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Multigenerational Theoretical Study of Isoprene Peroxy Radical 1–5-Hydrogen Shift Reactions that Regenerate HO_x Radicals and Produce Highly Oxidized Molecules

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Abstract

A computational protocol is employed to glean new insight into the kinetics of several 1,5-hydrogen atom (H) shift reactions subsequent to first- and second-generation OH/ O₂ additions to isoprene. The M06–2X density functional was initially used with the Nudged Elastic Band (NEB) method to determine the potential energy surface of OH/O₂ addition reactions, the 1,5-H shift reactions, and the fragmentation exit channels. The Master Equation Solver for Multi-Energy Well Reactions (MESMER) was applied to determine the rate constants for OH addition and the 1,5-H shifts. M06–2X was capable of quantifying the rate constants of OH addition to the first and second double bonds of isoprene with deviations less than 17% from the experimentally determined values. However, M06–2X underestimated the 1,5-H shift rate constants of second-generation isoprene peroxy radicals. Consequently, MN15, ωB97X-D, and CBS-QB3 methods were employed to compute average barrier heights to first- and second-generation 1,5-H shifts. In the first generation, the rate constants of H abstraction by β-(1,2) and (4,3) isoprene hydroxy-peroxy radicals from the neighboring hydroxyl group are 1.1×10^{-3} and $2.4 \times 10^{-3} \text{ s}^{-1}$, respectively. These values are determined primarily by the barrier of the H shift reaction and, to a smaller albeit nonnegligible extent, by the stability of the resulting alkoxy radical and the exit barrier leading to C–C bond dissociation. In contrast, the average second-generation rate constant of 1,5-H shifts from H–R–OH sites to the peroxy radical is $1.8 \times 10^{-1} \text{ s}^{-1}$, with tunneling playing the significant role of increasing this value relative to first-generation 1,5-H shifts. Under low NO_x conditions, first-generation isoprene oxidation reactions may recycle HO_x at levels ranging from 10 to 30% due in large part to 1,5-H shifts, with the recycling efficiency being sensitive to HO₂ concentrations and temperature. HO_x recycling is expected to increase to levels beyond 80% in second-generation reactions of oxidized isoprene species because of isoprene epoxidiol (IEPOX) formation and further 1,5-H shifts that are kinetically favorable.

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Keywords

Isoprene; HO_x recycling; Tunneling; Density Functional Theory; Nudged Elastic Band (NEB); DIMER method; Simplified Generalized Simulated Annealing (SGSA) method

1. Introduction

The hydroxyl radical (OH) plays an essential role in the removal of volatile organic compounds (VOCs) from the troposphere. Isoprene is a VOC released to the troposphere in substantial amounts by deciduous trees and other vegetation and, except for methane, is the most abundant VOC emitted into the troposphere by molar concentration.(1,2) Thus, it is important for the success of air quality models to understand the fate of isoprene and oxidants in the atmosphere. Recent studies of the OH radicals above forested regions have shown that atmospheric models underpredict the concentration of OH radicals.(3,4) The underestimation may be larger than a factor of 4 in many cases,(4–6) although a recent study has suggested that typical OH measurements may overestimate concentrations by a factor of 2.(7) The inadequacy is largely due to the complex multigenerational atmospheric chemistry of isoprene involving a variety of free radical addition, abstraction, and isomerization reactions at multiple sites with each successive oxidation step giving rise to a new generation of products. Given the OH consumption and recycling tendency of isoprene in oxidation mechanisms, it has been proposed that isoprene acts as a buffer over tropical forests, which can mitigate the concentration of the OH in the troposphere.(8)

Elaborate mechanisms for the reaction of the OH-induced oxidation of isoprene have been proposed.(9,10) The initial step involves the addition of the OH radical and oxygen (O₂) to one of the double bonds, which gives rise to eight isoprene hydroxy-peroxy radical isomers with varying yields.(11) In the absence of NO_x, the peroxy radicals may either react with HO₂ or isomerize typically via 1,5- and 1,6-hydrogen (H) atom shifts that may regenerate the OH radical and/or continue the oxidation process.(12) Scheme 1 illustrates the HO₂ addition reaction and two hydrogen shift reactions, which have been proposed to occur in the first-generation oxidation of isoprene.(13) The 1,5-H shift is suggested to be one of the main pathways leading to methyl vinyl ketone (MVK) and methacrolein (MACR), although other pathways may be significant.(14)

The computed rate constants for the 1,6-H shift shown in Scheme 1 are estimated to be several orders of magnitude greater than those for the 1,5-H shift,(9) although the yields of the precursor δ -peroxy radical isomers are approximately 5% under atmospheric conditions and the yield of HPALDs subsequent to a 1,6-H shift is only 25%.(12) Despite the diminished yields during each step of the oxidation, the 1,6-H shifts are still relevant to first-generation isoprene chemistry because a dynamic equilibrium exists between all peroxy radical isomers. Consequently, any reacted δ -peroxy radicals via 1,6-H shifts may be replenished by the reestablishment of equilibrium and therefore give rise to higher than expected HPALD yields. Da Silva et al. have computed the 1,5-H shift rate constants to be 4.8×10^{-4} and $5.0 \times 10^{-4} \text{ s}^{-1}$ for β (1,2) and (4,3) isoprene peroxy radical isomers, respectively, at 298 K by averaging barrier heights using two composite methods (G3SX/

