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Citation: Goldman, Jacob et al. "Correct Symmetry Treatment for X + X Reactions Prevents Large Errors in Predicted Isotope Enrichment." *Journal of Physical Chemistry A* 123, 12 (March 2019): 2320-2324 © 2019 American Chemical Society

As Published: <http://dx.doi.org/10.1021/acs.jpca.8b09024>

Publisher: American Chemical Society (ACS)

Persistent URL: <https://hdl.handle.net/1721.1/123203>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

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Correct Symmetry Treatment for X+X Reactions Prevents Large Errors in Predicted Isotope Enrichment

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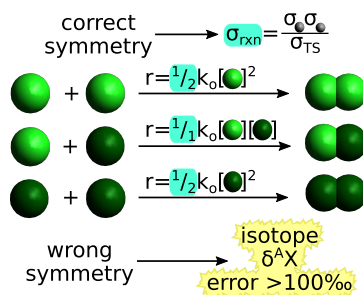
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Abstract

Confusion over how to account for symmetry numbers when reactants are identical can cause significant errors in isotopic studies. An extraneous factor of two in the reaction symmetry number, as proposed in literature, violates reaction equilibrium and causes huge enrichment errors in isotopic analysis. In actuality, no extra symmetry factor is needed with identical reactants.



This paper was published in *Journal of Physical Chemistry A* on March 20, 2019
with doi: 10.1021/acs.jpca.8b09024

1 Introduction

The rate of consumption of molecule A, r_A , in a bimolecular reaction can be calculated with $r_A = -k[A][B]$. If the two reactants are identical, a stoichiometric coefficient of two appears in front of the equation for the consumption of A: $r_A = -2k[A]^2$. The rate coefficient k is often computed using transition state theory (TST) at the high pressure limit:¹

$$k(T) = \kappa \sigma_{rxn} \frac{m_{TS}}{m_A m_B} \frac{k_B T}{h} \frac{q_{TS}^{\ddagger\dagger}/V}{\left(q_A^\dagger/V\right) \left(q_B^\dagger/V\right)} e^{\left(\frac{-E_o}{k_B T}\right)} \quad (1)$$

where κ is the tunneling factor, σ_{rxn} is the reaction symmetry number, m is the number of accessible optical, or ‘mirror image’, isomers of a molecule or transition state, k_B is Boltzmann’s constant, h is Planck’s constant, E_o represents the difference in zero point energy between the transition state and reactants, q represents the partition function of molecule or transition state with $E = 0$ at its zero point energy, \dagger indicates removal of the symmetry in the rotational partition function to form σ_{rxn} , and \ddagger indicates the removal of one degree of freedom corresponding to the reaction coordinate.

This article focuses on a discrepancy in defining the reaction symmetry number, σ_{rxn} , when used in TST with two identical reactants. With different reactants, σ_{rxn} is defined according to eq 2 with σ_X being the rotational symmetry number of X .

$$\sigma_{rxn} = \frac{\sigma_B \sigma_A}{\sigma_{TS}} \quad (2)$$

Competing theories exist for the correct value of σ_{rxn} when the two reactants are identical. A highly-cited article by Pollak and Pechukas in 1978 argues that σ_{rxn} should be increased by a factor of two when A and B are identical, since the reactants could be translationally interchanged.² This assertion conflicted with the previous recommendation by Bishop and Laidler who used an alternative method to correct for reaction symmetry, reaction path degeneracy (RPD).³ RPD is the number of ways a reaction can proceed with different atoms

and is equivalent to the combination of symmetry and optical isomers terms in eq 1. When reactants are identical, the RPD algorithm will interchange the two molecules and count the number of possible pathways twice. To prevent double-counting due to molecule interchangeability, Bishop and Laidler recommend dividing the RPD by two when the reactants are identical.³ These two competing perspectives on how to deal with identical reactants have persisted in the literature. A widely-cited review⁴ recommends multiplying the reactant symmetry numbers by a factor of two, referencing Pollak and Pechukas, though many studies involving identical reactants do not mention, and likely do not include, this factor of two.⁵⁻⁹

Though a factor of two mistake can impact many phenomena, it causes huge errors in isotopic enrichment since the disputed factor of two is much larger than most non-hydrogen kinetic isotope effects.¹⁰

This paper uses two methods to explain proper symmetry treatment in reaction kinetics. We first show that the factor of two proposed by Pollak and Pechukas causes thermodynamic inconsistencies in the equilibrium constant and then describe how this error creates huge discrepancies in isotopic enrichment, using $\text{Cl} + \text{Cl} \longrightarrow \text{Cl}_2$ as an example.

2 Methods

When estimating rate coefficients, we use TST, shown in eq 1. Reactions in this paper are analyzed at the high pressure limit, since errors in the reaction symmetry number would impact reaction rates at both the low and high pressure limit. When reactions are barrierless, the transition state structure is defined along the reaction path by variational TST.¹¹ This approach leads to the same relative rate coefficients for $\text{O} + \text{O}_2 \longrightarrow \text{O}_3$ as an alternative approach which involved analysis of metastable O_3 .¹²

To evaluate the correct method for treating symmetry numbers, this work varies the reaction symmetry number, shown in eq 2, by either adding or not adding a factor of two.

The two different rate coefficients derived from the different treatments of eq 2 are evaluated for thermodynamic equilibrium and for determining isotopic enrichment. To isolate the effect of symmetry numbers, examples are chosen which highlight the variation introduced in reaction symmetry number.

The usage of symmetry numbers in this work leads to the same rates as the full treatment of rotation with nuclear spin degeneracy at the classical limit.^{4,13}

3 Results and Discussion

3.1 Thermodynamic Derivation

The extra factor of two recommended in Ref. 2 leads to inconsistencies in equilibria. To show this, we plug eq 1 into the definition of equilibrium constant for the reaction $2\text{B} \longrightarrow \text{BB}$ and compare that to the equilibrium constant for this reaction derived from the Gibbs free energy. We can then determine if an extra factor of two appears when evaluating the forward reaction symmetry number, $\sigma_{f,rxn}$.

The equilibrium constant, K_c , is the ratio of forward, k_f , and reverse, k_r , rate coefficients. Substituting k_f and k_r obtained from eq 1 results in

$$K_c = \frac{k_f}{k_r} = \frac{\sigma_{f,rxn} m_{\text{BB}}}{\sigma_{r,rxn} m_{\text{B}}^2} \frac{q_{\text{BB}}^\dagger/V}{\left(q_{\text{B}}^\dagger/V\right) \left(q_{\text{B}}^\dagger/V\right)} e^{\left(\frac{-E_{rxn}}{k_{\text{B}}T}\right)} \quad (3)$$

where $\sigma_{f,rxn}$ is the reaction symmetry number in the forward direction, $\sigma_{r,rxn}$ is the equivalent in the reverse direction, and E_{rxn} is the difference between the zero point energies of the product and reactants. The tunneling factors and transition state partition function cancel out since neither affects equilibrium.

