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Impact of the size and degree of branching of alkanes on the rate rules approach: the case of isomerizations

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Abstract

The accurate and high-throughput generation of kinetic data for combustion detailed chemical kinetic models remains a challenge given the large size of these models. For large organic molecules, the majority of kinetic data of the kinetic models are estimated using quantitative structure activity relationships within reaction classes and reaction rate rules approaches. In this work, we question the limits of the rate rule approach for the isomerization reaction classes, using electronic structure calculations and reaction rate theories. Systematic calculations were performed to investigate the effect of the size and the degree of branching of alkyl radicals on the rate coefficients and their consequences on the rate rule approach. Our computed kinetic data show that when the size of alkyl group is increased, the rate coefficients remains close to each other. This allows the use of methyl as representative models of larger alkyl groups to investigate the influence of increasing the degree of branching. The computed rate coefficients for 1,3- and 1,4-H-atom shifts show that the increase of the branching level, with spectator methyl groups in the transition state cyclic structure can strongly increase the rate coefficients, up to several orders of magnitude. Consequently, a single rate rule is not feasible for any degree of branching of a reaction belonging to the same isomerization reaction class. As variation in rate coefficients are important, this would lead to an explosion of the number rate rules as a function of branching in 5-, 6-, and 7-membered cyclic transition states. A new approach is demonstrated and proposed where model transition states are tabulated, and methyl groups are assumed as alkyl groups and all combinations of substitutions in the model TSs, for a given reaction class, are included in a table with associated ab initio rate coefficients. The automation of the construction of such tables is possible and could be an interesting high-throughput / high-accuracy alternative to on-the-fly ab initio calculations of kinetic parameters.

Keywords: H-atom shifts, rate rules, kinetic model generation, theoretical chemistry

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1. Introduction

The development of reliable detailed kinetic models is crucial to understand, simulate and predict the combustion properties of fuels, from their global combustion parameters (ignition delay times, laminar burning velocities, *etc.*) to their pollutants, over a large range of temperatures and pressures. Detailed kinetic models are therefore important tools in the design of low-emission, high efficiency combustion systems operating with sustainable alternative fuels. The development of these combustion kinetic models for liquid fuel surrogates leads to reaction mechanisms that contains thousands of elementary reactions and species for which, thermochemical and kinetic data are required [1]. These data can be found in experimental databases, estimated from semi-empirical correlations, or calculated using theoretical chemical kinetics. In large kinetic models, i.e. models that do not belong to the core chemistry reaction bases, the majority of these parameters comes from correlations. Indeed, it is not possible to find experimental data for each reactions of the mechanism in the literature [2]. In addition, biofuel combustion models need to include an increasing number of chemical functions for which there is little experimental data compared to hydrocarbons.

The manual assembly or the automatic generation of large (bio)fuels combustion models is based on core chemistry reaction bases, with known thermo-kinetic data, and reactions classes that require the fast and high-throughput calculation of thermochemical and kinetic data with correlations [2]. Thermodynamic data can be efficiently estimated using the group additivity method proposed by Benson [3]. The kinetic data are calculated within the framework of reaction classes, with associated rate rules. It can be noted that theoretical calculations, based on quantum chemistry, statistical thermodynamics and reaction rate theories can be used to accurately compute these data, on the fly [4] or to store them in databases. However, this approach remains limited to about ten heavy atoms. Therefore, for larger molecules, these theoretical methods are mostly used to define or refine reaction rate rules [5].

The definition of rate rules is based on reaction similarity. Generic rate constants can be derived from semi-empirical correlations, defined within a kinetic model, and built to simulate a set of experimental data [6]. Rate rules can also be defined using an accurate rate coefficient obtained from experiments or calculated using quantum chemistry to estimate the rate constants for a family of similar reactions [7]. Semi-empirical correlations are mostly based on classical free-energy relationships or on the thermo-kinetic methods of Benson and coworkers. One of the most used free-energy relationships is the Evans-Polanyi method: the pre-exponential factor A is considered constant for a family of reactions, whereas the activation energy is estimated using a

linear relationship between E_A and the enthalpy of reaction [1, 2]. Benson's thermo-kinetic methods can also be applied to estimate the entropy and enthalpy of activation, based on estimated variations in the geometries, energies and partition functions between the reactant(s) and the transition state (TS). Rate rules based on such techniques are widely used to estimate kinetic parameters in automatically generated or manually assembled combustion kinetic models [6, 8-11].