CBS-QB3).(15) For the same isomers, Peeters et al. have recently reported the 1,5-H shift rate constants to be 6.5×10^{-4} and $1.2 \times 10^{-3} \text{ s}^{-1}$ using a combined coupled cluster//quadratic configuration interaction method (CC//QC).(9) They also used the M06-2X density functional and showed that its barriers were within <2% of the CC//QC values. Given that average peak daily ambient concentrations of HO₂ in pristine environments are approximately 5E8 molecules/cm³ (or 20 ppt)(16) and the rate constant for HO₂ addition to similar sized organic peroxy radicals is $1.6 \times 10^{-11} \text{ s}^{-1}$.(17) the effective first-order rate constant for HO₂ addition is $8.1 \times 10^{-3} \text{ s}^{-1}$ at 298 K and is assumed to dominate over isomerization and lead to lower-volatility hydroxy hydroperoxides while consuming HO_x species. Given Scheme 1, the relative branching of 1,5-H shifts, 1,6-H shifts, and HO₂ addition reactions in first-generation isoprene chemistry is important to discern because it represents the first opportunity for HO_x species to be recycled, which plays a central role in the oxidation of VOCs in the atmosphere.

It should be noted that density functionals and even higher level CC methods still suffer from uncertainties, particularly during bond breaking events and other cases involving nondynamical electron correlation.(18) Substantial systematic errors may therefore be present within the realm of single-reference methods and ideally should be accounted for in resulting calculations by comparing results with experimental measurements whenever available. While many density functionals such as M06-2X have been tested to be reliable using large data sets,(19) there is no guarantee that they will not give rise to errors outside of the bounds of the mean unsigned error range for a particular molecular system of interest. Even a reasonably small uncertainty of 1 kcal/mol in the barrier height (the gold standard for electronic structure calculations) may give rise to a factor of ~5 difference in the rate constant.

The situation changes dramatically in second-generation isoprene oxidation reactions. Scheme 2 illustrates several second-generation isoprene peroxy radical reactions occurring in low NO_x environments. Once again, HO₂ may add a hydrogen atom to yield another hydroperoxide group and give rise to a highly oxidized molecule (HOM) with a formula of C₅H₁₂O₆. This low-volatility species is thought to play an important role in new particle formation and growth.(20) Alternatively, the second-generation peroxy radical has several different sites to abstract from, including a carbon site containing a hydroxyl group. The hydrogen atom from a H-C-OH group (α site) is significantly more labile than that from a methyl group, and consequently, the H shift may lead to other highly oxidized species with formulas of C₅H₁₀O₅₋₇. The C₅H₁₀O₅ compound has been observed by chemical ionization mass spectrometry (CIMS) in the gas phase and determined to be an important contributor to isoprene-derived secondary organic aerosol (SOA).(21) If the compound is the epoxide shown in Scheme 2, it may hydrolyze in the particle phase like isoprene epoxydiols (IEPOXs).(22) The rate constant for the 1,5-H shift reaction shown in Scheme 2b was estimated to be >0.1 s⁻¹ from a box model fit to CIMS measurements and corroborated with quantum chemical calculations.(23) The stark increase of this rate constant relative to first-generation isomerization reactions is intriguing because it introduces new oxidative pathways after two OH additions. Furthermore, the reaction may regenerate HO_x, which may then continue to oxidize other species. Box models however possess uncertainties in the highly coupled parameters that comprise the model, and it can be difficult to abstract rate

constants using model fits to experimental data in certain cases with a high level of certainty. It is therefore important to scrutinize these reactions further with additional techniques to determine their role in HOM production and HO_x recycling.

In this paper, 1–5-H shift reactions of first- and second-generation isoprene peroxy radicals are investigated using a diverse combination of quantum chemical and kinetic calculations, and the results are compared with recent studies. A computational protocol based on density functional theory (DFT) was employed to investigate the 1–5-H shift, starting from the addition of OH/O₂ to isoprene. DFT has found widespread use in the biological and physical sciences because the methods are quite accurate and only incur a modest computational cost. (24) However, as stated above, many challenges remain to improve density functionals so that they may describe long-range interactions and the breaking of covalent bonds with a higher degree of accuracy. (25) DFT methods have been applied in previous computational studies on the 1–5-H shift mechanism, resulting in a range of rates. (9,13,15) The methods adopted in this work attempt to build upon previous studies by (1) identifying an additional reactive intermediate in the exit channel of alkoxy radical decomposition in first-generation isoprene oxidation chemistry, (2) determining that the M06–2X density functional may underestimate 1,5-H shift rate constants that have been measured in second-generation isoprene chemistry, (3) obtaining barrier height averages with some recently developed density functionals and methods to try and mitigate systematic errors, and (4) conducting a temperature-dependent comparison study of the first- and second-generation reaction dynamics so that pathways to HO_x recycling and HOM production may be better understood. The results of the calculations may also inform the chemistry of larger and more complex species such as aromatic compounds and higher-order terpenes so that air quality models may better capture their reaction dynamics.