To determine whether $\sigma_{f,rxn}$ contains the factor of two recommended by Pollak and Pechukas,² we derive the equilibrium constant in a different way based on the definition that at equilibrium the Gibbs free energy, G , is at a minimum in a constant temperature

and pressure system. The change in G can be represented by a constant temperature and pressure chemical potential, μ .

$$dG = -2\mu_B + \mu_{BB} = 0 \quad (4)$$

The chemical potential of a pure species j , μ_j , can be derived from its partition function, Q_j . Neglecting intermolecular forces with the ideal gas assumption, the partition function can be put in terms of a single molecule's partition function, q_j , and the number of those molecules, N_j . Since the molecules are also indistinguishable, a factor of $N_j!$ appears, which can be simplified by Stirling's approximation, $N_j! \approx \left(\frac{N_j}{e}\right)^{N_j}$, as shown in eq 5.¹⁴

$$Q_j = \frac{q_j^{N_j}}{N_j!} \approx \left(\frac{eq_j}{N_j}\right)^{N_j} \quad (5)$$

If species j represents a mixture with m_j optical isomers of equal concentration, energy and reactivity, then the partition function (Q_j) can be separated into the product of each isomer i , $Q_j = \Pi_i^{m_j} Q_{j,i} = (Q_{j,i})^{m_j}$, which is simplified with Stirling's approximation in eq 6.

$$Q_j = \left(\frac{q_j^{N_j/m_j}}{(N_j/m_j)!}\right)^{m_j} \approx \left(\left(\frac{eq_j}{N_j/m_j}\right)^{N_j/m_j}\right)^{m_j} = \left(\frac{m_j eq_j}{N_j}\right)^{N_j} \quad (6)$$

Since μ_j can equivalently be defined using Gibbs or Helmholtz free energy,¹⁴ μ_j can be found using Q_j and eq 6.

$$\mu_j = \left(\frac{\delta A}{\delta N_j}\right)_{T,V,N_i} = -RT \left(\frac{\delta \ln Q_j}{\delta N_j}\right)_{T,V,N_i} \approx -RT \ln \frac{m_j q_j}{N_j} \quad (7)$$

Substituting the chemical potentials for B and BB from eq 7 into the equilibrium relationship in eq 4 results in

$$\frac{N_{BB}}{N_B^2} = \frac{m_{BB} q_{BB}}{m_B^2 q_B^2} \quad (8)$$

Since the partition function of an ideal gas molecule is proportional to volume, each term

in eq 8 can be divided by volume to obtain concentrations, $C_j = \frac{N_j}{V}$, and the equilibrium constant, K_c .¹⁴

$$\frac{C_{BB}}{C_B^2} = \frac{m_{BB} (q_{BB}/V)}{m_B^2 (q_B/V)^2} = K_c \quad (9)$$

There is no special factor of two in eq 9 due to translational indistinguishability, and this equation is analogous to the equilibrium constant for a reaction with two different reactants.

We then extract the symmetry and zero point energy from the partition functions, $q_j = \frac{q_j^\dagger}{\sigma_j} e^{E_{o,j}/k_B T}$, to get eq 9 into the same form to compare with eq 3.

$$K_c = \frac{\sigma_B^2 m_{BB} (q_{BB}^\dagger/V)}{\sigma_{BB} m_B^2 (q_B^\dagger/V)^2} e^{\left(\frac{-E_{rxn}}{k_B T}\right)} \quad (10)$$

Equating eq 10 with eq 3 results in

$$\frac{\sigma_B^2}{\sigma_{BB}} = \frac{\sigma_B^2/\sigma_{TS}}{\sigma_{BB}/\sigma_{TS}} = \frac{\sigma_{f,rxn}}{\sigma_{r,rxn}} \quad (11)$$

By equating these two equilibrium constants, no factor of two appears in the definition of $\sigma_{f,rxn}$ even if $A = B$. Ref. 14 includes a derivation for K_c when $A \neq B$, which results in the same conclusion.

Interchange of the identical reactants, postulated by Pollack and Pechukas as the reason for the factor of two,² is already accounted for when going from an ensemble partition function to a molecular partition function in eq 5. Since the RPD algorithm accounts for the interchange, it must be removed by halving the RPD for reactions with identical reactants, as recommended by Bishop and Laidler.³

Due to this thermodynamic inconsistency, kinetic simulators that estimate reverse kinetics using equilibrium and forward kinetics will also incorrectly double the reverse rate of reaction if the factor of two recommended by Pollack and Pechukas is used for the forward reaction. Section S2 of the Supporting Information shows how including an erroneous factor

of two affects reverse reaction rates in ethane pyrolysis.

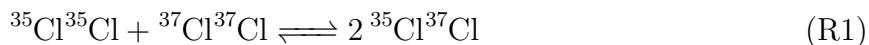
3.2 Isotopic Enrichment

In many fields a factor of two error in a computed rate coefficient can have modest effects, but when studying isotopic enrichment, it dominates any realistic enrichment. Increasing the rate coefficients of reactions with identical reactants by the extra factor of two proposed in some literature^{2,4} leads to unphysical behavior which is significantly inconsistent with experimental isotopic enrichment values of identical reactant reactions.¹⁵ As a simple example, consider chlorine atom recombination involving ^{35}Cl and ^{37}Cl which has three distinct reactions depending on the isotopes involved. By analyzing the rates of these three reactions, we show that adding the factor of two to eq 2 creates unrealistic isotopic enrichment.

To isolate the effect of the factor of two, this example makes several simplifying assumptions:

1. The reactions occur at the high pressure limit, so variable lifetimes of excited states, like in atmospheric ozone,¹⁶ would not be expected, and we can use canonical TST (eq 1) to estimate the rate coefficients.
2. Mass-dependent kinetic isotope effects for isotopic chlorine are negligible ($< 5\%$ change in rate coefficient for non-hydrogen isotopes¹⁰) when compared to deviations expected by doubling a rate coefficient, so they are omitted from this simple model.
3. Non-symmetry based mass-independent isotope effects, e.g. nuclear field shift and magnetic properties, are also negligible when compared to deviations expected by doubling a rate coefficient,¹⁰ so they are also omitted from this model.