Theoretical calculations can also be used as a basis for determining semi-empirical rate rules [12-15]. The *ab initio* computation of rate constants for a set of reactions belonging to the same reaction class is often used for the definition of rate rules. Given the balance that needs to be found between accuracy and the size of the system with the theoretical methods, rate rules are mostly defined from the calculation of the rate constant on a minimal structure [15]. Truong [16] proposed the reaction class transition state theory (RC-TST) approach for the calculation of a reaction constant k_1 from a known reaction constant k_2 by using *ab initio* correction factors and applied it for H-abstractions and other reaction classes of interest for combustion. Dean and co-workers proposed rate rules for alkyl + O₂ reactions, including, additions, concerted elimination, isomerizations, *etc.*, [7]. Based on a systematic calculation of the high-pressure rate constants, a rate rule is derived from a set of reaction of a given reaction class (mean rate constant value). An interesting point is raised by the latter study, in the case of alkylperoxy (RO₂) isomerizations. In this case, a large set of reactions can be built for each reaction class. For example, a rate rule for 1-4p isomerizations of RO₂ radicals was proposed by Villano *et al.* [7]. They found that the rate rule predicts the computed individual rate constants within a factor of 2 for a set of 7 reactions of different R, except for R = ethyl, the minimal structure of 1-4p, that is slower than the rate rule by a factor of 3.7 at 500 K (and was therefore excluded from the rate rule definition). This result is particularly striking as most rate rules derived from theoretical calculations are performed on minimal size structures to allow a high-level calculation. This raises questions on the conclusion that can be made within the uncertainty of the rate constant calculations and the validity of a rate rule approach for any size and degree of branching of a reaction belonging to the same reaction class.

This work aims at answering these questions by focusing on the simplest isomerizations of alkyl radicals (1-3, and 1,4-H-atom shifts). Starting from a minimal size transition state structure, these systems allow to vary the size of the lateral alkyl groups and the degree of branching of the alkyl radical, while systematically varying the nature of the radical carbon and of the transferred H-atom (primary, secondary, and tertiary). As it will be shown, this

leads to a very large number of structural combinations.

Several experimental [17-19] and theoretical literature studies have been reported over the years for alkyl isomerizations, which allows us to have some perspective on these reactions. Semi-empirical rate rules for these reactions classes are illustrative and widely used. Curran et al. [20] used

$$E_A = \Delta_r H + RSE + E_{ABS} \quad (1)$$

to estimate activation energies of isomerizations in their heptane combustion model. In Equation (1), E_A is the sum of the strain-free energy to abstract the H-atom (E_{ABS}) with the Ring Strain Energy (RSE) of the cyclic transition state and, in the case of endothermic reactions, the enthalpy of reaction ($\Delta_r H$). In this rate rule, the pre-exponential factor is calculated from the difference in the entropy due to the loss of internal rotors in the cyclic transition state. E_{ABS} is approximated using an Evans-Polanyi [7] expression.

Matheu et al [14] developed Evans-Polanyi relationships from theoretical calculations for alkyl isomerizations. Davis and Francisco [21] investigate all possible H-shifts for the n-alkyl radicals, from 1-ethyl to 1-octyl radicals. In their study, they highlighted the importance of considering different conformations of transition states (axial and equatorial) in the rate parameter calculation, since both paths can occur. Wang et al. [22] calculated modified Arrhenius parameters for 1,2 to 1,7 H-shift reactions in alkyl radicals at the CBS-QB3 level of theory, creating a rate rule based on the ring size and the radical nature of the reactant and product. The presence of substituents on the non-reactive part of the cyclic transition state was not considered as a parameter in these studies

In this study, we first examine the influence of the size of the substituent on the rate coefficients in 1,3 H-shift reactions of alkyl radicals. The small number of heavy atoms in the minimal size structure (1-propyl) for this reaction class will also allow us to perform a high-level calculation to better define the uncertainties in the level of calculation used in this work. Based on this discussion, the influence of the degree of branching in 1,4 H-shift reactions will be discussed. The validity of a single set of reaction class and rate rule to describe the isomerization reactions of alkanes of any size and degree of branching will be discussed. Based on the conclusions of this work, an alternative to, fast, reaction rate rules and expensive on-the-fly calculations will be proposed: the tabulated TS approach.

2. Method

Canonical transition state theory was used to calculate the high-pressure rate coefficients:

$$k(T) = L\kappa(T)[k_b T/h] \cdot [q^\ddagger/q_r] \exp(-\Delta E^\ddagger/RT) \quad (2)$$

where L is the statistical factor, $\kappa(T)$ is the tunneling correction factor, q^\ddagger and q_r are the partition functions of the transition state structure and the reactant, and ΔE^\ddagger is the difference of energy at 0 K between the TS and the reactant.

