Article

Collision Efficiency Parameter Influence on Pressure-Dependent Rate Constant Calculations Using the SS-QRRK Theory

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

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The system-specific quantum Rice–Ramsperger–Kassel (SS-QRRK) theory (*J. Am. Chem. Soc.* **2016**, *138*, 2690) is suitable to determine rate constants below the high-pressure limit. Its current implementation allows incorporating variational effects, multidimensional tunneling, and multistructural torsional anharmonicity in rate constant calculations. Master equation solvers offer a more rigorous approach to compute pressure-dependent rate constants, but several implementations available in the literature do not incorporate the aforementioned effects. However, the SS-QRRK theory coupled with a formulation of the modified strong collision model underestimates the value of unimolecular pressure-dependent rate constants in the high-temperature regime for reactions involving large molecules. This underestimation is a consequence of the definition for collision efficiency, which is part of the energy transfer model. Selection of the energy transfer model and its parameters constitutes a common issue in pressure-dependent calculations. To overcome this underestimation problem, we evaluated and implemented in a bespoke Python code two alternative definitions for the collision efficiency using the SS-QRRK theory and tested their performance by comparing the pressure-dependent rate constants with the Rice–Ramsperger–Kassel–Marcus/Master Equation (RRKM/ME) results. The modeled systems were the tautomerization of propen-2-ol and the decomposition of 1-propyl, 1-butyl, and 1-pentyl radicals. One of the tested definitions, which Dean et al. explicitly derived (*Z. Phys. Chem.* **2000**, *214*, 1533), corrected the underestimation of the pressure-dependent rate constants and, in addition, qualitatively reproduced the trend of RRKM/ME data. Therefore, the used SS-QRRK theory with accurate definitions for the collision efficiency can yield results that are in agreement with those from more sophisticated methodologies such as RRKM/ME.
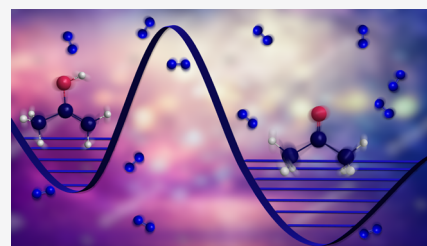
1. INTRODUCTION

Conventional theoretical kinetic studies cover temperature-dependent and pressure-dependent rate constants.[1] Linde-mann described the pressure-dependent scheme as a sequence of two steps (reaction R1). The first step is an excitation process where the reactant molecule A collides with a molecule of the bath gas M to form the energized molecule A^*. The second step is 2-fold: the energized molecule A^* can deactivate by colliding with another molecule M or it can react to form the product P.[2] Pressure-dependent reactions are common in a variety of chemical environments and applications,[3] such as combustion, atmospheric chemistry, and chemical vapor deposition, but an accurate theoretical treatment represents a challenge that has demanded comprehensive studies.[3]

$$A + M \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} A^* + M \tag{R1}$$

$$A^* \overset{k_2}{\rightarrow} P$$

The study of pressure-dependent reactions extends conventional transition state theory (TST) by considering other rate constants, that is, k_1, k_{-1}, and k_2, as shown in reaction R1. This description combines a collisional energy transfer model and an energy-resolved microcanonical TST (μTST) to calculate

the rate constants k_{-1} and k_2, which describes the relaxation and formation of the final product from the energized molecule, respectively. The rate constant k_1 is computed from the equilibrium constant $K_{eq} = k_1/k_{-1}$ once the value of k_{-1} is known.[4,5]

Considering the different energy transfer models, the master equation (ME) methodology is perhaps the most rigorous. For a given species, it involves a set of differential equations that describes the evolution of the distribution of the internal states of energy with time.[6] This method has enabled the computation of temperature- and pressure-dependent rate constants from first principles with good accuracy, allowing satisfactory modeling of experimental data.[7] Another energy transfer approach is the modified strong collision (MSC) model.[8,9] The MSC model considers that not all but just a fraction of the collisions—determined by the collision

efficiency— is strong enough to exchange the energy required for the reaction to proceed.[10]

There are different methods to compute energy-resolved rate constants. Rice−Ramsperger−Kassel−Markus (RRKM) is a rigorous theory and together with ME (RRKM/ME) has become the benchmark for pressure-dependent rate constant calculations. The quantum Rice−Ramsperger−Kassel (QRRK) theory is not as rigorous but requires a lower computational cost,[11] which has made the QRRK/MSC method suitable for fast initial estimations.[12] The recently developed system-specific QRRK (SS-QRRK) theory[13−15] allows for the incorporation of variational effects, multidimensional tunneling, and multistructural torsional anharmonicity in the low-pressure rate constants via estimation of these effects in the previously calculated high-pressure limit rate constants. Including these effects in ME calculations requires considerable extra effort.[11] Multidimensional tunneling methods can be crucial to accurately describe certain chemical reactions even at relatively high temperatures (∼700 K),[16,17] and multistructural anharmonicity can be pronounced in reactions involving complex molecules in the high-temperature regime;[18,19] these effects can be efficiently incorporated in low-pressure rate constant calculations by the SS-QRRK theory,[14,15] justifying the need for further improvements of this methodology.

However, there is a drawback in the energy transfer model used by the SS-QRRK theory:[14,15] one of the collision efficiency definitions (there are two options in the original SS-QRRK/MSC approach) yields underestimated rate constant values when dealing with large molecules at high temperatures. Different authors have already reported the nature of this problem,[9,12,20] and in general, the difficulty is choosing the appropriate collision efficiency formula together with the energy transfer parameter.[11] We address this topic in section 2.2.

In order to improve the performance of the original SS-QRRK theory and broaden its applicability,[13−15] we attempted to improve the MSC model by testing two alternative definitions for the collision efficiency parameter in the computation of rate constants for unimolecular reactions. The two alternative forms of the collision efficiency parameter refer to the work of Gilbert et al.,[21] albeit Dean et al.[12,20] explicitly described one of these two expressions. The reactive systems selected in this study were the propen-2-ol unimolecular tautomerization to acetone (i-C_3H_5OH → CH_3COCH_3), previously studied by us,[22] and the decomposition of 1-propyl ($CH_3CH_2CH_2^{\bullet}$ → C_2H_4 + $CH_3^{\bullet}$), 1-butyl ($CH_3(CH_2)_2CH_2^{\bullet}$ → C_2H_4 + $C_2H_5^{\bullet}$), and 1-pentyl ($CH_3(CH_2)_3CH_2^{\bullet}$ → C_2H_4 + $C_3H_7^{\bullet}$) radicals. By computing the pressure-dependent rate constants for species with an increasing number of atoms, we can systematically determine the application limit of the alternative approaches proposed in this work.