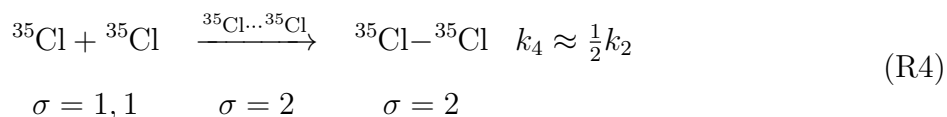
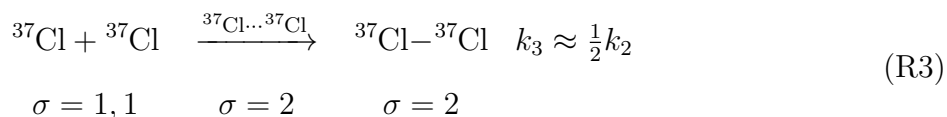
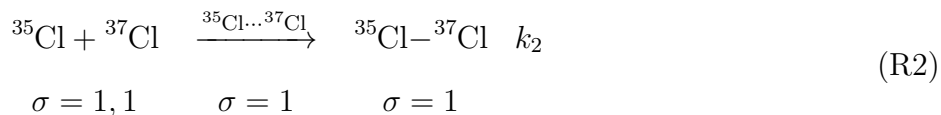
Suppose we start with a system of Cl atoms at a ^{37}Cl abundance of $\alpha = \frac{^{37}\text{Cl}}{^{37}\text{Cl}+^{35}\text{Cl}}$. When they finish recombining, we expect to have a system full of Cl_2 molecules. If no kinetic isotope effects occur, the products should be in isotopic equilibrium shown by reaction R1 with the equilibrium relationship given in eq 12.



$$K_c = \frac{[^{35}\text{Cl}^{37}\text{Cl}]^2}{[^{35}\text{Cl}^{35}\text{Cl}][^{37}\text{Cl}^{37}\text{Cl}]} \approx \frac{\sigma_{3535}\sigma_{3737}}{\sigma_{3537}^2} = 4 \quad (12)$$

Solving eq 12 for α , given isotopologue concentrations of $[^{37}\text{Cl}^{37}\text{Cl}] = c\alpha^2$ and $[^{35}\text{Cl}^{35}\text{Cl}] = c(1-\alpha)^2$, results in isotopologue ratios $[^{35}\text{Cl}^{35}\text{Cl}] : [^{35}\text{Cl}^{37}\text{Cl}] : [^{37}\text{Cl}^{37}\text{Cl}] \approx (1-\alpha)^2 : 2\alpha - 2\alpha^2 : \alpha^2$. Note that this ratio is exactly the same as predicted by combinatorics if one randomly chooses pairs of balls from a population where $P_{blue} = \alpha$ and $P_{red} = 1 - \alpha$.

These values can be compared with the products obtained from a kinetic model using TST rate coefficients to see the impact of adding the extra symmetry factor. Reactions R2-R4 show three chlorine recombination reactions using different isotopes of chlorine. The symmetry numbers of the reactants, product, and transition state, σ , are used to find the ratio of reaction rate coefficients, k_i , using eqs 1 and 2. Here all the $\sigma = 2$ factors are from rotational symmetry; the extra factor of two proposed by Pollack and Pechukas has not been included.²



If we assert that there is an initial system with 50% ^{35}Cl and 50% ^{37}Cl , eq 12 would predict a product distribution of 25% $^{37}\text{Cl}-^{37}\text{Cl}$, 50% $^{35}\text{Cl}-^{37}\text{Cl}$, and 25% $^{35}\text{Cl}-^{35}\text{Cl}$ based on thermodynamics. From a kinetics perspective, this same product ratio occurs when k_2 is

twice as large as k_3 and k_4 , which is caused by changes in the rotational partition functions due to molecular symmetry. In this example, the transition states for reactions R3 and R4 are symmetric ($\sigma = 2$) whereas the one for reaction R2 is not ($\sigma = 1$), creating the difference in rate coefficient.

This lack of enrichment caused by molecular symmetry agrees with previous analysis which indicates that the difference in rate coefficients in reactions R2-R4 just represents relative probabilities of forming symmetric and asymmetric molecules¹⁷ which cancels out in the classical limit when determining fractionation and enrichment factors. Some compounds, like O₃, do achieve fractionation between symmetric and asymmetric isotopologues. However, these observed enrichments are not caused by the symmetry factor discussed here. Instead the observed small enrichments are likely due to other effects, such as tunneling.¹⁸

If the method of Ref. 2 is applied to reactions R2-R4, k_3 and k_4 would be doubled, and all three reactions would have equal rates leading to a 33% accumulation of each Cl₂ isotopologue. This would significantly favor symmetrical products and deviate from isotopic equilibrium in reaction R1. Having an asymmetric transition state, described in Section S1 of the Supporting Information, provides the same conclusion as for the chlorine recombination system.

3.3 Enrichment Error

Given that substituting non-hydrogen isotopes typically modifies rate coefficients by only a few percent,¹⁰ the introduction of a factor of two to some rate coefficients can lead to significant errors at natural abundance. To quantify this error, we compare the change in enrichment between reactants and products with and without the factor of two proposed by Pollak and Pechukas.²

For the chlorine recombination reaction described above whose reactants have an isotopic ratio of $R_r = \frac{^{37}\text{Cl}}{^{35}\text{Cl}}$, the rates of reactions R2-R4 without the factor of two, given by eqs 13-15, can be used to find product enrichments.

$$r_{R4} = k_{R4} [^{35}\text{Cl}]^2 \quad (13)$$

$$r_{R2} = k_{R2} [^{35}\text{Cl}] [^{37}\text{Cl}] \approx 2R_r k_{R4} [^{35}\text{Cl}]^2 = 2R_r r_{R4} \quad (14)$$

$$r_{R3} = k_{R3} [^{37}\text{Cl}]^2 \approx R_r^2 k_{R4} [^{35}\text{Cl}]^2 = R_r^2 r_{R4} \quad (15)$$

A factor of two appears in eq 14 since the rate coefficient for reaction R2 is twice that of reaction R4. Using eqs 13-15, the ratio of the nonstandard to standard isotope in the products is

$$R_p = \frac{^{37}\text{Cl}}{^{35}\text{Cl}} = \frac{r_{R2} + 2r_{R3}}{2r_{R4} + r_{R2}} = \frac{2R_r + 2R_r^2}{2 + 2R_r} = R_r \quad (16)$$

Since R_p is equal to R_r , no enrichment occurs without the factor of two suggested by Pollak and Pechukas.