In this study, the CBS-QB3 [23] level of calculation was systematically used. This level of theory was chosen because of the large size of several alkyl radicals and the large number of reactions computed (more than a hundred). The validity of this choice has been verified and is described below. Torsional modes were treated as hindered rotors, using the 1D-HR-U method [24], based on B3LYP/6-311G(d,p) relaxed scans. Other vibrational modes were treated as harmonic oscillators and scaled by a factor of 0.99. The tunneling correction factors were calculated using Eckart method, which was shown to agree with more sophisticated methods for H-shifts in n-alkyls due to error cancelations [19]. Canonical rate constants were fitted between 500 and 1500 K. All the kinetic calculations were performed with the ThermRot code [24] and all electronic calculations were done with Gaussian 16 [25].

To understand the uncertainties in the rate constant calculation using the method described above, a very high level of calculation based on the ANL-F12 method proposed by Klippenstein et al. [26] was used. This method was applied to compute the rate constant of three H-shift reactions: 1,3-H-shift and 1,2-H-shift reactions in n-propyl, and 1,1-H-shift reaction in ethyl. The geometries and vibrational frequencies were calculated at the CCSD(T)-F12/cc-pVDZ-F12 level of theory. Complete basis set (CBS) extrapolation of CCSD(T)-F12 single point calculation was performed with cc-pVTZ-F12 and cc-pVQZ-F12 basis sets. Corrections for core-valence interaction, higher-order excitation (CCSDT(Q)), anharmonic vibrations and relativistic effects were also included. The relaxed scans for single bonds torsion rotational corrections were performed at B2PLYP/cc-pVTZ level. More details of this method can be found in the supplementary material. Table 1 presents the computed energy barriers at the ANL-F12 and CBS-QB3 methods, along with other levels of theory for the 1,3-H-shift reaction in n-propyl.

Table 1: Energy barriers for 1,3-H-shift in n-propyl

	ANL-F12	CBS-QB3	W1U	G4
E (OK), kcal/mol	40.6	40.1	40.0	40.6

It can be observed that the CBS-QB3 energy barrier is close to the values calculated at higher levels. The computed rate coefficients calculated with the ANL-F12 are close to the CBS-QB3 ones ($\pm 20\%$), with a maximum factor of 2.1 at 500K for the 1,2-H-shift reaction in ethyl. These factors come from both energy and entropy differences and are presented in

more details in the supplementary material. The highest difference observed between the rate coefficients computed at the two levels of theory, a factor of 2.1, was ascribed for the uncertainty of the absolute CBS-QB3 rate constants calculated in this paper.

3. Results and Discussion

3.1. 1,3-H-atom shifts

The first cases studied are the reactions with 4-membered ring TS structures, as represented in the

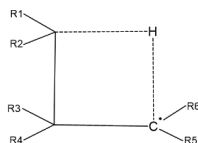


Figure 1.

Fig. 1. Model of four membered ring TS structure.

This model TS is first used to check the influence of the size of R_1 substituents on the rate coefficients. In this paper, the reactions are named in a Nyx format, where N is the number of members in the TS cycle, and y and x represent the nature of radical in the reactant and the product respectively (with p being used for primary, s for secondary and t for tertiary) [26]. Note that the presence of ‘spectator’ ring substituents (R_3 and R_4) is also systematically explored here. In some cases, multiple transition state structures were found due to equatorial and axial conformations of the substituents in the cyclic TS structures. In these cases, all the TS conformers were considered in the kinetic constant (see Figure S1).

The high-pressure kinetic constants were systematically computed for the 4pp, 4ps and 4pt reactions and are given in supplemental material. Figure 2 presents the impact of the size of the substituent R_1 on the computed rate coefficient.

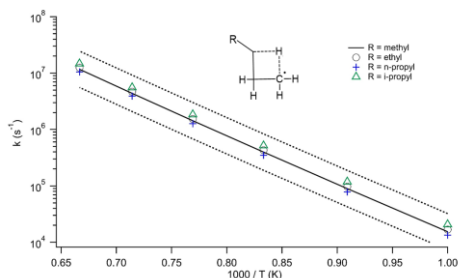


Fig. 2. Influence of R_1 substituent size on the 4ps rate constant. Dashed lines represent the uncertainty associated with the $R=CH_3$ calculation.

Figure 2 shows that the variation in the size (from C_1 to C_3) of R_1 , linked to the C-atom bearing the H-atom that is transferred, does not yield noticeable changes in the computed rate constants. Figure 3 and S3 shows that it is also the case for ‘spectator’ alkyl group (R_3) and R_5 group, respectively.

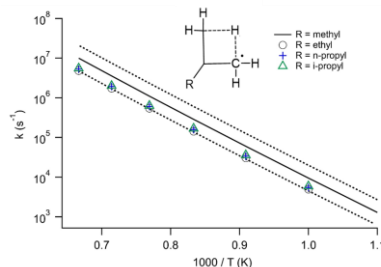


Fig. 3. Influence of R_3 substituent size on the 4ps rate constant. Dashed lines represent the uncertainty associated with the $R=CH_3$ calculation.

