational cost compared to more sophisticated methodologies such as RRKM/ME. For a detailed discussion about the advantages and disadvantages of the collision efficiencies tested here, the reader may refer to our previous study of thermally activated reactions [21].

3.5.5. Unimolecular pressure dependent rate constants for the second route of the HO $\dot{O}$ -assisted propen-2-ol tautomerization

The second route of the HO $\dot{O}$ -assisted tautomerization (purple dashed lines in Fig. 1(b)) initiates with an exothermic reaction ($-32.33 \text{ kJ mol}^{-1}$) toward the species L, a species that requires additional energy (39.91 or $46.68 \text{ kJ mol}^{-1}$ via the saddle points K and M, respectively shown in Fig. 1) to eventually react. In consequence, the adduct L likely achieves collision-stabilization, and thermal activation would be the only option to overcome the adjacent barriers. Because of this, pressure-dependent rate constants of the second route only involves unimolecular reactions.

Fig. 9 displays the rate constants of the most illustrative steps of the second route of the HO $\dot{O}$ -assisted tautomerization: R2. 3f, R2. 2f, R2. 4f and R2. 2r, which were computed using the SS-QRRK/MS-Dean approach for unimolecular reaction as indicated in our previous work [21]. The step R2. 2r (Fig. 9(a), dashed line) shows a negative temperature dependence that might be due to its submerged barrier. Another notable case is the step R2. 3f (Fig. 9(a), solid line), which slightly waves at the lowest pressures studied (0.001 and 0.01 atm) before achieving a steady-state value; this behavior might be related to the complexity of the conformational space of the involved stationary points since the start of the waving approximately coincide with the maxima of

multistructural anharmonicity highlighted in Fig. 2. The pressure-dependent rate constants of Fig. 9(b) (steps R2. 2f with solid lines and step R2. 4f with dashed lines) represent the standard behavior, becoming asymptotic at high temperatures.

Overall, pressure has particular effects in the second route of the HO $\dot{O}$ -assisted tautomerization at temperatures as low as 400 K attributed to the unique features of the PES. Numerical data of Fig. 9 are provided in Section 6.5 of the SM.

Fig. 9. Low pressure rate constants for the second route of the HO $\dot{O}$ -assisted tautomerization computed with the SS-QRRK/MS-Dean approach for unimolecular reactions [21]. (a) Steps R2. 3f (solid lines) and R2. 2r (dashed lines). (b) Steps R2. 2f (solid lines) and R2. 4f (dashed lines).

3.6. Stepwise against concerted HO $\dot{O}$ -assisted propen-2-ol tautomerization

Fig. 10 compares the different rate constants of the HO $\dot{O}$ -assisted propen-2-ol tautomerization: overall stepwise (sum of the first and second stepwise routes), first stepwise route, second stepwise route, and those of the concerted reaction previously reported by us [15]. The values for the second route and overall stepwise rate constants are shown in Section 8 of the SM, where the procedure of the computations of the rate constants is also described.

The second route does not play any significant role in the conditions tested: at 3000 K and 100 atm, it has the maximum contribution with only 8.0 % of the total flux, which decreases to 0.3 % at 200 K and the same pressure. As a result, the rate constants of the overall stepwise HO $\dot{\text{O}}$ -assisted tautomerization are practically equal to those of the chemical activated mechanism as illustrated with the green line and blue dots in Fig. 10. The overall rate constant values of the stepwise HO $\dot{\text{O}}$ -assisted propen-2-ol tautomerization vary slightly with the change of pressure, similar to the chemically activated mechanism and as in the concerted case. Therefore, Fig. 10 with data at 0.01 atm illustrates well the global behavior of the sets of rate constants over the whole temperature and pressure ranges.

Fig. 10. Rate constants for the overall stepwise (green line), first stepwise route (blue dots), second stepwise route (purple line), and concerted (red line) HO $\dot{\text{O}}$ -assisted propen-2-ol tautomerization at 0.01 atm.

The stepwise mechanism has a higher contribution to the HO $\dot{\text{O}}$ -assisted propen-2-ol tautomerization than the concerted step by around 4-6 times between 300 K and 900 K, and between 2-5 times for the remaining temperatures. The differences arise from the reduction of the

energy barrier by 8.2 kJ mol⁻¹ when going from the concerted to the chemical activated path and, to a lesser extent, to the sum of the contribution of the two stepwise processes.