If the factor of two is applied, the rate coefficients of all three reactions R2-R4 are equal, leading to the factor of two disappearing in eq 14. The subsequent eq 16 would become

$$R_p = \frac{^{37}\text{Cl}}{^{35}\text{Cl}} = \frac{r_{R2} + 2r_{R3}}{2r_{R4} + r_{R2}} = \frac{R_r + 2R_r^2}{2 + R_r} \quad (17)$$

which does not simplify down to R_r indicating some type of enrichment error is created. Since enrichment is defined as the ratio of sample to standard minus one, the change in enrichment from including the error would just be a function of the standard enrichment, R_{std} and the original sample enrichment, R_r .

$$\delta_{products} - \delta_{reagents} = \frac{1}{R_{std}} \left(\frac{R_r + 2R_r^2}{2 + R_r} \right) - \frac{R_r}{R_{std}} = \frac{R_r^2 - R_r}{(2 + R_r) R_{std}} \quad (18)$$

Given a starting enrichment near the standard enrichment, $R_r \approx R_{std}$, eq 18 reduces to $(R_{std} - 1) / (2 + R_{std})$.

Though the example here uses chlorine, this equation can be applied to different atomic

recombination reactions by using the corresponding R_{std} . For $^{37}\text{Cl}/^{35}\text{Cl}$, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, and $^{34}\text{S}/^{32}\text{S}$ with R_{std} of 0.320, 0.0111,¹⁹ 0.0037,²⁰ and 0.045,²¹ the enrichment errors from Pollak and Pechukas’s doubling of the symmetry number are 293‰, 491‰, 497‰, and 467‰ respectively. These predicted enrichments are much larger than typically observed experimentally.¹⁰

This enrichment error is of similar magnitude to the 500‰ enrichments recently computed to occur in $\text{S}_2 + \text{S}_2 \longrightarrow \text{S}_4$ and $\text{S}_4 + \text{S}_4 \longrightarrow \text{S}_8$.²² This suggests that these very large enrichments²² associated with the X + X reactions might arise from a factor of two mistake like that identified in this paper (though these reactions are more complicated than the simplistic examples presented here; see Supporting Information S3). We suspect that in reality the isotopic enrichment due to the reactions $\text{S}_2 + \text{S}_2$ and $\text{S}_4 + \text{S}_4$ is much smaller than the recently reported value.²² This insight opens the field to investigate other explanations for the anomalous sulfur enrichment in Archean earth.

In addition to the errors caused by estimating reaction symmetry in Refs. 2 and 22, a similar factor of two error for B + B reactions can arise when doing kinetic Monte Carlo simulations if the conversion from bulk rate coefficients to probabilistic rate coefficients is not done correctly (see Section S4 of the SI for the proper implementation).

3.4 Non-isotopic Impacts

In addition to isotopic studies, a factor of two error in rate coefficients of B + B reactions obtained from TST can create substantial changes in non-isotopic phenomena. This factor can alter major product concentrations by over 15% in pyrolysis simulations of hydrocarbons (shown in Section S2 of the Supporting Information). Even in the atmosphere, where many of the reactions have been quantified experimentally, detectable concentrations of large peroxy dimerization products,^{23,24} whose formation rate in models would typically be estimated using TST, indicates that including an extra factor of two could also impact estimation of how much a substance forms lower volatility products, affecting secondary organic aerosol

formation.

4 Conclusion

- The interchangeability of identical reactants, which justified doubling the reaction symmetry number in Ref. 2, is already accounted for when determining the reactant concentrations.
- Including a factor of two in reaction symmetry number for identical reactants causes thermodynamic inconsistency when applying transition state theory in both forward and reverse directions.
- Adding a factor of two in reaction symmetry number for reactions with identical reactants causes unphysical predicted isotopic enrichments well over 100‰ for many elements.
- For B + B reactions, the rate calculation method of Ref. 2 is incorrect; the method of Ref 3 is correct.

Acknowledgement

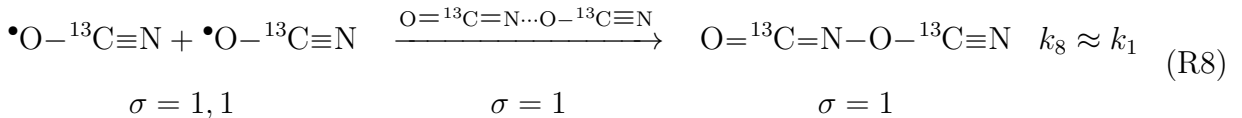
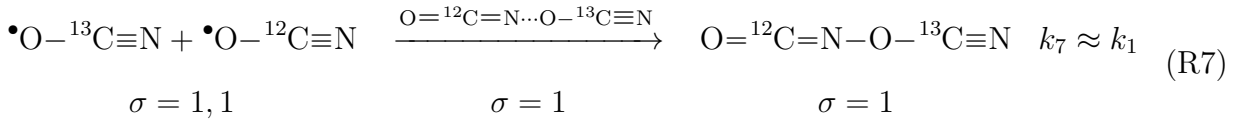
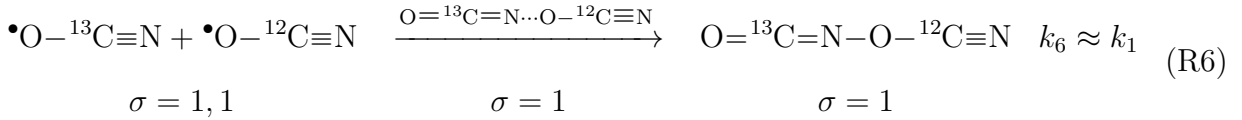
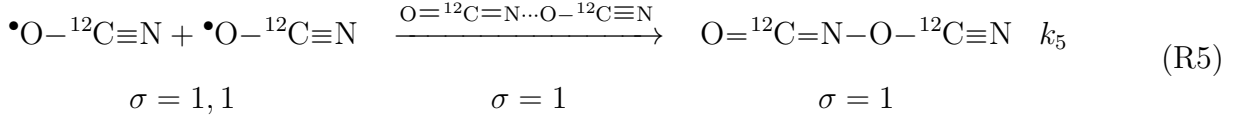
The Authors thank Kunting Eddie Chua and reviewers for helpful discussion. This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. 1122374 and the Gas Phase Chemical Physics Program of the US Department of Energy, Office of Basic Energy Sciences, Geosciences, and Biosciences (under award number DE-SC0014901). The Authors declare no competing interests.