Variations in the size and shape of R groups of the model TS of Figure 1 shows that the computed rate constants always fall within the uncertainty limits of the minimal size case, where a methyl group is used. Table 2 presents the variation in energy and entropy barriers as the size of R is increased.

Table 2: Computed energy and entropy barriers for

	R1			
	Methyl	Ethyl	<i>n</i> -Propyl	<i>i</i> -propyl
E_a 0K (kcal/mol)	38.5	38.2	38.3	37.6
ΔS^\ddagger_{298K} (cal/mol K)	-4.1	-4.2	-4.5	-5.0

reactions presented in Figure 2

A compensation effect is observed as the size of the alkyl chain increases, the activation energy is slightly decreased while the pre-exponential factor increases from entropy variations [21, 22]. From our systematic investigation of the effect of the size of R on the rate constant, it can be concluded that, for isomerization reactions, a methyl group is a suitable model to represent an alkyl group. The influence of the degree of branching on the validity of the rate rule approach can therefore be studied using this assumption.

In the case of 1,3-H-shifts in alkyls, all the combinations of $R_1 = CH_3$ and H of Figure 1 were considered and their kinetic parameters were computed (27 combinations). This leads to reversible

4pp, 4ps, 4pt, 4ss, 4st, 4tt rate parameters (variations in R1/R2 and R5/R6). For each rate 4xy reaction, the influence of 0, 1 or 2 methyl group in R₃ and R₄ was systematically explored. All kinetic data are available in supplemental material (Fig. S4 to S7, S14 Table S8). As expected, we found the following ranking in the computed rate constants 4xp < 4xs < 4xt because of the well-known variations in C-H bond energies going from a primary to a tertiary H-atom.

Figure 4 presents the effect of increasing the branching on 4ps rate constant, by successively adding spectator methyl groups in R₃ and R₄ positions.

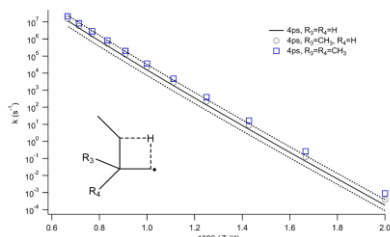


Fig. 4. Influence of R₃ and R₄ substituents on the 4ps rate constant. Dashed lines represent the uncertainty associated with the R₃ = R₄ = H calculation.

The inclusion of 1 or 2 methyl groups at R₃ and R₄ leads to sensitive changes in the simplest rate constant where R₃ = R₄ = H (k_{HH}). Adding 1 substituent (R₃ = CH₃) leads to an increase of a factor of 2 at 500 K. When 2 spectator CH₃ groups are added, the rate coefficient is increased by a factor of 5 at 500 K, compared to k_{HH} . These effects are also observed for other reaction classes with varying degrees of impact (Figure S4-S7).

As already observed with the substituent size variation, the increase in the number of substituents on the cyclic TS also decreases the activation energy while increases the entropy difference between the TS and the reactive (Table S4-S5). However, the differences are not always compensated as in the case of substituent size variations, which leads to distinguishable constants. Therefore, it seems that increasing the degree of branching of an alkyl radical tends to rule out the possibility of a single rate rule meaningful for any degree of branching. We further explored this hypothesis for all the possible 1,4-H-atom shifts of alkyl radicals at different degrees of branching.

3.2. 1,4-H-atom shifts

1,4-H-atom internal transfers occur through five-membered cyclic TS structures.

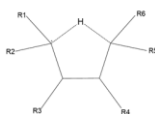


Fig. 5: Model of 5-membered ring TS structure

From the model TS depicted in Figure 5, if R₃ and R₄ are H-atoms, the combinations of R_i = H or CH₃ leads to the classical 5xy rate rules, i.e., if all R_i = H, except R₅ = CH₃, the minimal structure for the 5ps rate rule is defined. The number of combinations for R_i = H or CH₃ leads to 24 model TS structures. Within a single 5xy rate rule, increasing the degree of branching significantly increases the complexity of the calculation of the rate constant. For example, in the 5ps reaction class, with two spectator alkyl groups at R₃ and R₄, 2 reactants and 8 TS need to be included in the calculation of the elementary rate coefficient (Figure 6).