4. Conclusions

A theoretical kinetic study of the $\dot{\text{H}}$ - and $\text{HO}\dot{\text{O}}$ -assisted stepwise tautomerizations of propen-2-ol into acetone was performed based on electronic structure calculations at the CCSD(T)/aug-cc-pVTZ//M06-2X/cc-pVTZ *ab initio* level and using the multistructural torsional variational transition state theory with small-curvature tunneling corrections. Furthermore, the system-specific Rice-Ramsperger-Kassel (SS-QRRK) theory [18,19] and the modified strong collision (MSC) model were used to account for pressure effects, covering a wide temperature and pressure ranges.

The $\dot{\text{H}}$ -assisted tautomerization proceeds in two steps and involves the formation of an intermediate radical, which results from the addition of the hydrogen atom into the double bond of propen-2-ol. The first step of the $\dot{\text{H}}$ -assisted tautomerization (R 1. 1f) shows a rate constant slightly sensitive to the temperature due to its low energy barrier of 6.04 kJ mol⁻¹. The rate constants for the reactions of the intermediate radical (R 1. 1r and R 1. 2f) portray a well-defined Arrhenius behavior with values in agreement with those previously reported in the literature [41].

The $\text{HO}\dot{\text{O}}$ -assisted tautomerization takes place in four steps with two possible routes for the formation of acetone; the route with the highest energy barrier shows larger rate constants at temperatures above 800 K as the result of a positive effect exerted by multistructural anharmonicity on the reactivity. Therefore, the role of the multiple conformers in the $\text{HO}\dot{\text{O}}$ -assisted stepwise tautomerization, and reactions with larger molecules, has to be considered to describe the reaction mechanism accurately. Another relevant feature is the reverse rate constant of the reaction for

acetone formation (second route), which presents a non-Arrhenius behavior with a minimum at around 800 K because of the presence of a submerged barrier which is connected with the reactants acetone and HO $\dot{\text{O}}$ by an acetone $\cdots$ HO $\dot{\text{O}}$ complex.

It was shown that the original SS-QRRK/MS-C implementation [18,19] underestimates the bimolecular stabilization rate constants of the $\dot{\text{H}}$ -assisted tautomerization at temperatures above 1200 K with deviations of up to three orders of magnitude at 2800 K when compared with the benchmark Rice-Ramsperger-Kassel-Markus/master equation (RRKM/ME) method. The authors recently described a similar problem in the investigation of the unimolecular propen-2-ol tautomerization [21]. This failure had its roots in the overestimation of the normalized number of states above the threshold energy - a parameter denoted in the literature as F_E . The underestimation of the rate constants was fixed by implementing two alternative definitions of collision efficiency, one by Gilbert et al. [22] (Eq. (3)) and another one by Dean et al. [23,24] (Eq. (4)); our implementation was useful when determining pressure effects in thermally activated reactions [21], and it was extended in this work for the investigation of bimolecular reactions. The implementations with the alternative collision efficiency definitions were denoted as SS-QRRK/MS-C-GCA and SS-QRRK/MS-C-DCA approaches, respectively.

The SS-QRRK/MS-C-GCA approach worked well when compared with the method RRKM/ME, since it alleviated the underprediction of the bimolecular stabilization rate constant k_{stab} obtaining a maximum deviation of only 4.5 at 2000 K and 100 atm. On the other hand, the SS-QRRK/MS-C-DCA approach turned underprediction into overprediction (with a maximum deviation of 39.5 at 2800 K and 0.1 atm), which resulted in an unsatisfactory performance for the $\dot{\text{H}}$ -assisted tautomerization. We also replaced the analytical approximation to compute F_E with a more accurate numerical integration. However, it only has an appreciable influence (of one order of

magnitude) when using the original SS-QRRK/MS-C approach and diminishes to a factor of 1.7 after implementing the collision efficiency of Gilbert et al. [22].

In the chemically activated HO $\dot{\text{O}}$ -assisted tautomerization (green dashed line in Fig. 1(b)), the energized adduct does not stabilize ($\text{H}^* + \text{M} \rightarrow \text{H} + \text{M}$), and the population of final products (acetone + HO $\dot{\text{O}}$) dominates during most of the stages of the simulation. As a result, k_{stab} is negligible for the majority of the conditions of temperature and pressure tested.