Overview of Supplemental Information

- S1 Shows how the factor of 2 affects reactions with non-symmetric transitions states
- S2 Evaluates the impact of applying a factor of 2 to B + B reactions on ethane pyrolysis
- S3 Discusses the causes of sulfur isotope enrichment
- S4 Clarifies the difference between the two methods used for defining probabilistic rate coefficients in B + B reactions

S1 Asymmetric B + B reaction

Reactions with an asymmetric transition state have more possible reaction channels than reactions with symmetric ones, which could potentially affect how we treat isotopic reactions. Here we use the asymmetric recombination of NCO radicals, which is analogous to propargyl recombination important in aromatic formation.⁸ NCO radicals have two resonance forms, $\bullet\text{O}-\text{C}\equiv\text{N} \longleftrightarrow \text{O}=\text{C}=\text{N}\bullet$, which allows a radical recombination reaction to occur with an asymmetric transition state, giving an asymmetrical product, $\text{O}=\text{C}=\text{N}-\text{O}-\text{C}\equiv\text{N}$. There are four possibilities for asymmetric radical recombination with two carbon isotopes, ^{12}C and ^{13}C , shown below.



The symmetry numbers, σ , are used to find the ratio of reaction rate coefficients, k_i , using transition state theory (Equations 1 and 2 in the main text). These σ 's are from the

rotational partition functions and do not include the extra factor of 2 proposed in some literature.^{2,4} The four reactions are expected to have approximately identical rates, since the symmetry numbers of reactants and transition states are identical across the reactions. The only difference is in a heavy isotope which is not located at reaction center.

A 50:50 mixture of starting reactants, $\bullet\text{O}-^{12}\text{C}\equiv\text{N}$ and $\bullet\text{O}-^{13}\text{C}\equiv\text{N}$, would yield the four products with approximately equal concentrations. The two products with exactly one ^{13}C , from Reactions R7 and R6, together make up 50% of the total products in this system. This would lead to 25% of products with no ^{13}C atoms, 50% of products with one ^{13}C atom, and 25% of products with two ^{13}C atoms, as one would expect from combinatorics.

If a factor of 2 was added to reactant symmetries that had the same labeling, as proposed in literature,^{2,4} the rate coefficients for Reactions R5 and R8 would be twice as big as those for Reactions R7 and R6. This would lead to the fraction of products with no ^{13}C atoms, one ^{13}C atom, and two ^{13}C atoms to each be 33%. Like the chlorine recombination case, this leads to much more isotope segregation than would be expected from random collisions or kinetic isotope effects.

S2 Impact on ethane pyrolysis

Isotopic systems are not the only systems which could be affected by mistakes in rate coefficients. Large kinetic mechanisms, where many rate coefficients are estimated using symmetry numbers, could also have a substantial impact. To quantify the effect of doubling the rates of B + B reactions, the Reaction Mechanism Generator software package was used to create an ethane pyrolysis model with the specifications of the example ‘minimal’ included in the software package.²⁵ This model was used to simulate pyrolyzing a mixture of 10mol% ethane in helium at 1273 K and 2 bar for 0.1 seconds.

This model was then compared to one where each reaction involving identical reactants had the rate doubled. The difference in predicted production of methane is shown in Figure

S1.

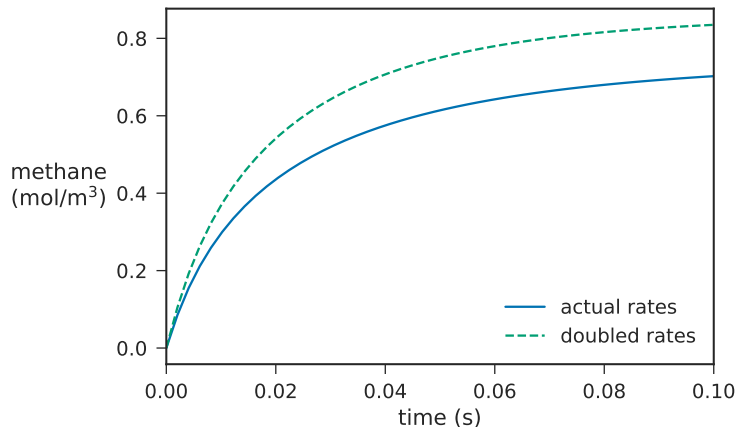


Figure S1: The difference in methane concentration between the original model and the one with doubled self-reaction rate coefficients.

The model with the doubled rates produced 19% more methane than the standard model. This is caused by the methyl recombination reaction, $\text{CH}_3 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_6$, which had twice the rate of the control in both forward and reverse directions. Despite not having two identical reactants, the rate of reverse reaction ends up doubled since it is estimated from the forward rate and equilibrium constant in common chemical kinetic solvers like Chemkin and Cantera. The methyl radicals formed from ethane degradation then abstract a hydrogen from other molecules to form methane.

Since the model only had a few reactions involving two identical reactants, the change in other properties, like the overall ethane conversion, shown in Figure S2, is very minor.

S3 Symmetry analysis of S_2 and S_4 self-reactions

This section is intended for readers interested in more details about the causes of the apparent symmetry effect in a 2017 paper published in Proceedings of the National Academy of Science,²² which is referred to as ‘the PNAS paper’ in this section.

Symmetry effects on enrichment were noted in two reactions, $\text{SS} + \text{SS} \longrightarrow \text{S}_4$ and $\text{S}_4 +$

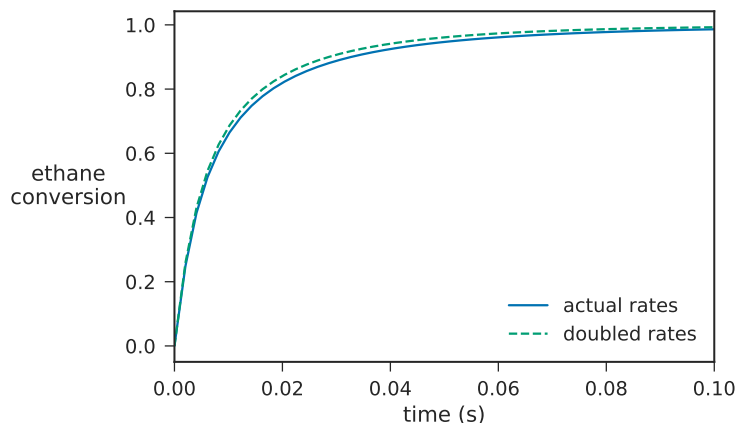
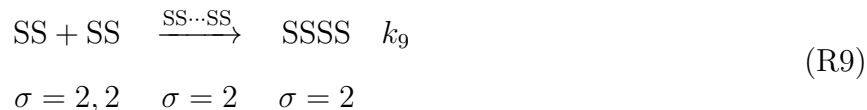