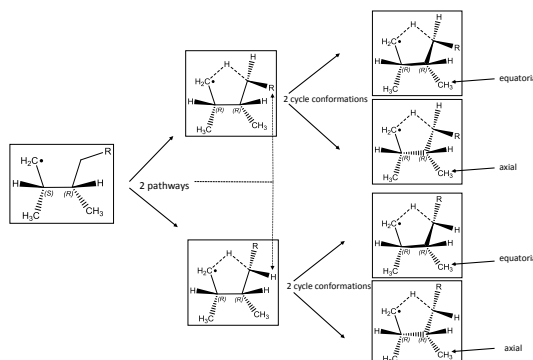


Fig. 6. Number of conformers to include in the calculation of the elementary reaction for the (S)(R) stereoisomer reactant. The same structural behavior occurs for the (S)(S) reactant.

As illustrated in Figure 6, the combination of 2 different cyclic conformations of the TS and of the possible configurations of the CH₃ with regard to the chiral centers leads to an increase of the distinguishable pathways that need to be included in the rate constant calculations. In addition, the (S)(S) stereoisomer, whose mirror image is the (R)(R) isomer, possesses a different energy than the (R)(S) configuration and also need to be included with its 4 additional indistinguishable TS pathways. Except for the 5pp, 5pt and 5tt rate constant calculations (without any spectator methyl), all the computed rate constant includes multiple transition state structures. In the general case, for 5ss (R₁=alkyl, R₂=H, R₅=alkyl, R₆=H), with R₃ = R₄ = alkyl group, 2 reactants and 16 indistinguishable TS structures are required to compute the elementary rate constant. As we use methyl groups as representative models of all possible alkyl groups, symmetry artificially arise and diminish the number of TS structures that have to be considered. Nevertheless, in this case, 12 TS structures were included in the rate constant calculation. For all kinetic parameters reported in this study, all configurations and conformations were included in the rate coefficient calculations. This multiple pathway is a challenge for on the fly

theoretical calculations of kinetic data with automated methods.

We compared our computed high-pressure rate coefficients to experimental data [17,18] available for 1,4-H-shifts (Figure S16) and found that they are in agreement.

For all 1,4-H-shifts reactions classes (5pp, 5ps, 5pt, 5ss, 5st, 5tt), the rate coefficients were calculated with all possible combinations of R_3 and R_4 spectator groups. This leads to a 6×4 matrix of model TS structures (see Table S8). For example, the 5pp reaction class features 4 structures of model TSs (Figure 7).

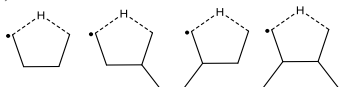


Fig. 7: Structures belonging to the 5pp reaction class with increasing degree of branching.

The reactions involving the TS structures of Figure 7 could be defined as a reaction class with a single reaction rate rule if the presence of spectator alkyl groups was negligible. The comparison of computed rate constants is performed in Figure 8.

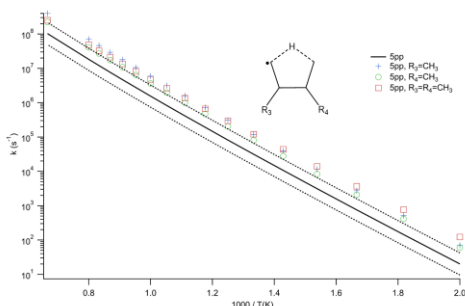


Fig.8: influence of R_3 and R_4 substituents on the 5pp rate constant. Dashed lines represent the uncertainty associated with the $R_3 = R_4 = H$ (k_{HH}) calculation.

At 500K, the addition of 1 methyl group on the simplest 5pp structure leads to an increase of k_{HH} of a factor ≈ 3 (either in R_3 or R_4) and a factor of 6 when $R_3=R_4=CH_3$. This is consistent with the trends observed for 1,3-H-atom shifts. However, if the effects were not very marked in 4xy reaction classes, the influence of spectator alkyl groups in 1,4-H-atom shifts appear consistently strong. Interestingly, the presence of spectator alkyl groups on the TS ring leads to a greater impact on 5xy's k_{HH} rate constants as this effect is increased with the reactivity induced by the substitution. Figure 9 and 10 depicts these effects for 5ss and 5st reaction classes.

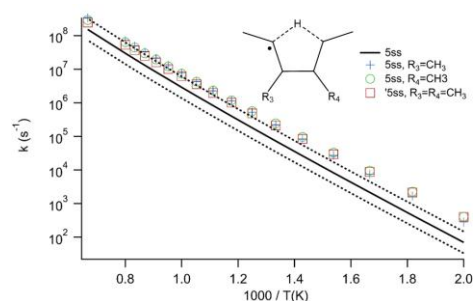


Fig.9: influence of R_3 and R_4 substituents on the 5ss rate constant. Dashed lines represent the uncertainty associated with the $R_3 = R_4 = H$ (k_{HH}) calculation.