2. THEORETICAL AND COMPUTATIONAL METHODOLOGY

2.1. Ab Initio and Initial Rate Constant Calculations.
In our previous work on the propen-2-ol unimolecular tautomerization into acetone,[22] we performed electronic structure calculations at the CCSD(T,FULL)/aug-cc-pVTZ//CCSD(T)/6-31+G(d,p) level of theory using the Gaussian09 package[23] to explore the potential energy surface. Canonical variational transition state rate constants at the high-

pressure limit (HPL) with small curvature tunneling correction were computed using Polyrate 2016-2A,[24] and multistructural torsional anharmonicity was included with partition functions obtained with MSTor.[25] Pressure effects were estimated with the original SS-QRRK/MSC formulation,[14,15] which is implemented in Polyrate 2016-2A.[24] For more details related to the calculations we carried out, the reader is referred to the original publication.[22]

In this work, we initially recomputed the pressure-dependent rate constants for the propen-2-ol tautomerization with the original SS-QRRK/MSC formulation[14,15] and taking HPL rate constants from our previous study[22] but using this time a bespoke Python[26] code. The pressures considered were 0.00526, 0.1, 1.0, 10.0, and 100.0 atm. We used a de-energization temperature dependence given by the form $\alpha = \theta(T/300)^{0.85}$ cm^{-1},[27] with $\theta = 300$ cm^{-1} and $\theta = 300$ cm^{-1} for nitrogen and argon, respectively. The Lennard−Jones parameters are $\sigma = 3.798$ Å and $\varepsilon/k_B = 71.4$ K for nitrogen and $\sigma = 3.542$ Å and $\varepsilon/k_B = 93.3$ K for argon.[28] In the case of propen-2-ol, the Lennard−Jones parameters were those of n-propanol as stated in our previous work,[22] $\sigma = 4.549$ Å and $\varepsilon/k_B = 576.7$ K.

2.2. Definition of the Collision Efficiency Parameter.
The code[13] that implements the original SS-QRRK/MSC approach[14,15] allows the user to use two ways to compute the collision efficiency, which are given by eqs 1 and 2

$$\frac{\beta_c}{1 - \beta_c^{1/2}} = \frac{|\langle E_{all} \rangle|}{F_E k_B T} \tag{1}$$

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

where F_E is the normalized Boltzmann-weighted number of unimolecular states above the threshold energy, k_B is the Boltzmann constant, T is the temperature, $\langle \Delta E_{all} \rangle$ is the average vibrational energy transferred during both energization and de-energization processes, and α is the average energy transferred only during the deactivation process. Troe[29] was the first to introduce eq 2, and eventually Gilbert and Smith[30] recommended this expression. Therefore, eq 2 can be referred as the Troe−Gilbert−Smith approximation.

The two definitions for the collision efficiency implemented in the MSC model differ in the energy transfer parameters $\langle \Delta E_{all} \rangle$ and α, which are related by $\langle \Delta E_{all} \rangle = \gamma - \alpha$, with γ being the average energy transferred in the activation process (formation of A^* in reaction R1).

We chose to work with eq 2 because the literature offers values of α rather than values of $\langle \Delta E_{all} \rangle$ for the physical conditions encountered in our work. However, eq 1 might also contribute to the underestimation of the value of the pressure-dependent rate constants we describe.[20,21] It is important to bear in mind that the two alternative definitions of collision efficiency we tested in this work took as reference eq 2.

Although one can use different theoretical[31] or experimental[32] methods to obtain the energy transfer parameters $\langle \Delta E_{all} \rangle$ and α, kinetic modelers usually look at the literature for these values of the system under investigation. In many cases, this search fails and then two scenarios are possible. First, the final model implements parameters of a similar system, or second, the parameters just fit experimental data at certain conditions of pressure and temperature, expecting that the model can predict the kinetic behavior at those and other temperatures and pressures. As a result, the value of $\langle \Delta E_{all} \rangle$ or α introduces

the largest uncertainty in fall-off computations using either ME or MSC energy transfer models.[11]

As stated by Gilbert et al.[21] and Dean et al.,[12,20] eq 2 leads to inaccurate results of β_c when the reactive system achieves high values of F_E, that is, at high temperatures, thereby underestimating β_c; this underestimation is especially pronounced in large systems. As a result, the MSC model does not allow one to accurately estimate the pressure effects at high temperatures in systems with many degrees of freedom (i.e., higher than C_2 hydrocarbons). An alternative formulation for fixing the underestimation of β_c is given by eq 3

$$\beta_{c,\Delta} = \left(\frac{\alpha}{\alpha + F_E k_B T}\right)^2 \frac{1}{\Delta} \tag{3}$$

In eq 3, the term Δ can be considered as a correction factor to yield a new definition of the collision efficiency, $\beta_{c,\Delta}$. In this work, two different expressions for Δ and therefore two alternative definitions for β_c have been tested. The first one belongs to the work of Gilbert et al.,[21] who proposed the following correction factor

$$\Delta = \int_0^{E_0} f(E) \left[1 - \frac{F_E k_B T}{\alpha + F_E k_B T} \exp\left(-\frac{E_0 - E}{F_E k_B T}\right)\right] dE \tag{4}$$

where E_0 is the threshold energy or Tolman activation energy and $f(E)$ is the up and down collisional model, which, in our case, has an exponential formulation given by eq 5[21]

$$f(E) = \frac{1}{F_E k_B T} \exp\left(-\frac{E}{F_E k_B T}\right) \tag{5}$$

Equation 5 is an approximation that has been used to obtain analytical solutions of the ME in the low-pressure range.[21] Inserting $f(E)$ (eq 5) into eq 4 and solving the integral by the analytical procedure presented in Section 1 of the Supporting Information, one gets eq 6

$$\Delta = 1 - \exp\left(-\frac{E_0}{F_E k_B T}\right)\left(1 + \frac{E_0}{\alpha + F_E k_B T}\right) \tag{6}$$

In our approach, eq 6 takes as input the value of F_E derived from the MSC model and calculates Δ to obtain $\beta_{c,\Delta}$ by eq 3; in a subsequent step, the pressure-dependent rate constants are calculated using the SS-QRRK theory[14,15] but using $\beta_{c,\Delta}$ as input.

The second definition used for the collision efficiency parameter uses the correction factor Δ explicitly presented by Dean et al.,[12,20] which is a function of F_E and the vibrational density of states, $\rho_v(E)$. Equations 7–10 show this dependency

$$\Delta = \Delta_1 - \left(\frac{F_E k_B T}{\alpha + F_E k_B T}\right)\Delta_2 \tag{7}$$

$$\Delta_1 = \frac{\int_0^{E_0} \rho_v(E)\exp[-E/(k_B T)]dE}{\Delta_N} \tag{8}$$

$$\Delta_2 = \frac{\int_0^{E_0} \rho_v(E)\exp[-E/(k_B T)]\exp[-(E_0 - E)/(F_E k_B T)]dE}{\Delta_N} \tag{9}$$

$$\Delta_N = \int_0^{\infty} \rho_v(E)\exp[-E/(k_B T)]dE \tag{10}$$

The vibrational density of states, $\rho_v(E)$, was computed by means of the Whitten–Rabinovitch approximation[33]

$$\rho_v(E) = \frac{[E + a(E)E_Z]^{s-1}}{(s-1)! \prod_{i=1}^{s}(h\nu_i)} \tag{11}$$

In eq 11, s is the number of vibrational degrees of freedom, α is an empirical energy-dependent factor, E_Z is the zero-point energy, and ν_i is the vibrational frequency of the normal mode i. The integrals of eqs 8, 9, and 10 were solved numerically in the Python[26] code to obtain the final Dean et al.[12,20] correction factor (Δ) of eq 7. Next, Δ is used in eq 3 to obtain $\beta_{c,\Delta}$, as we did with the former definition for β_c.