2. Methods

All electronic structure calculations were performed with Gaussian's G09 and G16 software. (26,27) G09 was used for all electronic structure calculations of the first-generation isoprene + OH oxidation potential energy surface (PES) involving the M06–2X density functional, while G16 was used to compute first- and second-generation 1,5-H shift barriers using several other density functionals, including the recently released MN15 (28) (as will be described further below). The M06–2X functional has become quite popular in recent years due to its ability to describe long-range interactions and barrier heights with a high level of accuracy for large test data sets. (29,30) G09 was interfaced with software that implements the Nudged Elastic Band (NEB), (31–33) Improved DIMER method (IDM) (34) and Simplified Generalized Simulating Annealing (SGSA) methods. (35)

One of the key elements of the computational method was the application of the NEB algorithm to construct a detailed PES so that transition states and reactive intermediates may be readily identified along the entire reaction path. During a NEB calculation, a number of images on the reactive pathway are optimized while maintaining equal spacing between neighboring images using spring forces, thereby creating an “elastic band”. The perpendicular component of the force is projected out during the optimization. The calculations are intensive because a typical pathway may contain 30 images or more and

consequently are usually conducted using a smaller basis set. The IDM was used to refine the transition state structures identified in the NEB calculations.

The NEB program that was used is a modified version of the original program from Alfonso and Jordan.(31) For each NEB calculation, 31 intermediate images were generated using Materials Studio.(36) Materials Studio uses the method of Halgren and Lipscomb(37) to interpolate between the defined reactants and products. This modified version of the NEB has been parallelized, which permits ten intermediate images to be run simultaneously, each image using eight processors. Thus, each cycle of the NEB calculation requires merely three gradient calculations and a speed up to almost 10-fold. The NEB computer program has been modified to include variable spring constants, climbing image, and the FIRE optimizer.(38) The FIRE optimizer improves the rate of convergence of a NEB calculation, and it was the optimizer of choice in all NEB calculations. The NEB calculations were stopped when all important maxima along the NEB trajectory had gradients in the range of 1.0×10^{-3} to 4.0×10^{-3} Hartrees/Bohr. The minima along the calculated NEB reaction path were then optimized using the maug-cc-pVTZ basis set with an ultrafine integration grid. The estimated transition states were refined using IDM and the maug-cc-pVTZ basis set with the fine integration grid. The convergence criterion of the gradient in the DIMER calculation was 4.5×10^{-4} Hartrees/Bohr. Both the NEB and DIMER methods do not need a Hessian matrix but require only the calculation of gradients of the energy. This makes these methods computationally expedient for finding the minimum-energy path between a set of reactants and products and potent for discovering unforeseen intermediates along a reaction coordinate.

For all G09 calculations of first-generation OH chemistry, the M06-2X hybrid meta exchange–correlation functional(15) was paired with either the 6-311+g** or the maug-cc-pVTZ basis set.(16,17) The smaller basis set (6-311+g**) was used in the NEB calculations in order to expedite the mapping of the entire reaction pathway. The larger maug-cc-pVTZ basis set was used for greater accuracy in all final geometry optimizations and harmonic frequency calculations of the stationary and transition states. For these latter calculations, an ultrafine integration grid was used where the SCF was required to converge to 1.0×10^{-8} Hartrees and the gradient of the energy was required to be smaller than 4.5×10^{-4} Hartrees/Bohr. The sign of the force constants from the frequency calculations enabled the characterization of the molecular structure as either a stationary or transition state. All of the force constants for all stationary states (minima on PES) were positive, and the refined transition state structures had only one negative force constant (and consequently one imaginary frequency).

Kinetic rate constant computations were conducted using the Master Equation Solver for Multi-Energy well Reactions (MESMER v. 4.0).(39) Master equation approaches are uniquely poised to describe nonequilibrium kinetics involving multiple reactive intermediates along a reaction coordinate. The approach obtains microcanonical rate coefficients for all reactions between all wells and therefore captures reversible dynamics in a complex system so that a full kinetic description may be provided. MESMER takes into account energy dissipative processes caused by molecular collisions, which may influence reaction dynamics.(11) In solving the master equation, a matrix describing the population

evolution within and between potential energy wells is diagonalized, yielding a set of eigenvalues. In many instances, the eigenvalues separate into two distinct groups: internal energy relaxation eigenvalues (IEREs) and chemically significant eigenvalues (CSEs). The IEREs represent rapid energy relaxation processes within wells, while the CSEs represent the slower conversion of species between wells. Most eigenvalues are IEREs, which are large in absolute value, while a minute number consist of small-valued CSEs. MESMER invokes the Bartis–Widom method(40) to obtain phenomenological rate coefficients, which is appropriate in the limit of the separation between IEREs and CSEs. When the eigenvalues begin to merge, alternative approximations or methodologies may be required.(41)

The vibrational frequencies, geometrical coordinates, and ZPE-corrected energies were used as input to MESMER in order to obtain first- and second-order rate constants. The bath gas employed in all MESMER calculations was N₂. The Lennard-Jones collision parameters for N₂ that were used were $\epsilon = 91.85$ K and $\sigma = 3.92$ Å,(42) while all other C5 species were assumed values similar to hexane of $\epsilon = 289.2$ K and $\sigma = 4.37$ Å.(43) The exponential down approach with a value of $E_{\text{down}} = 200$ cm⁻¹ was used to model the energy transfer. The value of the exponential down parameter is near the middle range of values suggested for nitrogen. Temperature-dependent calculations for the OH addition to isoprene and Isop-OOH as well as both first- and second-generation 1,5-H atom transfers were conducted where the pressure was set to 760 Torr.