A strong impact of the presence of spectator alkyl group is computed: if only one spectator methyl group is present ($R_3=CH_3$ or $R_4 = CH_3$), a factor of ≈ 4 compared to k_{HH} is observed at 500 K. If $R_3=R_4=CH_3$, this factor increases (factor of 6). At 1000 K, these differences reduced to factors of 2. These effects of increased reactivity of alkyls with higher degrees of branching are more pronounced for the internal transfer of tertiary H-atom.

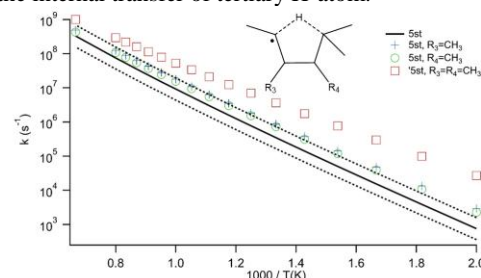


Fig.10: influence of R_3 and R_4 substituents on the 5st rate constant. Dashed lines represent the uncertainty associated with the $R_3 = R_4 = H$ (k_{HH}) calculation.

Figure 10 clearly shows that the presence of spectator substituents dramatically increases the rate coefficient values compared to the lowest minimal TS model. This behavior is also observed for 5ps, 5pt, and 5tt reactions (Figures S8-S12). Our calculations generally show that the presence of spectator alkyl groups on the most substituted reactants leads to noticeable decreases in energy barriers.

Table 3 presents an example of such energy and entropy barrier variations for the 5ps reactions (Figure 5, $R_1=R_2=R_5=H$ and $R_6 = CH_3$).

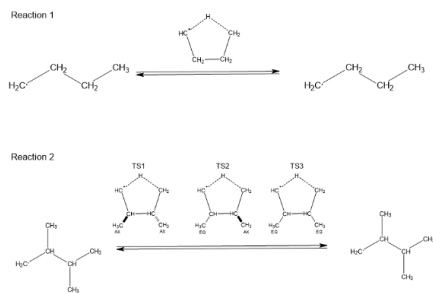
Table 3: Computed energy and entropy barriers for 5ps reactions with different 0 or 1 spectator substituents. E_A in kcal/mol and ΔS_{298K}^\ddagger in cal/mol.K

Substituent	$R_3=R_4=H$	
	CH_3 eq	CH_3 ax
R1	H	H
R2	H	H
E_A	22.0	22.3
ΔS_{298K}^\ddagger	-8.9	-9.1

Substituent	R ₃ =CH ₃ , R ₄ =H			
R	CH ₃ ax	CH ₃ ax	CH ₃ eq	CH ₃ eq
R1	CH ₃ ax	CH ₃ eq	CH ₃ ax	CH ₃ eq
R2	H	H	H	H
E _A	21.9	22.0	22.7	21.0
ΔS [‡] _{298K}	-10.1	-10.5	-10.8	-9.7

The remaining cases of 5ps reactions (R₃=H, R₄=CH₃ and R₃=R₄=CH₃) are given in Table S7. In the example of Table 3, the multiplicity of pathways is again highlighted. The substitution of a H-atom by a CH₃ at R₃ leads to 2 additional pathways compared to the case with 0 spectator CH₃. Lower energy barriers also appear in equatorial orientations, while the entropy barrier is only slightly decreased for the lowest energy conformer.

This trend is general in our calculations, TS with more substituents in equatorial position are more stable, resulting in lower activation energy and higher rate constants. Pre-exponential factor are also highly affected by changing the number of spectator alkyl group in the TS structure. With more substituents on the cycle, this parameter can be multiplied by a factor of 10 (Table S9). One can suppose that the difference observed could be due to the differences in individual statistical factors (n_e) for a studied reaction with and without spectator substituents. We observed that the contribution of variations in n_e has an effect on the kinetic constant, but is not the main cause of difference in the rate coefficients. Figure 11 presents the example of reaction 5pp with and without two methyl groups



attached to the cyclic TS.

Fig. 11. Two 5ps reactions with different degrees of substitution.

The first reaction, with no CH₃ group, has only one TS configuration, while the second reaction has three possible TS configurations, shown as TS1, TS2 and TS3. The first reaction has a n_e of 1, since the reactant has no chiral isomer and an external symmetry of 1 and the TS has a chirality of 2 and an external symmetry of 2. The second reaction has three possible pathways, therefore the total rate constant is calculated as

$$k_T = k_{TS1} + k_{TS2} + k_{TS3} \quad (3)$$

The values for n_{eTS1} , n_{eTS2} and n_{eTS3} are $\frac{1}{2}$, 1 and $\frac{1}{2}$ respectively. If k_{TS1} , k_{TS2} and k_{TS3} tends to a similar value k_j , Equation (3) can be rewritten as:

$$k_T = n_{eTS1}k_1 + n_{eTS2}k_1 + n_{eTS3}k_1 \quad (4)$$

Hence, the constant of the second reaction would be greater by a factor of 2 over the first reaction constant, uniquely based on pathway counting from symmetry and chirality. However, the factor observed is higher, varying from 6 to 2.4 from 500K to 1000K, which indicates that the statistical factor is not the only parameter influencing the variations in the rate constants.