The alternative collision efficiency definitions were implemented with the SS-QRRK theory.[14,15] In the first stage, we computed the correction factor Δ by either the Gilbert et al.[21] (eq 6) or Dean et al.[12,20] (eq 7) equations, as previously described. Then the corrected collision efficiency value was obtained by eq 3, thus replacing the original definition used by the MSC model, β_c, by a new one, $\beta_{c,\Delta}$ in a newly written SS-QRRK/MSC code. The code has been written in Python[26] as described in Section 2 of the Supporting Information, where it is also provided. Hereafter, the combination of the SS-QRRK theory[14,15] and the MSC model using the correction factor of Gilbert et al.[21] and Dean et al.[12,20] will be denoted as the SS-QRRK/MSC-Gilbert and SS-QRRK/MSC-Dean approaches, respectively. The original approach[14,15] will be labeled just as SS-QRRK/MSC.

2.3. Comparison with RRKM/ME Pressure-Dependent Rate Constants. To assess the accuracy of the two SS-QRRK/MSC approaches proposed in this work, we compared their results with those of RRKM/ME calculations using two reactive systems and considering the temperature and pressure ranges from 200 to 3000 K and from 0.01 to 100.0 atm, respectively. The first reactive system is the unimolecular propen-2-ol unimolecular tautomerization (same system mentioned in section 2.1). RRKM/ME pressure-dependent rate constants were computed with the ChemRate software.[34] Vibrational, rotational, and energy data were taken from our previous study,[22] with the enthalpies of formation from the NIST database.[35] One-dimensional tunneling coefficients, as calculated by ChemRate,[34] were neglected since our objective is to compare the performance of the approaches we implemented against the performance of the RRKM/ME method when estimating pressure effects. For SS-QRRK/MSC calculations, we used HPL rate constants computed by ChemRate software[34] using TST (HPL rate constants already calculated in our previous study[22] were not considered in this comparison in section 3.2.1 since they included other effects). Nitrogen was the bath gas, with parameter values of the energy transfer model as presented in section 2.1.

The second reactive system was that studied by Ding et al.,[36] who computed the pressure-dependent rate constants for the decomposition (β-scission) of 1-propyl, 1-butyl, and 1-pentyl radicals into ethylene and the respective radical: methyl, ethyl and 1-propyl radical, accordingly. The temperature and pressure ranges were the same as those considered for the first reactive system. With nitrogen as the bath gas, the energy transferred during the deactivation process was considered constant and given by $\alpha = 200$ cm^{-1}. The collision parameters

selected were those of the corresponding hydrocarbons propane, butane, and pentane, which are presented in Table 1.

Table 1. Lennard−Jones Parameters[28] for the Hydrocarbon Radicals Studied in This Work[a]

species	σ (Å)	ε/k_B (K)
propane (1-propyl radical)	5.118	237.1
n-butane (1-butyl radical)	4.687	531.4
n-pentane (1-pentyl radical)	5.784	341.1

[a]Propane, n-butane, and n-pentane were the references for the species indicated in parentheses.

3. RESULTS AND DISCUSSION

Figure S1 of the Supporting Information shows the potential energy profile of the propen-2-ol tautomerization. The reaction has a well-defined barrier with an adiabatic value of 54.0 kcal mol^{-1}. Additional results and discussions about the potential energy surface and rate constants can be found in our previous work;[22] here, we focus on the analysis of implementing the two proposed SS-QRRK/MSC approaches previously described in section 2.2. We obtained all results presented below using nitrogen as the bath gas.

3.1. Pressure Effects in the Propen-2-ol Unimolecular Tautomerization. *3.1.1. Pressure-Dependent Rate Constants.* Figure 1 shows the SS-QRRK/MSC[14,15] pressure-dependent rate constants for the propen-2-ol tautomerization to acetone calculated as described in section 2.1. Numerical values are provided in Sections 4.1 and 5.1 of the Supporting Information considering nitrogen and argon as the bath gases, respectively. The original SS-QRRK/MSC approach[14,15] implemented in our Python code captures the expected relative decrease in rate constants as pressure decreases due to the lack of collisions to repopulate the excited adduct as fast as it reacts. However, there is a local temperature maximum in the pressure-dependent rate constants followed by a decrease when temperature goes beyond a certain value (i.e., 1800 K at 0.00526 atm). In our work on other reactive systems, we observed that this maximum arises at lower temperatures as the number of atoms in the involved molecules increases and is not particular of the system under investigation: it has been also described by other authors in the study of the hydrogen shift isomerization of oxygenated C_5 hydrocarbons.[37]

The trend depicted in Figure 1 for the pressure-dependent rate constants is not expected and is attributed to the collision efficiency definition used by the initial MSC model approach (eq 2). Relations like eqs 1 and 2 are approximations obtained from solving the ME in the low-pressure limit, and experimental values of β_c are qualitative in nature with availability limited to a certain number of chemical systems.[11] This work aims to help with the problem of selecting an appropriate collision efficiency expression to avoid the underestimation of rate constants described above.

The collision efficiency β_c shows an inverse relationship with the normalized Boltzmann-weighted number of unimolecular states above the threshold energy, F_E, defined as[38]

$$F_E = \int_{E_0}^{\infty} \frac{\rho(E)}{\rho(E_0)} \exp[-(E - E_0)/(k_B T)] \frac{dE}{k_B T} \tag{12}$$

The determination of F_E requires knowledge of the unimolecular species density of states, $\rho_v(E)$, and it is obtained
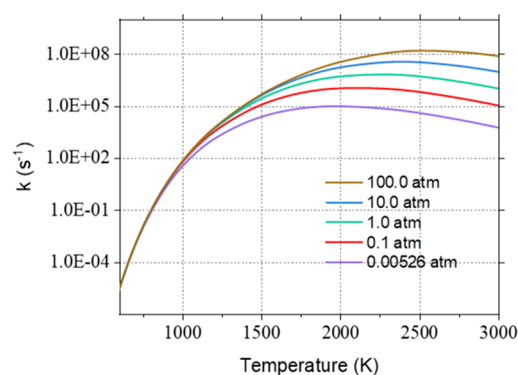

Figure 1. Pressure-dependent rate constants with nitrogen as the bath gas computed with the original SS-QRRK/MSC approach[14,15] for the propen-2-ol unimolecular tautomerization to acetone.

by the Whitten−Rabinovitch approximation,[33] which only considers the vibrational frequencies, as indicated by eq 11. Considering that the empirical factor a is independent of the energy and introducing eq 11 in eq 12, we obtain

$$F_E = \sum_{i=0}^{s-1} \frac{(s-1)!}{(s-1-i)!} \left(\frac{k_B T}{E_0 + a(E_0)E_Z} \right)^i \tag{13}$$

Bao and Truhlar[38] studied the uncertainty introduced by considering the empirical factor as energy independent. These authors compared rate constants obtained using eq 13 and those obtained by solving eq 12 numerically, that is, considering $a(E)$. The results indicate that for small molecules and reactions with energy thresholds above 30 kcal mol^{-1}, the differences are negligible at all temperatures. In other cases, the underestimation of the pressure-dependent rate constants using eq 13 could be of a factor of 2.0−5.8 at high temperatures (2200−2400 K). In this work, we attempted to alleviate the underestimation introduced by the original SS-QRRK/MSC approach, making the application of the SS-QRRK theory[14,15] as general as possible. Therefore, we adopted the numerical integration of eq 12 because it meets our objectives.