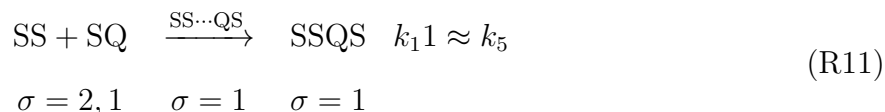
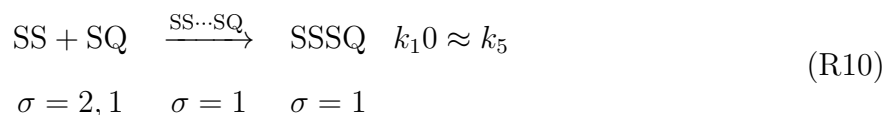
Figure S2: The difference in ethane conversion between the original model and the one with doubled self-reaction rate coefficients.

$S_4 \longrightarrow S_8$. Here we describe why we think these reactions should not cause nearly as much enrichment as originally proposed. In both of these reactions, we first represent S_4 as the minimum energy acyclic form (i.e., C_{2v} symmetry with $\sigma = 2$), which is separated from another acyclic form by a small barrier as described in the PNAS paper. We then discuss the case for cyclic S_4 and for a non-rigid S_4 which can switch between different structures at room temperatures. We use S to represent the most abundant sulfur isotope and Q to represent any other sulfur isotope. Like the original work, we assume that there is a very low abundance of Q, so reactions between two molecules containing Q can be neglected.

S3.1 $SS + SS \longrightarrow S_4$

The PNAS paper analyzes three reactions involving SS self-reaction, shown by Reactions R9 to R11 with symmetry numbers assigned based on the rigid and linear S_4 . Here we analyze these three reactions using reaction symmetry described in Equation 2 of the main text and then compare with what the PNAS paper suggested.





Since there is a loss of symmetry in both a reactant and the transition state in the labeled Reactions R10 and R11 relative to Reaction R9, all three reactions have a reaction symmetry number of 2. Since heavy-atom kinetic isotope effects are small, the rate coefficients for all three reactions would be approximately equal, and no enrichment would be expected from symmetry, which corresponds to the relative rates used in previous models, which the PNAS paper discusses.^{22,26}

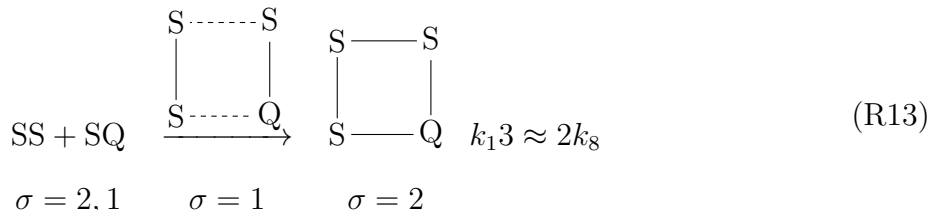
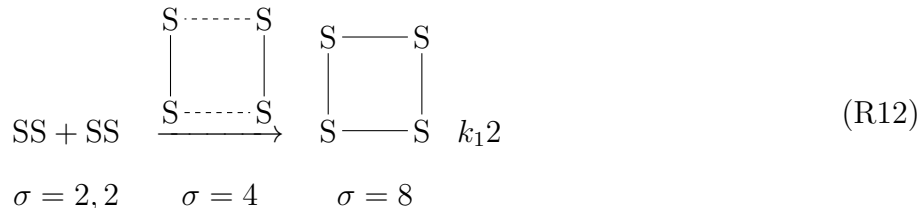
One hypothesis in the PNAS paper states that the rates of Reaction R9 should be twice of either Reaction R10 or Reaction R11 by arguing that metastable S_4 has all the conformational possibilities present in forming SSSQ and SSQS. This leads to counting both indistinguishable reaction pathways that form SSSS.²² The sulfur system discussed in the PNAS paper is rather complicated and does not use exactly the same methods for estimating rate coefficients as discussed in the main text of this manuscript. However, it appears to us that the PNAS paper made a similar factor of 2 mistake as one would make if one used the Pollak and Pechukas method.² Our paper has shown that rearrangements which result in indistinguishable conformations do not lead to an increase in reaction symmetry number or a change in the final reaction rate. Since this rearrangement should not change the kinetics, the rate coefficient for formation of isotopically enriched SSSQ and SSQS should be equal to that of SSSS.

The PNAS paper also notes that S_4 , SSSQ, and SSQS are not rigid molecules, which can make the rigid rotor approximation for finding the symmetry number incorrect. Using this non-rigidity, the PNAS paper arrives at a hypothesis that the partition functions for S_4 , SSSQ, and SSQS are equal, which appears to result from a decrease in the symmetry of S_4 .

Looking at this viewpoint from the perspective of reaction symmetry, we do not obtain the same result, and find our result consistent with previously reported rate coefficients.

Contrasting the argument in the PNAS paper, non-rigid molecules can still have symmetry.¹³ If there is an effect of non-rigidity on molecular symmetry, it would likely increase the number of symmetry operations, as is the case with many non-rigid compounds like NH_3 and H_2O_2 ,²⁷ lowering the corresponding molecules' partition function. Using NH_3 as an example, NH_3 's most stable form is non-planar, but since it can undergo low barrier inversion tunneling, it switches between its two non-planar forms by going through a planar transition. With this inversion tunneling, the symmetry properties of NH_3 become identical to that of the planar BF_3 ,²⁷ increasing the number of symmetry operations. Similarly, S_4 's most stable conformation is not cyclic, but it can interconvert between two forms through a cyclic transition. Counting this non-rigid effect would likely give S_4 the same symmetry operations available in its cyclic structure, increasing its symmetry number as well.