Therefore, our calculations show that a single rate rule is not feasible for any degree of branching of a reaction belonging to the same isomerization reaction class and that a rate rule based only on minimal TS structure models is not sufficient. This study suggest that a new rate rule should be defined each time that a spectator alkyl group is added in the cyclic TS. Given that, 5-, 6- and 7-membered ring TS are the most favored isomerizations pathways and that they can involve oxygen atoms, this would lead to too many rate rules. We propose here a new approach where the model TS are tabulated. In this approach, methyl groups are assumed as alkyl group surrogates and all combinations of substitutions in the model TSs, for a given reaction class, are included in a table with associated theoretical rate coefficients. Tables S8 and S9 provide such tabulated TS model data for 1,3- and 1,4-H-atom shifts in alkyl radicals. Figure S16 also compares this method with experimental results and a single rate rules approach. We anticipate that this approach will be useful for the improvement of kinetic data in reaction mechanism generators. Considering all the combinations of substituents for all the reaction classes will lead to a very large number of calculations, a difficult task to do by hand. The emergence of deep learning algorithms makes it possible to consider the automation of these calculations allowing to build large databases of tabulated TS models for any reaction classes. The tabulated data could include computed parameters to perform master equation calculations and account for pressure dependence in rate coefficients. This alternative to on the fly calculations of kinetic parameters is worth exploring given its high-throughput / high-accuracy potential.

4. Conclusions

In this work, the validity of a rate rule approach to estimate rate constants of isomerizations is thoroughly explored for 4- and 5-membered cyclic TS, using theoretical calculations. Computed rate constants for 1,3-H-atom shifts demonstrate that a methyl group is representative of an alkyl group of larger size. When the size of the alkyl chain

increases, the energy barrier decreases while the entropy barrier decreases. These effects compensate each other and lead to similar rate coefficients. The influence of the degree of branching in 1,3-H-atom shifts was systematically investigated and we show that the presence of spectator alkyl groups in the cyclic TS leads to sensitive variations in the rate coefficients, that in several cases tends to make the use of a single rate rule impractical.

This conclusion is further reinforced in 1,4-Hatom shifts. The increase of the level of branching, through the addition of spectator alkyl groups, systematically increases the value of rate coefficients compared to the cases with no spectator groups, up to several orders of magnitude. For higher level of branching, energy barriers tend to be lower and multiple conformers, i.e. pathways, of equivalent energies appear for the TS structures.

For internal H-atom transfers, it appears that a set of reaction class using a single rate rule is not feasible as the degree of branching increases. This also means that an ab initio rate rule defined only from calculations on unbranched radicals is not suitable for branched radicals. This conclusion implies that an additional rate rule is needed for each increment in the radical branching level. We propose here a new tabulated TS model approach as an alternative to rate rules and on-the-fly theoretical calculations in automatic generators of kinetic models.

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Supplementary material

Details on the ANL-F12 calculations, all computed Arrhenius parameters, additional comparisons of rate constants for 4xy and 5xy and tabulated TS models given in supplemental material.

References

[1] F. Battin-Leclerc, E. Blurock, R. Bounaceur, R. Fournet, *et al.*, Towards cleaner combustion engines through groundbreaking detailed chemical kinetic models *Chemical Society Reviews* 40 (2011) 4762-4782.
[2] R. Van de Vijver, N.M. Vandewiele, P.L. Bhoorasingh, B.L. Slakman, *et al.*, Automatic mechanism and kinetic model generation for gas- and solution- phase processes: a perspective on best practices, recent advances, and future challenges *International Journal of Chemical Kinetics* 47 (2015) 199-231.