In general, the values of F_E can be increased by two variables, temperature and number of normal modes, s (the number of normal modes is related to the molecule size or number of atoms). However, the definition of the collision efficiency given by eq 2, which is the one used by the original MSC model,[14,15] underestimates the values of this parameter in the high-temperature regime, as was already discussed, because of the large values of F_E of large reactive systems with many normal modes and at high temperatures. The overall result is an overestimation of pressure effects, yielding too low values for the pressure-dependent rate constants (Figure 1). Nonetheless, eq 2, and therefore the original SS-QRRK/MSC approach,[14,15] yields accurate results at intermediate temperatures[21] and for smaller reactive systems.[9] As an example, Jasper et al.[39] found that the Troe−Gilbert−Smith approximation (eq 2) accurately predicts the collision efficiency when running classical trajectories simulations for the decomposition of methane using different bath gases (H_2O, O_2, He, Ar, Kr, H_2, N_2, and CH_4 itself).

In general, the larger is the reactive system, the lower will be the temperature at which these wrong predictions will arise, thereby limiting the application of the SS-QRRK theory.[14,15] In the next section, we show how this behavior can be corrected
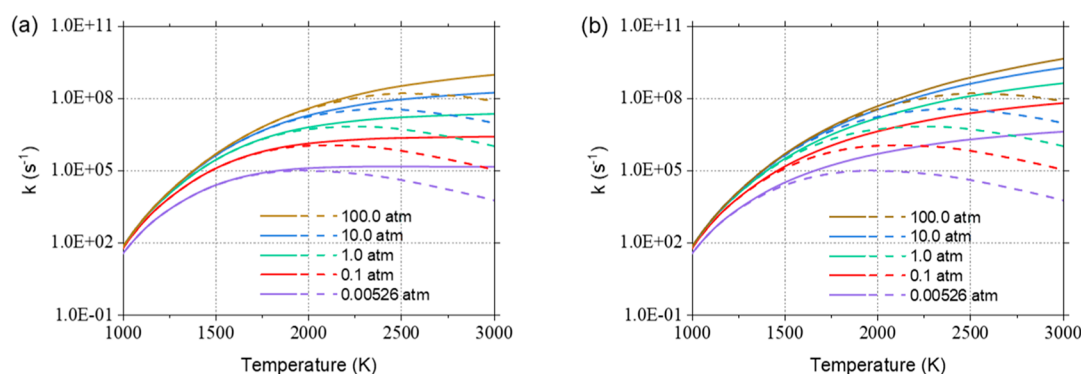
Figure 2. Pressure-dependent rate constants with nitrogen as the bath gas for propen-2-ol unimolecular tautomerization using the two alternative definitions for the collision efficiency parameter (solid lines): (a) SS-QRRK/MSC-Gilbert approach and (b) SS-QRRK/MSC-Dean approach.[12,20] Values computed with the original SS-QQRK/MSC approach[14,15] (dashed lines) are included for comparison.

using the previously described alternative definitions for the collision efficiency, as implemented in our bespoke code.

3.1.2. Alternative Definitions for the Collision Efficiency Parameter. To correct the erroneous trend introduced by the collision efficiency β_c defined in the original MSC model (eq 2), a correction factor denoted as Δ is implemented to obtain a different collision efficiency definition, $\beta_{c,\Delta}$ (eq 3). In this section, only the most important results of this implementation will be discussed; details about the two different correction factors used are described in section 2.2 and in Section 1 of the Supporting Information.

In short, two definitions of the collision efficiency, from the works of Gilbert et al.[21] and Dean et al.,[12,20] were tested, with the respective approaches used to compute the pressure-dependent rate constants denoted as SS-QRRK/MSC-Gilbert and SS-QRRK/MSC-Dean. Figures 2a and 2b, respectively, show their effect on the rate constants of the unimolecular tautomerization. Rate constants from Figure 1 are also illustrated with dashed lines for comparison purposes. In Figure 2a, the drop previously observed in the rate constants plotted in Figure 1 is no longer present, showing an asymptotic tendency in agreement with the expected behavior for this type of reaction. Therefore, the SS-QRRK/MSC-Gilbert approach (Δ from eq 6) fixes the underestimation introduced by the collision efficiency parameter used by the original MSC model (eq 2). At 0.00526 atm, which is the lowest pressure considered in this section, the correction of the rate constants becomes evident at around 1800 K. Overall, this correction accurately alleviates the effect of the increase of the term F_E in eq 3 by also increasing the value of $1/\Delta$. Numerical values of the corrected pressure-dependent rate constants shown in Figure 2a (solid lines) are given in Section 4.2 of the Supporting Information.

In Figure 2b, the SS-QRRK/MSC-Dean approach predicts a monotonic increase of the rate constants with temperature and thereby predicts higher values than the SS-QRRK/MSC-Gilbert approach due to its direct relation with the density of states; as a result, higher values of the collision efficiency ($\beta_{c,\Delta}$, eq 3) and pressure-dependent rate constants are obtained. Numerical values of the corrected pressure-dependent rate constants shown in Figure 2b (solid lines) are given in Section 4.3 of the Supporting Information.

The analysis of the rate constants plotted in Figure 2 also applies to the computed pressure-dependent rate constants using argon as the bath gas, whose trend is similar as shown in Figure S2 of the Supporting Information. Numerical values of

the pressure-dependent rate constants for the argon case are provided in Section 5.2 (SS-QRRK/MSC-Gilbert) and Section 5.3 (SS-QRRK/MSC-Dean) of the Supporting Information.

To exemplify the effect of temperature on the collision efficiency for the unimolecular tautomerization and thereby its effect in the pressure-dependent rate constants, Figure 3 shows the collision efficiency calculated by the original MSC model (eq 2) together with those obtained by the definitions by Gilbert et al.[21] (eq 6) and Dean et al.[12,20] (eq 7) in the 1000−3000 K temperature range. The collision efficiency obtained with eq 2 is much lower than that obtained with the other two formulations at temperatures beyond 1800 K, explaining the observed underestimation of the rate constants predicted by the original SS-QRRK/MSC approach.[14,15] At lower temperatures the three formulations predict the same results. The collision efficiency obtained with Gilbert et al.'s[21] formulation fixes the underestimation of this parameter within the whole temperature range, achieving a steady value of around 1.0×10^{-2} beyond 1800 K. Dean et al.'s[12,20] formulation also fixes the underestimation of the collision efficiency and achieves an asymptotic behavior close to 1.0 at higher temperatures, therefore predicting higher values for the rate constants than the former formulation. Similar results were obtained with argon as the bath gas, which are presented in Figure S3 of the Supporting Information.

The pressure-dependent reverse rate constants of the propen-2-ol unimolecular tautomerization can be derived from the equilibrium constants obtained from the HPL kinetic parameters and the corresponding pressure-dependent forward rate constants corrected with the most accurate approach. The accuracy of the different approaches tested will be addressed in the next section by comparing the SS-QRRK/MSC-Gilbert and SS-QRRK/MSC-Dean results with those of the more rigorous RRKM/ME method.