The other chemically activated rate constants, k_p for the formation of the final products and k_{rev} for the dissociation of the energized adduct back to the reactants, are well predicted for both tautomerizations by any of the SS-QRRK implementations employed in this work. These good predictions indicate the convenience of the method for computing microcanonical rate constants. Pressure effects of the HO $\dot{\text{O}}$ -assisted tautomerization presented unique features for the second route (purple dashed line in Fig. 1(b)). For instance, a subtle maximum in the rate constants of its first step, especially at low pressures, which coincides with the peak of multistructural anharmonicity at around 800 K. However, the chemically activated reaction (first route) makes the HO $\dot{\text{O}}$ -assisted stepwise tautomerization the main path to the formation of acetone, taking over the previously studied concerted mechanism, which has a barrier of 8.2 kJ mol⁻¹ higher in energy [15].

Our calculated rate constants are useful to prevent the use of analogies for the keto-enol tautomerization of propen-2-ol in kinetic modeling. This is the case of the HO $\dot{\text{O}}$ -assisted tautomerization, which is commonly modeled by using the corresponding tautomerization of vinyl alcohol [10]. Besides, the SS-QRRK/MS-C-GCA approach proposed in this work and implemented in our bespoke Python [35] code extends the scope of the SS-QRRK theory [18,19] to chemically activated reactions, which easily allows the inclusion of variational effects, multidimensional tunneling, and multistructural anharmonicity in the falloff region of chemical reactions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work was supported by King Abdullah University of Science and Technology (KAUST), Office of Sponsored Research (OSR) under Award No. OSR-2016-CRG5-3022. We thank the resources of the Supercomputing Laboratory at KAUST.

Supplementary Material

Supplementary Material. Additional details on the calculations we performed and all numerical results; ChemAc-SS-QRRK. Python code to compute pressure dependent rate constants of chemically activated reactions using the approaches proposed in this work; H-Assisted_SM. Input example Excel file for the code ChemAc-SS-QRRK.

References

- [1] K. Kohse-Höinghaus, P. Oßwald, T.A. Cool, T. Kasper, N. Hansen, F. Qi, et al., Biofuel combustion chemistry: From ethanol to biodiesel, *Angew. Chemie Int. Ed.* 49 (2010) 3572–3597.
- [2] S.M. Sarathy, P. Oßwald, N. Hansen, K. Kohse-Höinghaus, Alcohol combustion chemistry,

- Prog. Energy Combust. Sci. 44 (2014) 40–102.
- [3] K. Yasunaga, T. Mikajiri, S.M. Sarathy, T. Koike, F. Gillespie, T. Nagy, et al., A shock tube and chemical kinetic modeling study of the pyrolysis and oxidation of butanols, Combust. Flame 159 (2012) 2009–2027.
- [4] D.E. Couch, Q.L.D. Nguyen, A. Liu, D.D. Hickstein, H.C. Kapteyn, M.M. Murnane, et al., Detection of the keto-enol tautomerization in acetaldehyde, acetone, cyclohexanone, and methyl vinyl ketone with a novel VUV light source, Proc. Combust. Inst. (2020) 1-8.
- [5] C.A. Taatjes, N. Hansen, A. McIlroy, J.A. Miller, J.P. Senosiain, S.J. Klippenstein, et al., Chemistry: Enols are common intermediates in hydrocarbon oxidation, Science 308 (2005) 1887–1889.
- [6] S. So, U. Wille, G. da Silva, Atmospheric chemistry of enols: A theoretical study of the vinyl alcohol + OH + O₂ reaction mechanism, Environ. Sci. Technol. 48 (2014) 6694–6701.
- [7] J.M. Simmie, H.J. Curran, Energy barriers for the addition of H, $\dot{\text{C}}\text{H}_3$, and $\dot{\text{C}}_2\text{H}_5$ to CH₂=CHX [X = H, CH₃, OH] and for H-atom addition to RCH=O [R = H, CH₃, $\dot{\text{C}}_2\text{H}_5$, n-C₃H₇]: Implications for the gas-phase chemistry of enols, J. Phys. Chem. A 113 (2009) 7834–7845.
- [8] G. Da Silva, C.H. Kim, J.W. Bozzelli, Thermodynamic properties (enthalpy, bond energy, entropy, and heat capacity) and internal rotor potentials of vinyl alcohol, methyl vinyl ether, and their corresponding radicals, J. Phys. Chem. A 110 (2006) 7925–7934.
- [9] G. da Silva, J.W. Bozzelli, L. Liang, J.T. Farrell, Ethanol oxidation: Kinetics of the alpha-hydroxyethyl radical + O₂ reaction., J. Phys. Chem. A 113 (2009) 8923–8933.
- [10] G. da Silva, J.W. Bozzelli, Role of the α -hydroxyethylperoxy radical in the reactions of acetaldehyde and vinyl alcohol with HO₂, Chem. Phys. Lett. 483 (2009) 25–29.