A series of three different MESMER calculations were performed on the following systems: (1) isoprene + OH/HO-Isop-OOH + OH, (2) first-generation isoprene peroxy radical 1,5-H shifts (Scheme 1b), and (3) second-generation isoprene peroxy radical 1,5-H shifts (Scheme 2b). The first series involved computing the well-known OH addition rate constant to isoprene and its first-generation hydroxy-hydroperoxy derivative(44) in order to assess the accuracy of the computational protocol in this case. The first elementary step in the reaction crucially involves OH loosely associating with the π electrons of an isoprene double bond. This loosely bound complex has been given many names in the literature, including a supermolecule,(45) a van der Waals (vdW) complex,(46) and a prereactive complex.(47) Herein, these species will be referred to as vdW complexes. The reaction to form a vdW complex is barrierless and was treated within MESMER by the inverse Laplace transform method. In this work, the barrierless reactions were assumed to be limited by the rate at which the reactants collide. Thus, a value of 3.0×10^{-10} cm³molecule⁻¹ s⁻¹ was used for the pre-exponential factor. A value of 1.0×10^{16} molecules cm⁻³ was used for the excess concentration, which is sufficient to ensure the linearity of the master equation. For all 1,5-H shift reactions, the Eckart tunneling correction as presented by Miller(48) was used to account for hydrogen atom tunneling. The electronic partition function for the OH radical included the low-lying doubly degenerate excited state, separated from the doubly degenerate ground state by 139.7 cm⁻¹.(25) A grain size of 20 cm⁻¹ was used in all MESMER calculations, and all final products were treated as infinite sinks.

As will be discussed in the next section, the inadequate agreement between M06–2X calculations and experimental measurements of second-generation 1,5-H shifts motivated additional calculations using other recently developed density functionals and methods. For all 1,5-H shifts, calculations were performed using M06–2X, MN15, ω B97X-D, and CBS-

QB3 methods. The former method (M06–2X) is directly comparable to the work of Peeters et al.,(9) while the CBS-QB3 composite method was used by Da Silva et al.(15) An average barrier height was obtained using an equally weighted average of all four methods. The computational averaging implemented here is viewed as a way of minimizing systematic errors that may occur among the different functionals employed. Systematic errors in barrier heights of hydrogen transfer reactions have been observed in the study of Zhao and Truhlar(19) for 15 different DFT methods including M06–2X, which all displayed nonzero mean signed errors. The average barrier height was then used in subsequent MESMER calculations for the 1,5-H shift rate constants. As will be seen, this improved the agreement between the calculations here and measurements of second-generation 1,5-H shifts, and the averaging procedure was also applied to first-generation reactions.

3. Results and Discussion

3.1. Isoprene + OH and HO-Isop-OOH + OH Reaction Kinetics

The computational protocol previously described was initially applied to the OH addition to isoprene and 1-hydroxy-2-hydroperoxy-isoprene (β -(1,2)-HO-Isop-OOH). Figure 1 displays the PES for OH addition to both species. In Figure 1a, calculations were carried out for OH additions to carbon sites 1 and 4, which represent 96% of the initial hydroxy-isoprene isomers.(10) For isoprene OH addition, the OH initially forms a weak vdW complex by interacting with the π electrons of the double bond, forming a weak hydrogen bond (“T” style geometry; see Figure 2a). A very small submerged barrier to association is encountered before the adducts are produced. 1-HO-Isop $\cdot$ is observed to be several kcal/mol more stable than 4-HO-Isop $\cdot$ because a tertiary radical is produced in addition to the allylic resonance stability. The barrier height difference between the vdW complexes and TS₁ is well within the uncertainty range of M06–2X, which may hamper rate constant calculations.

The vdW complex that forms between OH and β -(1,2)-HO-Isop-OOH is significantly stronger than isoprene + OH, as shown in Figure 1b with the deeper well occurring at 8.1 kcal/mol. Figure 2b illustrates why this is the case because OH changes hydrogen bond allegiance from the π -electron system of the double bond to the neighboring hydroxy and hydroperoxy groups where it may form stronger hydrogen bonds. This modified geometry is better suited for the OH to add to the second double bond. The deeper-lying vdW complex and transition state will more favorably lead to the adduct relative to the first-generation reaction.

To quantify the rate constants, a MESMER calculation was set up for both PESs shown in Figure 1. For the OH addition to isoprene, only one vdW complex was implemented (vdW leading to 4-HO-Isop $\cdot$) along with both transition states (TS₁) and both products. The resulting calculation gives a rate constant of $5.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for OH addition at site 1 and $2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at site 4 at 298 K (see Table S1 in the Supporting Information). The results are very similar to those obtained by McGivern et al. (49) (5.6×10^{-11} and $3.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively), who computed energies at the CCSD(T)/6–311G**//B3LYP/6–31G** level. The branching ratio between the two rate constants is 2.2, which closely matches the factor of 2 difference in OH adduct yields at carbon sites 1 and 4 on isoprene.(50) Given that the two OH adducts (at carbons 1 and 4)