3.2. Benchmark of the SS-QRRK/MSC-Gilbert and SS-QRRK/MSC-Dean Approaches Against the RRKM/ME Method. *3.2.1. Propen-2-ol Unimolecular Tautomerization as the Reactive System.* Figure 4 shows the comparison between the pressure-dependent rate constants computed using the SS-QRRK (solid lines) and RRKM/ME (dashed lines) methods. For the SS-QRRK theory,[14,15] we used the collision efficiency of the original implementation[14,15] (Figure 4a, SS-QRRK/MSC approach) as well as the other two alternative definitions by Gilbert et al.[21] (Figure 4b, SS-QRRK/MSC-Gilbert approach) and Dean et al.[12,20] (Figure 4c, SS-QRRK/MSC-Dean approach). As mentioned in section
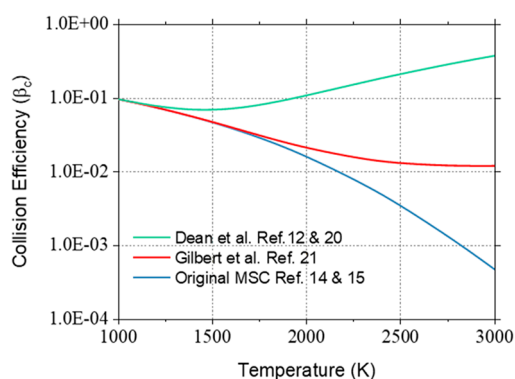
Figure 3. Collision efficiency parameter (β_c) calculated for the unimolecular tautomerization with nitrogen as the bath gas using the three different formulations described in this work.

2.3, we employed for the SS-QRRK/MSC calculations HPL rate constants calculated by ChemRate software,[34] which does not account for multidimensional tunneling, variational effects, and multistructural anharmonicity; this procedure allows us to make a more appropriate comparison since our previously computed HPL rate constants[22] would include those effects in the calculated low-pressure rate constants.

Similar to the results shown in Figure 1, the original SS-QRRK/MSC approach[14,15] tends to increasingly underestimate the value of the pressure-dependent rate constants as temperature increases (Figure 4a). At the lowest pressure tested, 0.01 atm, discrepancies start at around 2100 K, reaching an underestimation factor of 28.1 at 3000 K. At the highest pressure considered, 100.0 atm, discrepancies become evident

at around 2500 K, reaching an underestimation factor of 3.7 at 3000 K.

The SS-QRRK/MSC-Gilbert approach (Figure 4b) improves the results obtained with the original SS-QRRK/MSC[14,15] approach. The underestimation of the rate constants disappears even in the high-temperature limit, and the reported values show a steady behavior similar to that observed with the RRKM/ME method (same improvement depicted in Figure 2a). As a result, the underestimation at 3000 K is reduced to factors of 4.0 and 1.3 at 0.01 and 100.0 atm, respectively, representing a significant improvement (i.e., underprediction at 0.01 atm and 3000 K is seven times lower) in comparison with the SS-QRRK/MSC approach.[14,15]

The SS-QRRK/MSC-Dean approach (Figure 4c) also better reproduces the RRKM/ME method but with two further improvements compared to the SS-QRRK/MSC-Gilbert approach. First, the overestimation factor at 0.01 atm and 3000 K is further reduced to 3.0; Table 2 summarizes the

Table 2. Deviation Factors of the Pressure-Dependent Rate Constants for the Propen-2-ol Unimolecular Tautomerization Computed with the Different SS-QRRK/MSC Approaches and Taking the RRKM/ME Results As Benchmark

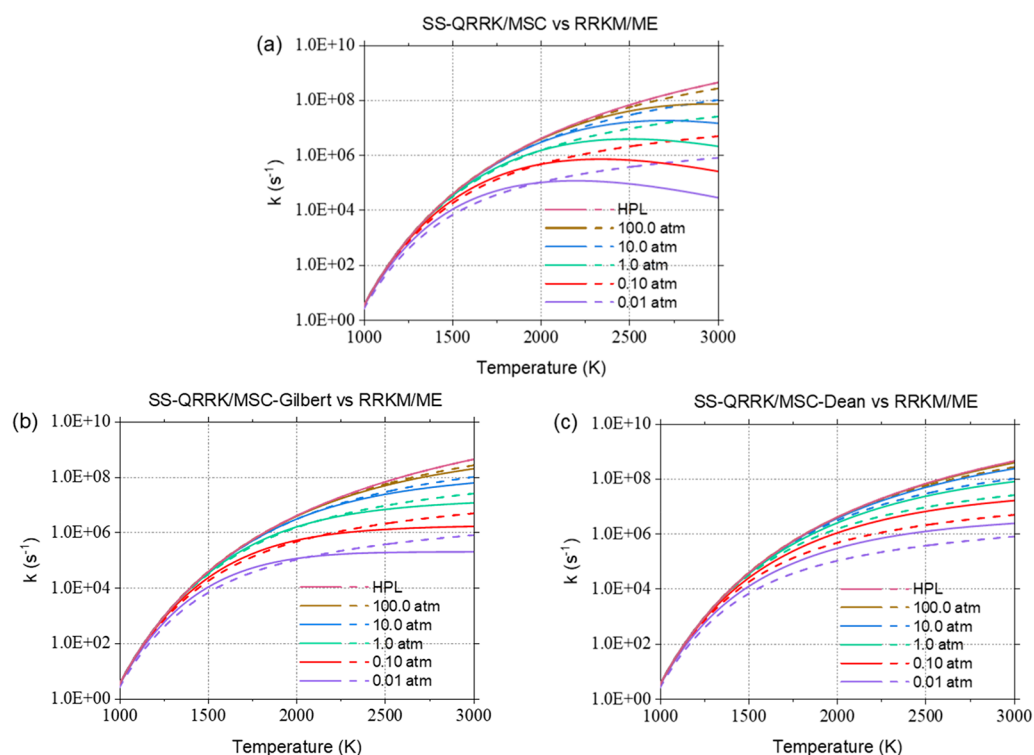| implementation	underestimation (u) or overestimation (o) factors at 3000 K	
	0.01 atm	100.0 atm
SS-QRRK/MSC	28.1 (u)	3.7 (u)
SS-QRRK/MSC-Gilbert	4.0 (u)	3.1 (u)
SS-QRRK/MSC-Dean	3.0 (o)	1.5 (o)