- [11] J. Zádor, A.W. Jasper, J.A. Miller, The reaction between propene and hydroxyl, *Phys. Chem. Chem. Phys.* 11 (2009) 11040.
- [12] N. Hansen, M.R. Harper, W.H. Green, High-temperature oxidation chemistry of n-butanol – experiments in low-pressure premixed flames and detailed kinetic modeling, *Phys. Chem. Chem. Phys.* 13 (2011) 20262–20274.
- [13] E. Grajales-González, M. Monge-Palacios, S.M. Sarathy, Theoretical kinetic study of the unimolecular keto–enol tautomerism propen-2-ol $\leftrightarrow$ acetone. Pressure effects and implications in the pyrolysis of tert- and 2-butanol, *J. Phys. Chem. A* 122 (2018) 3547–3555.
- [14] M. Monge-Palacios, E. Grajales-González, S.M. Sarathy, Formic acid catalyzed keto-enol tautomerizations for C₂ and C₃ enols: Implications in atmospheric and combustion chemistry, *Int. J. Quantum Chem.* 119 (2019) e25954.
- [15] M. Monge-Palacios, E. Grajales-González, S.M. Sarathy, Ab Initio, transition state theory, and kinetic modeling study of the HO₂-assisted keto–enol tautomerism propen-2-ol + HO₂ $\rightleftharpoons$ acetone + HO₂ under combustion, atmospheric, and interstellar conditions, *J. Phys. Chem. A* 122 (2018) 9792–9805.
- [16] C.K. Law, *Combustion Physics*, Cambridge University Press, New York, 2006, p. 740.
- [17] M. Zarzecki, J.G. Quintiere, R.E. Lyon, T. Rossmann, F.J. Diez, The effect of pressure and oxygen concentration on the combustion of PMMA, *Combust. Flame* 160 (2013) 1519–1530.
- [18] J.L. Bao, X. Zhang, D.G. Truhlar, Predicting pressure-dependent unimolecular rate constants using variational transition state theory with multidimensional tunneling combined with system-specific quantum RRK theory: A definitive test for fluorofom

- dissociation, *Phys. Chem. Chem. Phys.* 18 (2016) 16659–16670.
- [19] J.L. Bao, J. Zheng, D.G. Truhlar, Kinetics of hydrogen radical reactions with toluene including chemical activation theory employing system-specific quantum RRK theory calibrated by variational transition state theory, *J. Am. Chem. Soc.* 138 (2016) 2690–2704.
- [20] J.L. Bao, D.G. Truhlar, Variational transition state theory: Theoretical framework and recent developments, *Chem. Soc. Rev.* 46 (2017) 7548–7596.
- [21] E. Grajales-González, M. Monge-Palacios, S.M. Sarathy, Collision efficiency parameter influence on pressure-dependent rate constant calculations using the SS-QRRK theory, *J. Phys. Chem. A* 124 (2020) 6277–6286.
- [22] R.G. Gilbert, K. Luther, J. Troe, Theory of thermal unimolecular reactions in the fall-off range. II. weak collision rate constants, *Berichte der Bunsengesellschaft für Phys. Chemie* 87 (1983) 169–177.
- [23] A.Y. Chang, J.W. Bozzelli, A.M. Dean, Kinetic analysis of complex chemical activation and unimolecular dissociation reactions using QRRK theory and the modified strong collision approximation, *Zeitschrift für Phys. Chemie* 214 (2000) 1533–1568.
- [24] H.H. Carstensen, A.M. Dean, Chapter 4 The kinetics of pressure-dependent reactions, *comprehensive chemical kinetics* First edit., Elsevier, Amsterdam, The Netherland, 2007, p. 101–184.
- [25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, et al., *Gaussian 09*, Gaussian, Inc, Wallingford, CT, 2010.
- [26] Y. Zhao, D.G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class