[3] S.W. Benson, *Thermochemical kinetics*, Wiley, 1976.
[4] P.L. Bhoorasingh, B.L. Slakman, F. Seyedzadeh Khanshan, J.Y. Cain, *et al.*, Automated transition state theory calculations for high-throughput kinetics *The Journal of Physical Chemistry A* 121 (2017) 6896-6904.
[5] R. Sumathi, W.H. Green Jr, A priori rate constants for kinetic modeling *Theoretical Chemistry Accounts* 108 (2002) 187-213.
[6] K. Zhang, C. Banyon, U. Burke, G. Kukkadapu, *et al.*, An experimental and kinetic modeling study of the oxidation of hexane isomers: Developing consistent reaction rate rules for alkanes *Combustion and Flame* 206 (2019) 123-137.
[7] S.M. Villano, L.K. Huynh, H.-H. Carstensen, A.M. Dean, High-pressure rate rules for alkyl+ O₂ reactions. 1. The dissociation, concerted elimination, and isomerization channels of the alkyl peroxy radical *The Journal of Physical Chemistry A* 115 (2011) 13425-13442.
[8] C.W. Gao, J.W. Allen, W.H. Green, R.H. West, Reaction Mechanism Generator: Automatic construction of chemical kinetic mechanisms *Computer Physics Communications* 203 (2016) 212-225.
[9] V. Warth, N. Stef, P. Glaude, F. Battin-Leclerc, *et al.*, Computer-aided derivation of gas-phase oxidation mechanisms: application to the modeling of the oxidation of n-butane *Combustion and Flame* 114 (1998) 81-102.
[10] E. Ranzi, T. Faravelli, P. Gaffuri, A. Sogaro, Low-temperature combustion: automatic generation of primary oxidation reactions and lumping procedures *Combustion and flame* 102 (1995) 179-192.
[11] N.M. Vandewiele, K.M. Van Geem, M.-F. Reyniers, G.B. Marin, Genesys: Kinetic model construction using chemo-informatics *Chemical Engineering Journal* 207 (2012) 526-538.
[12] B. Sirjean, P.-A. Glaude, M. Ruiz-Lopez, R. Fournet, Theoretical kinetic study of thermal unimolecular decomposition of cyclic alkyl radicals *The Journal of Physical Chemistry A* 112 (2008) 11598-11610.
[13] M. Saeys, M.F. Reyniers, V. Van Speybroeck, M. Waroquier, *et al.*, Ab initio group contribution method for activation energies of hydrogen abstraction reactions *ChemPhysChem* 7 (2006) 188-199.
[14] D.M. Matheu, W.H. Green Jr, J.M. Grenda, Capturing pressure-dependence in automated mechanism generation: Reactions through cycloalkyl intermediates *International journal of chemical kinetics* 35 (2003) 95-119.
[15] M. Cord, B. Sirjean, R. Fournet, A. Tomlin, *et al.*, Improvement of the modeling of the low-temperature oxidation of n-butane: study of the primary reactions *The Journal of Physical Chemistry A* 116 (2012) 6142-6158.
[16] T.N. Truong, Reaction class transition state theory: Hydrogen abstraction reactions by hydrogen atoms as test cases *The Journal of Chemical Physics* 113 (2000) 4957-4964.
[17] W. Tsang, W.S. McGivern, J.A. Manion, Multichannel decomposition and isomerization of octyl radicals *Proceedings of the Combustion Institute* 32 (2009) 131-138.
[18] I.A. Awan, W.S. McGivern, W. Tsang, J.A. Manion, Decomposition and isomerization of 5-methylhex-1-yl radical *The Journal of Physical Chemistry A* 114 (2010) 7832-7846.
[19] B. Sirjean, E. Dames, H. Wang, W. Tsang, Tunneling in hydrogen-transfer isomerization of n-alkyl radicals *The Journal of Physical Chemistry A* 116 (2012) 319-332.

- [20] H.J. Curran, P. Gaffuri, W.J. Pitz, C.K. Westbrook, A comprehensive modeling study of n-heptane oxidation Combustion and flame 114 (1998) 149-177.
- [21] A.C. Davis, J.S. Francisco, Ab initio study of hydrogen migration across n-alkyl radicals The Journal of Physical Chemistry A 115 (2011) 2966-2977.
- [22] K. Wang, S.M. Villano, A.M. Dean, Reactivity-structure-based rate estimation rules for alkyl radical H atom shift and alkenyl radical cycloaddition reactions The Journal of Physical Chemistry A 119 (2015) 7205-7221.
- [23] J.A. Montgomery Jr, M.J. Frisch, J.W. Ochterski, G.A. Petersson, A complete basis set model chemistry. VI. Use of density functional geometries and frequencies The Journal of chemical physics 110 (1999) 2822-2827.
- [24] J. Lizardo-Huerta, B. Sirjean, R. Bounaceur, R. Fournet, Intramolecular effects on the kinetics of unimolecular reactions of β -HORO \cdot and HOQ \cdot OOH radicals Physical Chemistry Chemical Physics 18 (2016) 12231-12251.
- [25] M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, *et al.*, Gaussian 16 rev Gaussian Inc.: Wallingford, CT, USA (2016).
- [26] S.J. Klippenstein, L.B. Harding, B. Ruscic, Ab initio computations and active thermochemical tables hand in hand: Heats of formation of core combustion species The Journal of Physical Chemistry A 121 (2017) 6580-6602.