Figure 4. Comparisons between the pressure-dependent rate constants computed using the SS-QRRK/MSC (solid lines) and the RRKM/ME (dashed lines) methods. SS-QRRK/MSC method uses the collision efficiency definition of (a) the original approach[14,15] (eq 2), (b) Gilbert et al.[21] (eq 6), and (c) Dean et al.[12,20] (eq 7).
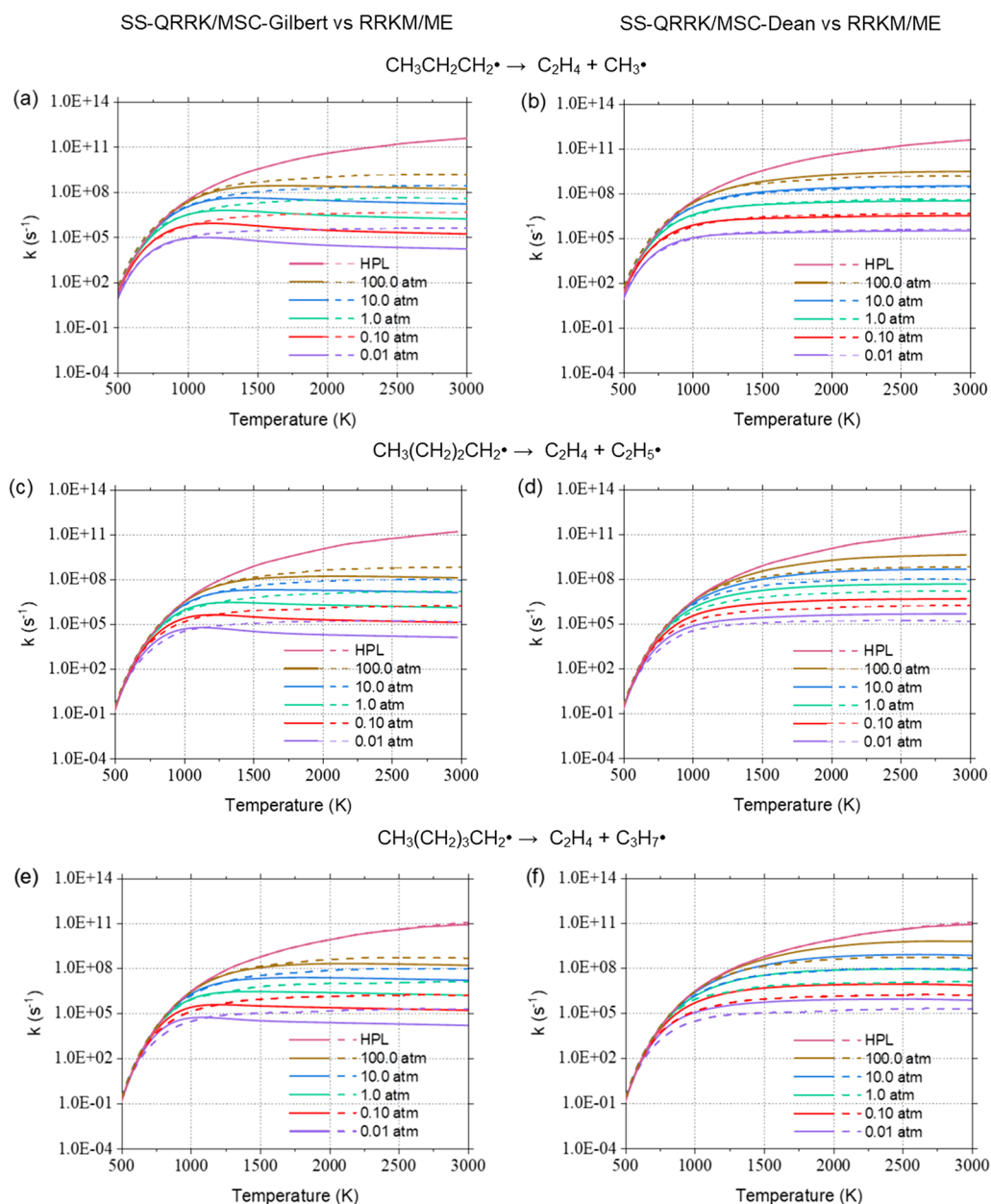
Figure 5. Comparisons between the pressure-dependent rate constants for the decomposition of three different alkyl radicals computed with the SS-QRRK/MSC (solid lines, this work) and RRKM/ME (dashed lines, Ding et al.[36]) methods. SS-QRRK/MSC method uses the collision efficiency definition of Gilbert et al.[21] given by eq 6 (panels a, c, and e) and Dean et al.[12,20] given by eq 7 (panels b, d, and f). 1-Propyl radical: panels a and b. 1-Butyl radical: panels c and d. 1-Pentyl radical: panels e and f.

discussed underestimation/overestimation factors with the different approaches used in this work for a closer comparison. Second, the SS-QRRK/MSC-Dean approach also reproduces better the general trend of RRKM/ME results with a monotonic increase of the rate constants in the high-temperature regime, while the SS-QRRK/MSC-Gilbert rate constants seem to achieve a more steady-state behavior. Numerical values of the data presented in Figure 4 are available in Section 8 of the Supporting Information.

The collision efficiency parameter determines the trends observed in Figure 4. Similar to the data shown in Figure 3, the MSC-Dean energy transfer model has the highest values for the collision efficiency parameter, leading to the highest values for the rate constants below the HPL and explaining the overestimation with respect to the RRKM/ME results. On the

other hand, one observes the opposite behavior for the original transfer model, which underestimates the RRKM/ME results.

3.2.2. Decomposition of Hydrocarbons as the Reactive System. Figure 5 shows the pressure-dependent rate constants for the decomposition (β-scission) of 1-propyl (C_3), 1-butyl (C_4), and 1-pentyl (C_5) radicals (solid lines in panels a and b, c and d, and e and f, respectively) computed using the SS-QRRK/MSC-Gilbert (panels a, c and e) and SS-QRRK/MSC-Dean (panels b, d and f) approaches. The figure also shows the benchmark values computed by Ding et al.[36] using the RRKM/ME method (dashed lines). These computations provide insights into the performance of the new SS-QRRK/MSC approaches as the size of the reactive system increases, which would help to determine if one could apply the SS-QRRK theory[14,15] to larger reactive systems.

We found similar trends to those observed for the unimolecular propen-2-ol tautomerization but with notable differences: pressure effects become important at lower temperatures (around 700 K in comparison to 1250 K for the propen-2-ol tautomerization), and the pressure-dependent rate constants reach steady values also at lower temperatures (around 1600 K).

The overestimation of the rate constants by the SS-QRRK/MSC-Gilbert approach becomes evident at around 750 K followed by an underestimation, as shown in Figure 5a, 5c, and 5e. We computed underestimation factors of 26.7, 12.9, and 10.3 for the decomposition of C_3, C_4, and C_5 radicals, respectively, at 0.01 atm and 3000 K, conditions of the highest deviations. This approach becomes in slightly better agreement with the RRKM/ME method as we increase the size of the reactant from C_3 to C_5.

The SS-QRRK/MSC-Dean approach reproduces with higher fidelity the trends of the RRKM/ME method as shown in Figure 5b, 5d, and 5f. The largest deviations occur at 100.0 atm and 3000 K, with underestimation factors of 2.1, 6.2, and 13.2 for the C_3, C_4, and C_5 radical decompositions, respectively. Less pronounced deviations occur at 0.01 atm and 3000 K, with underestimation factors of 1.3, 2.8, and 4.4 for the C_3, C_4, and C_5 radical decomposition reactions, correspondingly. Table 3 summarizes these deviation factors for both approaches, at pressures corresponding to their largest deviations, using RRKM/ME as benchmark for comparison purposes.

Table 3. Deviation Factors of the Pressure-Dependent Rate Constants for Decomposition of the C_3–C_5 Hydrocarbon Radicals Computed with the Different SS-QRRK/MSC Approaches and Taking the RRKM/ME Results as a Benchmark

	underestimation (u) or overestimation (o) factors at 3000 K		
implementation	C_3	C_4	C_5
SS-QRRK/MSC-Gilbert −0.01 atm	26.7 (u)	12.9 (u)	10.3 (u)
SS-QRRK/MSC-Dean −100.0 atm	2.1 (o)	6.2 (o)	13.2 (o)

The SS-QRRK/MSC-Dean approach has an outstanding performance, predicting the pressure-dependent rate constants for the C_3 radical decomposition (Figure 5b), with 2.1 being the largest overestimation factor value with respect to the RRKM/ME methodology. Although this approach shows the largest deviation for the C_5 radical decomposition at 100.0 atm and 3000 K with an overestimation factor value of 13.2, it shows good performance at pressures below 10.0 atm and temperatures as high as 2500 K (deviation factors less than 8.5), which are still common conditions in combustion chemistry experiments. The numerical values of the rate constants plotted in Figure 5 are available in Section 9 of the Supporting Information.