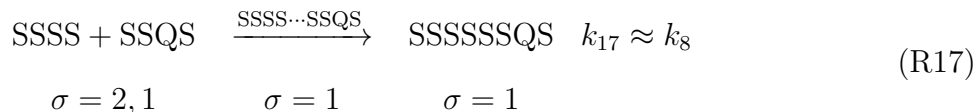
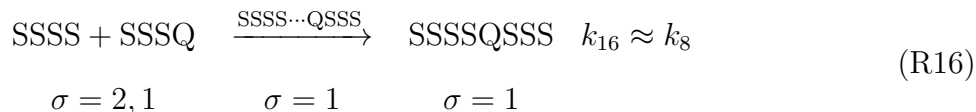
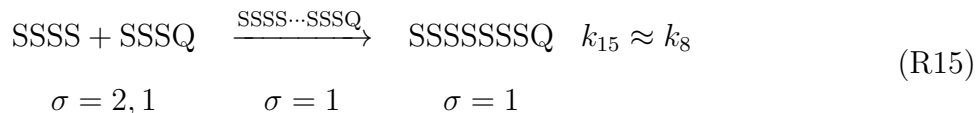
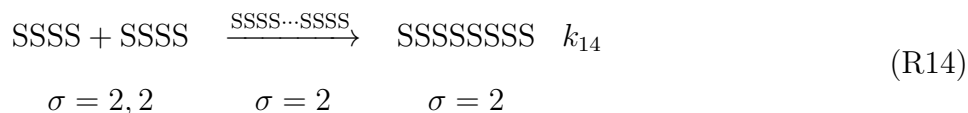
If we analyze S_4 as non-rigid, using the similar analogy to NH_3 (or equivalently analyze the direct cyclic formation, which creates the same effect), S_4 would have a symmetry number of 8, and $\text{SSQS} \longleftrightarrow \text{SSSQ}$, which are no longer distinct species, would have a symmetry number of 2, with their corresponding transition states having symmetry numbers of 4 and 1 respectively. This would give the labeled reaction twice the rate constant of the unlabeled reaction, as shown by Reactions R12 and R13.

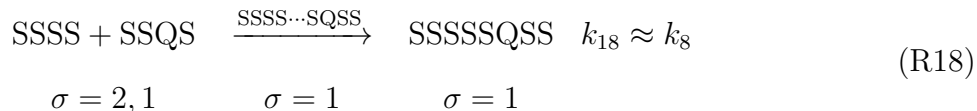


To compare with the rigid analysis, we can count SSQS and SSSQ as separate species by halving the combined species's partition function, halving the rate constant of Reaction R13, and creating a duplicate reaction forming the other structure, as is done in the PNAS paper. This would lead to three reactions with equal rate constants, which is the same as using the rigid structures in Reactions R9 to R11. Using this analysis in this instance, the rigid and non-rigid structures lead to the same relative rate constants since the non-rigidity proportionally increases the symmetry numbers of these three isotopologues.

S3.2 $S_4 + S_4 \longrightarrow S_8$

For the set of reactions forming S_8 , the PNAS paper uses three reactions, $S_4 + S_4$, $S_4 + SSSQ$ and $S_4 + SSQS$, and mentions that equal rate coefficients would correspond to no mass-independent fractionation.²² Looking more deeply at this reaction may indicate more complexity. Instead of three reactions, we represent this system as a set of 5 elementary reactions which form a linear eight sulfur compound. The linear S_8 compound, which has been well-characterized,²⁸ would likely form before any ring closure occurs, so this would more accurately represent elementary kinetics. The set of five reactions are shown below.





Based on standard transition state theory used in other parts of this work, which results in no mass-independent fractionation, Reactions R14 to R18 should have equal rates.

If the set of five reactions is lumped into the three reactions used in the PNAS paper, the two reactions involving a non-abundant isotopes, SSSS + SSSQ and SSSS + SSQS, would have a rate coefficient twice that of the reaction with only ^{32}S isotopes. Applying this difference in rate coefficients to Equation 14 in the PNAS paper²² leads to no enrichment.

Overall, this section provides multiple perspectives which indicate that the large enrichments described in the PNAS paper may have been due to some factor of 2 mistake in estimating molecular symmetry leading to similar enrichment errors as found by our analysis of the method by Pollak and Pechukas.²

S4 B + B treatment in kinetic Monte Carlo

There are two ways to formulate the conversion from bulk kinetic rates to stochastic rates for B + B reactions, and both are internally consistent. However, if one is half implemented, then an erroneous factor of 2 would be created for rate constants. This section describes the background and difference between the two methods of implementation. We first discuss how the A + B reaction was originally formulated by Gillespie, then describe how he implemented A + A reaction, and conclude with a valid alternative representation used in other work.

In the original Gillespie papers,^{29,30} he formulates the rate coefficient, c , for a stochastic reaction as the average probability that a unique combination will react in a given system per time. The total number of reactions over a given time dt in a volume V for a reaction with reactants A and B is $ABc dt/V$, given A and B are the number of reactants A and B respectively. For an ensemble of systems, the rate can then be described by the average, $\langle AB \rangle c dt/V$. Comparing this with the deterministic rate $k \langle A \rangle \langle B \rangle dt/V^2$ yields the relation-

ship $k = Vc\langle AB\rangle/\langle A\rangle\langle B\rangle$. At the deterministic limit, where $\langle AB\rangle = \langle A\rangle\langle B\rangle$, $c = k/V$.^{29,30}

Gillespie discusses this framework for a B + B reaction. The stochastic description of reaction rate becomes $(B(B - 1)/2!)cdt/V$. The factor of 2 prevents the doubling counting of pairs of molecules. When the ensemble of stochastic rates is set equal to the deterministic rate coefficient, we get $k\langle B\rangle^2/V^2 = \langle B(B - 1)\rangle cdt/2V$. At the deterministic limit for a Poisson distribution, where $\langle B\rangle^2 = \langle B(B - 1)\rangle$, this comes out to $c = 2k/V$.³⁰

One interesting thing to note about Gillespie’s formulation is that the factor of 2 which is used in converting the k to c is then eliminated when going from c to the probability of reaction, with the addition of 1/2. Some people have eliminated both factors entirely,³¹ which is also a valid way of implementing kinetic Monte Carlo, though it changes Gillespie’s definition of c .

If one were to only use the factor when determining c from k or when going from c to the reaction rate, the B + B reactions in that system would be off by a factor of 2, leading to errors similar to those discussed in this paper.