form with a computed rate constant of $8.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($k_{1,4}$ in Table S1) and represent an estimated combined yield of 96%, (10) the total isoprene + OH rate constant due to additions at all four carbon sites on isoprene is estimated to be $8.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from these results. The difference relative to the measured rate constant (51) is 17%, which is well within the uncertainty of the barrier calculations. In the benchmark studies of Zhao and Truhlar, (19) they determined that the average mean unsigned error (AMUE) of barrier heights computed with M06-2X over several large data sets was 1.06 kcal/mol. Consequently, a barrier height uncertainty of ± 1 kcal/mol was implemented for all species in subsequent temperature-dependent rate constant calculations (including the DFT averaging method) to provide the uncertainty range for the rate constant values. Because the barrier height appears in the exponential of rate constant expressions, its uncertainty gets amplified when rate constants are computed. For isoprene + OH at 298 K, a ± 1 kcal/mol barrier height uncertainty led to a $3.1 \times 10^{-11} < k_{\text{total}} < 1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ rate constant range. The temperature dependence of the OH + isoprene rate constants and over a 278–418 K temperature range was computed using MESMER and is shown in Figure S3 of the Supporting Information. It shows the expected trend of a mildly decreasing rate constant with increasing temperature for a submerged barrier. The slope of the Arrhenius plot in Figure S3 yields an activation energy of $-1090 \text{ cal mol}^{-1}$, which is comparable to the experimental measurement of $-813 \text{ cal mol}^{-1}$ as reported by Kleindienst et al. (52) and the Master Chemical Mechanism (MCM) fitted value of $-775 \text{ cal mol}^{-1}$. (53)

For second-generation OH addition to β -(1,2)-HO-Isop-OOH, the MESMER calculation was set up in a similar fashion with a barrierless reaction leading to the vdW complex, which is preceded by OH addition to the double bond. The computed rate constant at 298 K was $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Recent work by St. Clair et al. has shown that the β -(1,2)-HO-Isop-OOH isomer specific rate constant is $7.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which may indicate that the calculations are overestimating the rate in this case although the measured value is within the uncertainty range of the calculations. If the calculation is accurate, it may overestimate the overall rate because the computed rate constant assumes that all OH collisions are equivalent and eventually go through the transition state shown in Figure 1b. Electronic structure calculations of OH trajectories below the plane of the double bond (relative to the location of the polar OH and OOH groups) show that the vdW lies only 3.5 kcal/mol below the infinitely separated reactants' limit. This is similar to OH addition to isoprene, yet the TS lies only 1.8 kcal/mol below the separated reactants' limit (instead of 3.1 kcal/mol for isoprene), implying that its rate is going to be significantly slower than OH addition to either carbon site 1 or 4 in isoprene. If half of the attacking phase space results in OH weakly binding to β -(1,2)-HO-Isop-OOH, dissociations are more likely to occur before a reorientation event. A barrier of 3.5 kcal/mol gives an estimated rate constant of $1.6 \times 10^{10} \text{ s}^{-1}$ or a half-life of $\sim 40 \text{ ps}$, which is the time that it takes for C–C bond rotations. (54) In this case, the $\text{C}=\text{C} + \text{OH}$ vdW group would have to reorient, which may occur on an even longer time scale. This spatial asymmetry would reduce the effective computed rate roughly by a factor of 2 and would therefore represent better agreement with experimental work with a deviation of 12%. An Arrhenius plot over a 278–418 K temperature range (Figure S4 in the Supporting Information) shows that this reaction has a much larger negative activation energy of $-2110 \text{ cal mol}^{-1}$. All of this is a consequence of the ideal hydrogen bonding

geometry in the vdW complex that enables OH to add to the second double bond of HO-Isop-OOH more efficiently, as shown in Figure 2b.

3.2. First-Generation 1,5-H Shift Reaction Kinetics

Motivated by the results and insights gained from applying the M06-2X functional to OH addition chemistry, the computational protocol was adopted to explore 1,5-H shifts. Scheme 3 displays the full reaction pathways for the addition of OH to carbons 1 and 4 of isoprene that give rise to MVK and MACR, respectively, via a 1,5-H shift in the first-generation. The first two steps are identical to Figure 1. O₂ then forms a secondary vdW complex followed by formation of the peroxy adduct. The next step involves the 1,5-H shift from the neighboring hydroxy group. This is followed by C-C bond dissociation to yield formaldehyde that remains loosely associated (vdW₃) with the C4 radical. The final step involves the release of OH to form either MVK or MACR. Calculations were performed for two exit channel geometries (anti and syn). The anti geometry (double bond points away from the hydroperoxy group) gave slightly smaller H shift barriers relative to the syn geometry with the barrier to internal rotation being 1.5 kcal/mol. Consequently, only the PES of both reactions is displayed for the anti geometry in Figure 3 (both anti and syn PESs are given in the Supporting Information). The M06-2X/maug-cc-pVTZ barriers for the 1,5-H shifts were 21.3 and 20.4 kcal/mol, respectively. These barriers are very similar to those from calculations by Peeters et al.(9) and Da Silva et al.(15) However, using the NEB technique, an additional intermediate (vdW₃) was discovered here. This complex represents one of three intermediates in a series of three dissociative steps that produce MVK or MACR from the HOO-Isop-O• radical intermediate. The more detailed PES shown in Figure 3 suggests that the overall barrier to hydrogen atom transfer is determined by the relative energies of three states: TS₃ (initial H transfer barrier), HOO-Isop-O• (stability determines the extent of hydrogen atom tunneling), and TS₄ (exit barrier to produce dissociated products). The discussion below will illustrate the relative importance of these three states in determining the overall kinetics of first-generation H transfer. The TS₅ barrier is not expected to affect the kinetics to a great extent for two reasons. First, it is significantly smaller than the reverse barrier over TS₄, which indicates that the reverse reaction will not take place appreciably. Second, the magnitude of the forward barrier over TS₅ is much smaller than the initial H transfer reaction (TS₃), which predominantly sets the overall H transfer rate. For these reasons, vdW₃ and TS₅ were not included in the subsequent kinetics calculations.