In summary, the SS-QRRK/MSC-Dean approach shows an overall better performance, and it could be suited to compute unimolecular pressure-dependent rate constants for species that have around the same number of degrees of freedom as C_5 species. However, validation with a system that resembles as close as possible the one under study is recommended, as a given reaction may have unique features that may change these conclusions.

3.3. Advantages and Limitations of the Proposed SS-QRRK/MSC-Gilbert and SS-QRRK/MSC-Dean Approaches. The collision efficiency parameters defined by Gilbert et al.[21] and Dean et al.[12,20] improve the results of the original SS-QRRK/MSC approach[14,15] by correcting the underestimation of the pressure-dependent rate constants in the high-temperature regime; the SS-QRRK/MSC-Dean approach has a better performance overall, showing the same qualitative trends as the RRKM/ME method. Both approaches have the following general advantages.

- Extension of the applicability of the SS-QRRK theory[14,15] to larger molecules and across a wider temperature range. This is of special interest for reactions with pronounced variational effects, multi-dimensional tunneling, and/or multistructural torsional anharmonicity as these features can be simultaneously incorporated with the SS-QRRK theory.[14,15]

- Fast initial screening of large chemical reaction mechanisms: initial estimations of the pressure-dependent rate constants with a fast method (execution time on the order of seconds) would help to identify the most sensitive reactions that can be eventually addressed with a more robust and computationally demanding methodology, such as RRKM/ME (execution time on the order of hours).

Nonetheless, the collision efficiency definition studied in this work may fail under certain circumstances:

- The Whitten−Rabinovitch approximation for the density of states (eq 11) becomes inaccurate for very large molecules due to the presence of multiple conformational structures and coupled internal rotations; this would require a more comprehensive computational work.[38]

- The simplistic model of a single step for the activation and deactivation of the reactant (reaction R1) assumed by the MSC model may introduce further uncertainties in the determination of the pressure-dependent rate constants, especially at high temperatures.

- Increasing the size of the reactive system and thus the values of the normalized Boltzmann-weighted number of unimolecular states above the threshold energy makes corrections of the underestimation of the rate constants more difficult, especially at high temperatures. However, for hydrocarbons with up to 4 or 5 carbon atoms, accurate results can be obtained for temperatures as high as 2500 K, covering conditions of interest in atmospheric and combustion chemistry.

4. CONCLUSIONS

The system-specific quantum Rice−Ramsperger−Kassel theory/modified strong collision model (SS-QRRK/MSC)[13−15] approach was shown to underestimate the value of the pressure-dependent rate constants because of an inaccurate estimation of the collision efficiency, a parameter linked to the energy transfer model. This work explored the effect of two alternative definitions for the collision efficiency parameter using the SS-QRRK theory[13−15] in the calculation of pressure-dependent rate constants.

These definitions for the collision efficiency parameter belong to the works of Gilbert et al.[21] (eq 6) and Dean et al.[12,20] (eq 7), which coupled with the SS-QRRK theory[13−15] were denoted as the SS-QRRK/MSC-Gilbert and SS-QRRK/

MSC-Dean approaches, respectively. We tested these approaches to check their reliability for computing rate constants below the high-pressure limit by comparing their predictions to those of the more robust methodology Rice—Ramsperger—Kassel—Marcus/Master Equation (RRKM/ME), which served as the benchmark. Two model reactive systems were used for our comparison: propen-2-ol unimolecular tautomerization and decomposition (β-scission) of 1-propyl, 1-butyl, and 1-pentyl radicals to ethylene and the corresponding alky radical.

The SS-QRRK/MSC-Gilbert approach successfully corrects the underprediction of the pressure-dependent rate constants observed with the original SS-QRRK/MSC approach,[14,15] achieving an asymptotic behavior in the high-temperature regime. However, it does not reproduce qualitatively the trend of the RRKM/ME data, which shows a slight increase in the rate constants at high temperatures. On the contrary, the SS-QRRK/MSC-Dean approach not only corrects the underprediction of the pressure-dependent rate constants but also reproduces the trend of the RRKM/ME results at high temperatures showing a monotonic increase in the rate constants.

The SS-QRRK/MSC-Dean approach implemented in our bespoke code extends the applicability of the original SS-QRRK theory[14,15] by predicting accurate results across a broader set of conditions, that is, lower pressures and higher temperatures. It addresses the reactivity of larger molecules, such as C_4 and C_5 hydrocarbon species, more accurately. This implementation of SS-QRRK also allows the user to include reliably variational effects, multistructural anharmonicity, and multidimensional tunneling in the falloff region of chemical reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c02943.

> Mathematical solution of the correction factor (Δ) differential equation, Python code that implements the different approaches for computation of the pressure-dependent rate constants, potential energy surface of the propen-2-ol tautomerization, and pressure-dependent rate constants using argon as bath gas and the RRKM/ME method (PDF)

> Example Excel file to run the bespoke Python code, which implements the SS-QRRK/MSC approaches studied and proposed in this work (XLSX)

■ AUTHOR INFORMATION

Corresponding Authors

E. Grajales-González − *Physical Sciences and Engineering Division, Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal, Jeddah 23955-6900, Saudi Arabia;* ⃝ orcid.org/0000-0002-2317-0884; Email: edwing.grajalesgonzalez@kaust.edu.sa

M. Monge-Palacios − *Physical Sciences and Engineering Division, Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal, Jeddah 23955-6900, Saudi Arabia;* ⃝ orcid.org/0000-0003-1199-5026; Email: manuel.mongepalacios@kaust.edu.sa

Author

S. Mani Sarathy − *Physical Sciences and Engineering Division, Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal, Jeddah 23955-6900, Saudi Arabia;* ⃝ orcid.org/0000-0002-3975-6206

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpca.0c02943

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Pilling, M. J. Calculating the Pressure Dependence of Chemical Reactions. *Science* **2014**, *346*, 1183−1184.

(2) Pilling, M. J.; Seakins, P. W. *Reaction Kinetics*; Oxford University Press: New York, 1997.

(3) Jasper, A. W.; Pelzer, K. M.; Miller, J. A.; Kamarchik, E.; Harding, L. B.; Klippenstein, S. J. Predictive a Priori Pressure-Dependent Kinetics. *Science* **2014**, *346*, 1212−1215.

(4) Glowacki, D. R.; Liang, C.-H.; Morley, C.; Pilling, M. J.; Robertson, S. H. MESMER: An Open-Source Master Equation Solver for Multi-Energy Well Reactions. *J. Phys. Chem. A* **2012**, *116*, 9545−9560.

(5) Miller, J. A.; Klippenstein, S. J. Master Equation Methods in Gas Phase Chemical Kinetics. *J. Phys. Chem. A* **2006**, *110*, 10528−10544.

(6) Alexander, M. H.; Hall, G. E.; Dagdigian, P. J. The Approach to Equilibrium: Detailed Balance and the Master Equation. *J. Chem. Educ.* **2011**, *88*, 1538−1543.

(7) Nguyen, T. L.; Stanton, J. F. Three-Dimensional Master Equation (3DME) Approach. *J. Phys. Chem. A* **2018**, *122*, 7757−7767.

(8) Hinshelwood, C. N. *The Kinetics of Chemical Change in Gaseous Systems*; Oxford University Press: London, 1933.

(9) Troe, J. Predictive Possibilities of Unimolecular Rate Theory. *J. Phys. Chem.* **1979**, *83*, 114−126.