Bibliography

- (1) Karas, A. J.; Gilbert, R. G.; Collins, M. A. Rigorous Derivation of Reaction Path Degeneracy in Transition State Theory. *Chem. Phys. Lett.* **1992**, *193*, 181–184.
- (2) Pollak, E. L. I.; Pechukas, P. Symmetry Numbers, Not Statistical Factors, Should Be Used in Absolute Rate Theory and in Brøsted Relations. *J. Am. Chem. Soc.* **1978**, *100*, 2984–2991.
- (3) Bishop, D. M.; Laidler, K. J. Symmetry Numbers and Statistical Factors in Rate Theory. *J. Chem. Phys.* **1965**, *42*, 1688–1691.
- (4) Fernández-Ramos, A.; Ellingson, B. A.; Meana-Pañeda, R.; Marques, J. M. C.; Truh-

- lar, D. G. Symmetry Numbers and Chemical Reaction Rates. *Theor. Chem. Acc.* **2007**, *118*, 813–826.
- (5) McIntosh, G. J. A Theoretical Kinetic Model of the Temperature and pH Dependent Dimerization of Orthosilicic Acid in Aqueous Solution. *Phys. Chem. Chem. Phys.* **2012**, *14*, 996–1013.
- (6) Vandeputte, A. G.; Reyniers, M.-F.; Marin, G. B. Theoretical Study of the Thermal Decomposition of Dimethyl Disulfide. *J. Phys. Chem. A* **2010**, *114*, 10531–10549.
- (7) Tranter, R. S.; Klippenstein, S. J.; Harding, L. B.; Giri, B. R.; Yang, X.; Kiefer, J. H. Experimental and Theoretical Investigation of the Self-Reaction of Phenyl Radicals. *J. Phys. Chem. A* **2010**, *114*, 8240–8261.
- (8) Miller, J. A.; Klippenstein, S. J. The Recombination of Propargyl Radicals and Other Reactions on a C₆H₆ Potential. *J. Phys. Chem. A* **2003**, *107*, 7783–7799.
- (9) Babikov, D.; Semenov, A.; Teplukhin, A. One Possible Source of Mass-Independent Fractionation of Sulfur Isotopes in the Archean Atmosphere of Earth. *Geochim. Cosmochim. Ac.* **2017**, *204*, 388–406.
- (10) Dauphas, N.; Schauble, E. A. Mass Fractionation Laws, Mass-Independent Effects, and Isotopic Anomalies. *Annu. Rev. Earth Planet. Sci.* **2016**, *44*, 709–783.
- (11) Truhlar, D. G.; Garrett, B. C. Variational Transition-State Theory. *Acc. Chem. Res.* **1980**, *13*, 440–448.
- (12) Teplukhin, A.; Babikov, D. Several Levels of Theory for Description of Isotope Effects in Ozone: Symmetry Effect and Mass Effect. *J. Phys. Chem. A* **2018**, *122*, 9177–9190.
- (13) Gilson, M. K.; Irikura, K. K. Symmetry Numbers for Rigid, Flexible, and Fluxional Molecules: Theory and Applications. *J. Phys. Chem. B* **2010**, *114*, 16304–16317.

- (14) McQuarrie, D. A.; Simon, J. D. *Physical Chemistry: A Molecular Approach*; University Science Books, 1997.
- (15) Velivetskaya, T. A.; Ignatiev, A. V.; Yakovenko, V. V.; Vysotskiy, S. V. Experimental Studies of the Oxygen Isotope Anomalies ($\Delta^{17}\text{O}$) of H_2O_2 and Their Relation to Radical Recombination Reactions. *Chem. Phys. Lett.* **2018**, *693*, 107–113.
- (16) Mauersberger, K.; Erbacher, B.; Krankowsky, D.; Gunther, J.; Nickel, R. Ozone Isotope Enrichment: Isotopomer-Specific Rate Coefficients. *Science* **1999**, *283*, 370–372.
- (17) Bigeleisen, J.; Mayer, M. G. Calculation of Equilibrium Constants for Isotopic Exchange Reactions. *J. Chem. Phys.* **1947**, *15*, 261–267.
- (18) Ivanov, M. V.; Babikov, D. On Molecular Origin of Mass-Independent Fractionation of Oxygen Isotopes in the Ozone Forming Recombination Reaction. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 17708–17713.
- (19) Dunn, P. J. H.; Malinovsky, D.; Goenaga-Infante, H. Calibration Strategies for the Determination of Stable Carbon Absolute Isotope Ratios in a Glycine Candidate Reference Material by Elemental Analyser-Isotope Ratio Mass Spectrometry. *Anal. Bioanal. Chem.* **2015**, *407*, 3169–3180.
- (20) Junk, G. A.; Svec, H. J. *Nitrogen Isotope Abundance Measurements*; Chemistry-Radiochemistry ISC-1138, 1958.
- (21) Attendorn, H.-G.; Bowen, R. N. C. *Radioactive and Stable Isotope Geology*; Chapman & Hall: London, 1997.
- (22) Babikov, D. Recombination Reactions as a Possible Mechanism of Mass-Independent Fractionation of Sulfur Isotopes in the Archean Atmosphere of Earth. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 3062–3067.

- (23) Mentel, T. F.; Springer, M.; Ehn, M.; Kleist, E.; Pullinen, I.; Kurtén, T.; Rissanen, M.; Wahner, A.; Wildt, J. Formation of Highly Oxidized Multifunctional Compounds: Autoxidation of Peroxy Radicals Formed in the Ozonolysis of Alkenes – Deduced from Structure–Product Relationships. *Atmos. Chem. Phys.* **2015**, *15*, 6745–6765.
- (24) Zhang, X.; McVay, R. C.; Huang, D. D.; Dalleska, N. F.; Aumont, B.; Flagan, R. C.; Seinfeld, J. H. Formation and Evolution of Molecular Products in α -Pinene Secondary Organic Aerosol. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 14168–14173.
- (25) Gao, C. W.; Allen, J. W.; Green, W. H.; West, R. H. Reaction Mechanism Generator: Automatic Construction of Chemical Kinetic Mechanisms. *Comput. Phys. Commun.* **2016**, *203*, 212–225.
- (26) Pavlov, A.; Kasting, J. Mass-Independent Fractionation of Sulfur Isotopes in Archean Sediments: Strong Evidence for an Anoxic Archean Atmosphere. *Astrobiology* **2002**, *2*, 27–41.
- (27) Bunker, P. R.; Jensen, P. *Molecular Symmetry and Spectroscopy*, 2nd ed.; NRC Research Press: Ottawa, 2006.
- (28) Mayer, R. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Springer US: Boston, MA, 1977; pp 33–69.
- (29) Gillespie, D. T. A General Method for Numerically Simulating the Stochastic Time Evolution of Coupled Chemical Reactions. *J. Comput. Phys.* **1976**, *22*, 403–434.
- (30) Gillespie, D. T. Exact Stochastic Simulation of Coupled Chemical Reactions. *J. Phys. Chem.* **1977**, *81*, 2340–2361.
- (31) Goss, P. J. E.; Peccoud, J. Quantitative Modeling of Stochastic Systems in Molecular Biology by Using Stochastic Petri Nets. *Proc. Natl. Acad. Sci. U. S. A.* **1998**, *95*, 6750–6755.