MESMER calculations of the 1,5-H shift were conducted using the PESs given in Figure 3, commencing with the peroxy radical intermediate. The 1,5-H shift rates were initially computed with TS₃ only directly analogous to previous calculations that assumed barrierless exit channel reactions that do not impact the overall rate.(9,15) Under this assumption, the rate constants are 5.1×10^{-4} and $1.7 \times 10^{-3} \text{ s}^{-1}$ with Eckart tunneling factors of 1.0 and 1.3 for the (1,2)- and (4,3)-HO-Isop-OO• isomers at 298 K, respectively. Tunneling is limited in first-generation 1,5-H shifts because the alkoxy radicals are unstable and close in energy to TS₃, consequently giving rise to a negligible asymmetrical barrier to tunnel through. The computed rates are unsurprisingly similar to those computed by Peeters et al. (<33% difference for both isomers) using the same density functional and show that a much faster H

transfer rate occurs for the (4,3) isomer.(9) In contrast, the isomer-specific rates computed by Da Silva et al. are not very distinguishable at $\sim 5 \times 10^{-4} \text{ s}^{-1}$ for both isomers.(15)

Conceivably, the presence of a low TS₄ barrier similar in energy to TS₃ (as shown in Figure 3) may reduce the effective rate of hydrogen atom transfer because the intermediate alkoxy radical population may receive the hydrogen atom back (reverse reaction) or the C–C bond may fragment to yield MVK or MACR by proceeding over TS₄. In the limit that the free energy of activation ($G^\ddagger$) is identical for the reverse reaction over TS₃ and the forward reaction over TS₄ for a steady-state alkoxy radical population, the effective hydrogen atom transfer rate constant (k_{eff}) would be reduced by a factor of 2. This is evident in the steady-state approximation of the effective transfer rate,(11) $k_{\text{eff}} = k_3 k_4 / (k_{-3} + k_4) = k_3 / 2$, where the reverse transfer is equivalent to the C–C dissociation rate ($k_{-3} = k_4$) using the nomenclature from Figure 3. Conversely, if $G^\ddagger$ is negligibly small for the exit channel (i.e., k_4 is large relative to k_{-3} , which is the assumption used in previous calculations), $k_{\text{eff}} = k_3$ and the only relevant reaction is that of the actual hydrogen atom transfer.

In order to ascertain the importance of TS₄ on the overall reaction kinetics of isoprene oxidation, MESMER calculations were carried out by incorporating both TS₃ and TS₄. Unfortunately, the relative energy levels of TS₃, HOO-Isop-O[•], and TS₄ as shown in Figure 3 are so close together that there is not an adequate separation of IEREs and CSEs in the MESMER calculations to make the Bartis–Widom method valid in determining temperature-dependent phenomenological rate constants as described in the Methods section. In this case, the steady-state approximation of the HOO-Isop-O[•] population was invoked to determine the role of TS₄ in the effective rate. In this approximation, $k_{\text{eff}} = k_3 k_4 / (k_{-3} + k_4)$ is relatively insensitive to the energy of the alkoxy radical intermediate because it will affect k_{-3} and k_4 in equal measure and therefore cancel in the $k_4 / (k_{-3} + k_4)$ factor. This was observed to be the case in MESMER calculations where the intermediate HOO-Isop-O[•] energy level was lowered by 5–10 kcal/mol, which resulted in an average variation of the effective rate constant of less than 20.1% over a temperature range of 275–325 K for the (1,2)- and (4,3)-HO-Isop-OO[•] isomers. A decrease of 8 kcal/mol in the HOO-Isop-O[•] energy was necessary to get a separation of IEREs and CSEs for the entire temperature range studied. The Eckart tunneling correction factor was finally applied to this rate by conducting a MESMER calculation on the single hydrogen transfer reaction to obtain the final effective rate constant.

For both (1,2)- and (4,3)-HO-Isop-OO[•] isomers, the presence of TS₄ lowered the effective rate constants to 4.8×10^{-4} and $1.5 \times 10^{-3} \text{ s}^{-1}$ at 298 K. The slight difference relative to the simpler calculation involving only k_3 is a consequence of a smaller $G^\ddagger$ for k_4 versus k_{-3} . For (1,2)-HO-Isop-OO[•], $G^\ddagger_{-3} = 0.9 \text{ kcal/mol}$ and $G^\ddagger_4 = 0.0 \text{ kcal/mol}$, while $G^\ddagger_{-3} = 1.0 \text{ kcal/mol}$ and $G^\ddagger_4 = 0.7 \text{ kcal/mol}$ for (4,3)-HO-Isop-OO[•]. In these cases, the barrierless exit channel assumption that was used in previous studies is reasonable. However, uncertainties in the electronic structure calculations may be as large as 1 kcal/mol,(19) which may still render TS₄ significant in slowing H transfers of Isop-OO[•] and other peroxy radicals in the atmosphere. It is therefore important to quantify all intermediates and barriers in the reaction pathway, and in this regard, the NEB method has proven essential to understanding the underlying details concerning the first-generation oxidation chemistry of isoprene.