(10) Troe, J. Theory of Thermal Unimolecular Reactions at Low Pressures. II. Strong Collision Rate Constants. Applications. *J. Chem. Phys.* **1977**, *66*, 4758−4775.

(11) Bao, J. L.; Truhlar, D. G. Variational Transition State Theory: Theoretical Framework and Recent Developments. *Chem. Soc. Rev.* **2017**, *46*, 7548−7596.

(12) Chang, A. Y.; Bozzelli, J. W.; Dean, A. M. Kinetic Analysis of Complex Chemical Activation and Unimolecular Dissociation Reactions Using QRRK Theory and the Modified Strong Collision Approximation. *Z. Phys. Chem.* **2000**, *214*, 1533−1568.

(13) Bao, J. L.; Truhlar, D. G. Manual for SS-QRRK Utility Code. *SS-QRRK: A Program for System-Specific Quantum Rice-Ramsperger-Kassel Theory*; Department of Chemistry Chemical Theory Center and Supercomputing Institute, University of Minnesota: Minnesota, MN; 2017; pp 1−24.

(14) Bao, J. L.; Zhang, X.; Truhlar, D. G. 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 Fluoroform Dissociation. *Phys. Chem. Chem. Phys.* **2016**, *18*, 16659−16670.

(15) Bao, J. L.; Zheng, J.; Truhlar, D. G. 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.* **2016**, *138*, 2690−2704.

(16) Zhang, P.; Law, C. K. A Fitting Formula for the Falloff Curves of Unimolecular Reactions, II: Tunneling Effects. *Int. J. Chem. Kinet.* **2011**, *43*, 31−42.

(17) Monge-Palacios, M.; Grajales-González, E.; Sarathy, S. M. Formic Acid Catalyzed Keto-Enol Tautomerizations for C_2 and C_3 Enols: Implications in Atmospheric and Combustion Chemistry. *Int. J. Quantum Chem.* **2019**, *119*, No. e25954.

(18) Xing, L.; Wang, Z.; Truhlar, D. G. Multistructural Anharmonicity Controls the Radical Generation Process in Biofuel Combustion. *J. Am. Chem. Soc.* **2019**, *141*, 18531−18543.

(19) Duan, Y.; Monge-Palacios, M.; Grajales-Gonzalez, E.; Han, D.; Møller, K. H.; Kjaergaard, H. G.; Sarathy, S. M. Oxidation Kinetics of n-Pentanol: A Theoretical Study of the Reactivity of the 1-hydroxy-1-Peroxypentyl Radical. *Combust. Flame* **2020**, *219*, 20−32.

(20) Carstensen, H. H.; Dean, A. M. The Kinetics of Pressure-Dependent Reactions. In *Comprehensive Chemical Kinetics*; Green, N. J. B., Carr, R. W., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; Vol. *42*, Chapter 4, pp 101−184.

(21) Gilbert, R. G.; Luther, K.; Troe, J. Theory of Thermal Unimolecular Reactions in the Fall-off Range. II. Weak Collision Rate Constants. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 169−177.

(22) Grajales-González, E.; Monge-Palacios, M.; Sarathy, S. M. Theoretical Kinetic Study of the Unimolecular Keto-Enol Tautomerism Propen-2-ol ↔ Acetone. Pressure Effects and Implications in the Pyrolysis of Tert- and 2-Butanol. *J. Phys. Chem. A* **2018**, *122*, 3547−3555.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*, Revision d.01; Gaussian, Inc.: Wallingford, CT, 2010.

(24) Zheng, J.; Bao, L.; Meana-Pañeda, R.; Zhang, S.; Lynch, G. C.; Corchado, J. C.; Chuang, Y. Y.; Fast, P. L.; Hu, W. P.; Liu, Y. P.; et al. *POLYRATE 2016-2A*; University of Minnesota: Minneapolis, MN, 2016.

(25) Zheng, J.; Mielke, S.; Bao, J. L.; Meana-Pañeda, R.; Clarkson, K.; Truhlar, D. *MSTor: A Program for Calculating Partition Functions, Free Energies, Enthalpies, Entropies, and Heat Capacities of Complex Molecules Including Torsional Anharmonicity*, Version 2017b; University of Minnesota and IBM Almaden Research Center, Minneapolis, MN, and San Jose, CA, 2017.

(26) Python Software Foundation. Python Programming Language-Official Website; http://www.python.org/ (accessed May 20, 2020).

(27) Senosiain, J. P.; Klippenstein, S. J.; Miller, J. A. Reaction of Ethylene with Hydroxyl Radicals: A Theoretical Study. *J. Phys. Chem. A* **2006**, *110*, 6960−6970.

(28) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *Properties of Gases and Liquids*; McGraw-Hill Education: New York, 2001.

(29) Troe, J. Theory of Thermal Unimolecular Reactions at Low Pressures. I. Solutions of the Master Equation. *J. Chem. Phys.* **1977**, *66*, 4745−4757.

(30) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Science Inc.: London, 1990.

(31) Wang, H.; Wen, K.; You, X.; Mao, Q.; Luo, K. H.; Pilling, M. J.; Robertson, S. H. Energy Transfer in Intermolecular Collisions of Polycyclic Aromatic Hydrocarbons with Bath Gases He and Ar. *J. Chem. Phys.* **2019**, *151*, 044301.

(32) King, K. D.; Barker, J. R. Experiments on Collisional Energy Transfer. In *Comprehensive Chemical Kinetics*; Robertson, S. H., Ed.; Elsevier: Amsterdam, The Netherlands, 2019; Vol. *43*, Chapter 1 , pp 3−62.

(33) Whitten, G. Z.; Rabinovitch, B. S. Accurate and Facile Approximation for Vibrational Energy-Level Sums. *J. Chem. Phys.* **1963**, *38*, 2466−2473.

(34) Mokrushin, V.; Bedanov, V.; Tsang, W.; Zachariah, M. R.; Knyazev, V. D.; McGivern, W. S. ChemRate. *A Tool for RRKM/Master Equation Modeling*, Version 1.5.10; NIST, 2011.

(35) Linstrom, P. J.; Mallard, W. G. Gas Phase Thermochemistry Data. *NIST Chemistry WebBook; NIST Standard Reference Database Number 69*; National Institute of Standards and Technology, https://webbook.nist.gov/ (retrieved May 30, 2020).

(36) Ding, J.; Zhang, L.; Han, K. Thermal Rate Constants of the Pyrolysis of N-Heptane. *Combust. Flame* **2011**, *158*, 2314−2324.

(37) Xing, L.; Bao, J. L.; Wang, Z.; Wang, X.; Truhlar, D. G. Hydrogen Shift Isomerizations in the Kinetics of the Second Oxidation Mechanism of Alkane Combustion. Reactions of the Hydroperoxypentylperoxy OOQOOH Radical. *Combust. Flame* **2018**, *197*, 88−101.

(38) Bao, J. L.; Truhlar, D. G. Effect of Energy Dependence of the Density of States on Pressure-Dependent Rate Constants. *Phys. Chem. Chem. Phys.* **2018**, *20*, 30475−30479.

(39) Jasper, A. W.; Miller, J. A.; Klippenstein, S. J. Collision Efficiency of Water in the Unimolecular Reaction CH_4 $(+H_2O)$ ⇆ CH_3 + H $(+H_2O)$: One-Dimensional and Two-Dimensional Solutions of the Low-Pressure-Limit Master Equation. *J. Phys. Chem. A* **2013**, *117*, 12243−12255.