- functionals and 12 other function, *Theor. Chem. Acc.* 120 (2008) 215–241.
- [27] T.H. Dunning, Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.* 90 (1989) 1007–1023.
- [28] R.J. Bartlett, Coupled-cluster approach to molecular structure and spectra: a step toward predictive quantum chemistry, *J. Phys. Chem.* 93 (1989) 1697–1708.
- [29] J. Zheng, S. Zhang, J.C. Corchado, R. Meana-Pañeda, Y.Y. Chuang, E.L. Coitiño, et al., GAUSSRATE 17, University of Minnesota: Minneapolis, 2016.
- [30] J. Zheng, L. Bao, R. Meana-Pañeda, S. Zhang, G.C. Lynch, J.C. Corchado, et al., POLYRATE 2016, University of Minnesota: Minneapolis, 2016.
- [31] J. Zheng, T. Yu, E. Papajak, I.M. Alecu, S.L. Mielke, D.G. Truhlar, Practical methods for including torsional anharmonicity in thermochemical calculations on complex molecules: The internal-coordinate multi-structural approximation, *Phys. Chem. Chem. Phys.* 13 (2011) 10885.
- [32] J. Zheng, D.G. Truhlar, Quantum thermochemistry: Multistructural method with torsional anharmonicity based on a coupled torsional potential, *J. Chem. Theory Comput.* 9 (2013) 1356–1367.
- [33] J. Zheng, S. Mielke, J.L. Bao, R. Meana-Pañeda, K. Clarkson, D. Truhlar, MStor: A program for calculating partition functions, free energies, enthalpies, entropies, and heat capacities of complex molecules including torsional anharmonicity, Department of Chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, MN 55455. IBM Almaden Research Center, San Jose, CA 95120, 2017.
- [34] NIST, Precomputed vibrational scaling factors, available from:

- <<http://cccbdb.nist.gov/vibscalejust.asp>>, National Institute of Standards and Technology, 2016.
- [35] Python Software Foundation, Python Programming Language – Official Website, Available from: <<http://www.python.org/>>, pythonorg, 2019.
- [36] B.E. Poling, J.M. Prausnitz, J.P. O’Connell, Properties of gases and liquids, 5th ed., McGraw-Hill Education, New York, 2001.
- [37] Y. Duan, M. Monge-Palacios, E. Grajales-Gonzalez, D. Han, K.H. Møller, H.G. Kjaergaard, et al., Oxidation kinetics of n-pentanol: A theoretical study of the reactivity of the 1-hydroxy-1-peroxypentyl radical, *Combust. Flame* 219 (2020) 20–32.
- [38] J.R. Barker, Multiple-Well, multiple-path unimolecular reaction systems. I. MultiWell computer program suite, *Int. J. Chem. Kinet.* 33 (2001) 232–245.
- [39] J.R. Barker, Energy transfer in master equation simulations: A new approach, *Int. J. Chem. Kinet.* 41 (2009) 748–763.
- [40] L.K. Huynh, H.R. Zhang, S. Zhang, E. Eddings, A. Sarofim, M.E. Law, et al., Kinetics of enol formation from reaction of OH with propene, *J. Phys. Chem. A* 113 (2009) 3177–3185.
- [41] J. Zádor, J.A. Miller, Unimolecular dissociation of hydroxypropyl and propoxy radicals, *Proc. Combust. Inst.* 34 (2013) 519–526.
- [42] M. Monge-Palacios, S.M. Sarathy, Ab initio and transition state theory study of the $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2(^3\Sigma_g^-)/\text{O}_2(^1\Delta_g)$ reactions: yield and role of $\text{O}_2(^1\Delta_g)$, *Phys. Chem. Chem. Phys.* 20 (2018) 4478–4489.
- [43] M. Monge-Palacios, M.P. Rissanen, Z. Wang, S.M. Sarathy, Theoretical kinetic study of the formic acid catalyzed criegee intermediate isomerization: multistructural anharmonicity and atmospheric implications, *Phys. Chem. Chem. Phys.* 20 (2018) 10806–10814.

- [44] J. Troe, Predictive possibilities of unimolecular rate theory, *J. Phys. Chem.* 83 (1979) 114–126.
- [45] MATLAB, (R2019b), The MathWorks Inc., Natick, Massachusetts, 2018.
- [46] J.L. Bao, D.G. Truhlar, Effect of energy dependence of the density of states on pressure-dependent rate constants, *Phys. Chem. Chem. Phys.* 20 (2018) 30475–30479.