3.3. Second-Generation 1,5-H Shift Reaction Kinetics

For the second-generation 1,5-H shifts, the same methods were applied to determine fundamental differences relative to the first-generation kinetics. Figure 4 displays the 1,5-H shift barriers for two second-generation peroxy isomers computed at the M06-2X/maug-cc-pVTZ level. Additional 1,5-H shifts are possible where the peroxy radical is abstracted from the neighboring hydroxy group (analogous to the first-generation reactions), although the alkoxy radicals produced are considerably less stable (>10 kcal/mol) than the carbon-centered radicals and are therefore not considered further. As shown in Figure 3, the alkoxy radical products are only slightly more stable than the H shift barrier, which decreases the likelihood of hydrogen tunneling and increases the likelihood of the reverse reaction taking place, both of which give rise to slower H transfer rates. The opposite of these two effects occurs for second-generation Isop-OO $\cdot$ chemistry because of the stability of the carbon-centered radical products. The H transfer rates are therefore amplified, and subsequent reactions in Scheme 2 are more likely to irreversibly drive the products to HOMs. Epoxide ring closure is predicted to exhibit barriers of 10–12 kcal/mol.⁽⁵⁵⁾ Considering that O₂ addition competes with epoxide formation to a certain extent because the products derived from O₂ addition have been detected, the exit channels are expected to funnel away the product species displayed in Figure 4. Consequently, MESMER calculations were conducted on only the reactions shown in Figure 4 because the products represent an effective sink. The 1,5-H shift rate for (1,4)-(HO)₂-(2)-HOO-Isop(3)-OO $\cdot$ was 2.9×10^{-2} s⁻¹. While this is considerably faster than the first-generation rates, it is significantly slower than recent measurements by D'Ambro et al., which predict rate constants greater than 0.1 s⁻¹.⁽²³⁾ The overestimation of reaction barriers by M06-2X has been observed in several other reactions. For example, the barrier for the epoxide ring closure reaction that produces IEPOX is 17.1 kcal/mol using M06-2X/maug-cc-pVTZ, which is considerably greater than the 10–12 kcal/mol barriers reported with F12 methods⁽⁵⁵⁾ and the expected barrier (<10 kcal/mol) if the reaction is to compete with O₂ addition. Additionally, Piletic et al. were unable to account for the pressure-dependent behavior of isoprene peroxy nitrite dissociation because the calculated M06-2X exit barrier was 5.2 kcal/mol too high.⁽¹¹⁾ In the seminal work of Zhao and Truhlar,⁽¹⁹⁾ systematic errors of barrier heights in several large data sets were observed for M06-2X and 16 other density functionals due to the occurrence of nonzero mean signed errors. These examples suggest that the M06-2X functional while being increasingly adopted, may imprecisely describe certain bond-breaking events in atmospheric reactions.

3.4. Multimethod Averaging of 1,5-H Shift Barrier Heights

An attempt to improve the agreement of these calculations with experimental data was made by invoking several DFT and complete basis set methods in an averaging procedure. The M06-2X and CBS-QB3 methods have been applied in previous calculations^(9,15) and were included in the average. Two recently developed density functionals ω B97X-D and MN15 were also included^(56,57) with the thought that averaging the barrier height for the crucial 1,5-H shift reaction will cancel systematic errors to a certain extent. Zhao and Truhlar have shown that M06-2X gives rise to mean signed errors (systematic errors) in barrier heights that range from -0.81 to 0.77 kcal/mol in four different benchmark data sets.⁽¹⁹⁾ Other density functionals also possess mean signed errors, and averaging procedures may therefore

cancel some of these effects out. Table 1 displays all calculations using the four methods on four reactions: two isomers involved in first- and second-generation 1,5-H shifts. From the computed values, it is evident that M06–2X yields barrier heights that are above average for all reactions, while the recently developed MN15 functional gives rise to lower values. Both of these functionals have been shown recently to exhibit small errors in barrier heights in a comprehensive study examining 14 Minnesota density functionals.⁽⁵⁶⁾ The data also show that 1,5-H shifts preferably occur at the C4 site for both first- and second-generation chemistry (darker gray side in Table 1a,b). Furthermore, and most importantly, the average barrier heights for the 1,5-H shifts are smaller in the second generation relative to those in the first generation for both isomers. This was confirmed by higher-level double-hybrid PBE0-DH and single-point CCSD(T) calculations, each showing that the second-generation 1,5-H shift barrier was lower in energy by 1.7 and 1.2 kcal/mol, respectively, for the β -(1,2)-HO-Isop-OO[•] and (1,4)-(HO)₂-(2)-HOO-Isop-(3)-OO[•] isomers (light gray values in Table 1). The average values indicate that second-generation 1,5-H shifts are kinetically and thermodynamically favorable and will therefore give rise to higher rates of conversion.

MESMER calculations using the average barriers shown in Table 1 were conducted in the same manner with the same parameters as those described for the M06–2X calculations above. Tables S3–S6 in the Supporting Information display a summary of the rate constants using M06–2X only versus the values obtained by averaging the four listed methods. In the first generation, the first two reactions starting with the peroxy radical were considered in the kinetic scheme (peroxy radical $\rightarrow$ alkoxy radical $\rightarrow$ MVK/MACR + OH + formaldehyde vdW). Because the energy levels of TS₃, TS₄, and the alkoxy radicals are also very close in the average DFT calculations, the energy of the alkoxy radical intermediate was lowered by 8 kcal/mol in order to achieve a separation of CSEs and IEREs for the entire temperature range under study. As discussed above, the overall rate constant is relatively insensitive to the energy of the alkoxy radical in the steady-state approximation and when tunneling is ignored. The Eckart tunneling factors for all reactions were determined by conducting MESMER calculations on the first reaction only (peroxy radical $\rightarrow$ alkoxy radical) and then incorporated as a multiplicative factor to the steady-state rate constant to give the final overall rate constant.

Figure 5 displays the first-generation temperature-dependent rate constants of the 1,5-H shifts for the (1,2)- and (4,3)-isoprene peroxy radical isomers using the averaging procedure. Several other recent calculations of the first-generation 1,5-H shifts are also displayed. (9,13,15) The error bars represent a ± 1 kcal/mol uncertainty in the barrier height of H transfer, as described in section 3.1. The rate constants at 298 K are 1.1×10^{-3} and $2.4 \times 10^{-3} \text{ s}^{-1}$ for the (1,2)- and (4,3)-isoprene peroxy radicals, respectively, which are approximately a factor of 2 greater than the M06–2X values (see Tables S3 and S4 in the Supporting Information). The values lie between the early and later calculations of Peeters et al.^(9,13) for both isomers and exhibit an enhanced rate for the (4,3)-isoprene peroxy radical. In contrast, the rate constants for both isomers are not that distinguishable in the reported values of Da Silva et al.⁽¹⁵⁾ The effective first-order rate constant of HO₂ addition (assuming 20 and 40 ppt concentrations) to the peroxy radicals are also plotted.⁽⁵³⁾ The 40 ppt of HO₂ represents an upper bound concentration because many recent field campaigns have measured concentrations less than 40 ppt.⁽¹⁶⁾ The 20 ppt of HO₂ represents a more

realistic peak daily concentration of HO₂ that is typically measured in forested or remote areas(16) and is also displayed in Figure 5. The temperature dependence has a slight negative slope because the HO₂ reaction is barrierless. At 298 K and 20 ppt of HO₂, the effective first-order rate constant of HO₂ addition is $8.1 \times 10^{-3} \text{ s}^{-1}$.(53) A crossover of the rate constant plots for the 1,5-H shift and HO₂ addition occurs at 314 and 309 K for the (1,2)- and (4,3)-peroxy radicals, respectively. This implies that in hot climates with significant isoprene emissions, 1,5-H shifts are expected to play a significant role in recycling OH radicals during isoprene oxidation.

Because the rate constant calculations displayed in Figure 5 incorporate two reactions with an intermediate well (alkoxy radical) and the energies of the two barriers (TS₃ and TS₄) and the alkoxy radical possess uncertainties, it is important to assess the relative uncertainties from each step in the reaction coordinate to the overall rate constant. Figure 6 shows several calculations that were conducted by shifting energy levels by 1 kcal/mol for TS₃ (1,5-H shift barrier), the alkoxy radical, and TS₄ (barrier for C–C bond dissociation) for the (1,2)-isoprene peroxy radical isomer. As expected, the largest uncertainty for the overall rate constant is due to the barrier height of the initial 1,5-H shift. An increase or decrease of this barrier by 1 kcal/mol gives rise to a factor of 5–6 decrease or increase in the rate constant, respectively, for the entire temperature range. The relatively large uncertainty is a consequence of the barrier height appearing in an exponential term of the rate constant expression. Interestingly, the second most important factor in the uncertainty is the energy level of the alkoxy radical intermediate. A shift down in the energy of the intermediate by 1 kcal/mol leads to a factor of 2–3 increase in the overall rate because tunneling becomes more significant. The second barrier where the alkoxy radical fragments into formaldehyde and MVK affects the rate constant the least, with an increase of 1 kcal/mol leading to an approximate decrease of 20%. Once again, this final calculation had to be carried out by lowering the alkoxy radical intermediate energy level by 8 kcal/mol in order to achieve viable separation of the CSEs and IEREs while not affecting the overall rate in the steady-state approximation. The decrease in the rate constant in this case is due to the fact that both the forward and reverse reactions of the alkoxy radical intermediate compete to a certain extent. All of these uncertainties illustrate that modeling the entire PES accurately is necessary to obtain reasonable rate constants.

The 1,5-H shifts in second-generation isoprene oxidation chemistry change markedly. Figure 4 has already shown that similar barrier heights to the 1,5-H shifts are encountered in both first- and second-generation 1,5-H shifts. However, the rate constants are approximately 2 orders of magnitude greater for second-generation H shifts, as shown in Figure 7. At 298 K, (1,4)-(HO)₂-(2)-HOO-Isop-(3)-OO• transfers H at a rate of $1.7 \times 10^{-1} \text{ s}^{-1}$, while (1,4)-(HO)₂-(3)-HOO-Isop-(2)-OO• transfers H at a rate of $1.8 \times 10^{-1} \text{ s}^{-1}$. Both rate constants are essentially the same, yet the zero-point energy-corrected barriers as shown in Table 1b differ by 1.1 kcal/mol. A large source of the discrepancy is the fact that the (1,4)-(HO)₂-(2)-HOO-Isop-(3)-OO• H shift has an Eckart tunneling correction factor that is 1.6 times greater than that for (1,4)-(HO)₂-(2)-HOO-Isop-(3)-OO• (see Tables S5 and S6 in the Supporting Information). Most significantly, a reversal of the branching ratio between the 1,5-H shift and the HO₂ addition reaction occurs, although the temperature dependence of the rate constants is not as steep as the first-generation 1,5-H shift. The values from the averaged

barriers agree well with recent calculations and experiments of isoprene oxidation.(23) The trend that has emerged from the calculations shown in Figures 5 and 7 and recent calculations of the 1,6-H shift(9) is that $k_{1,6\text{-H shift}}(1\text{st gen.}) \approx 10k_{1,5\text{-H shift}}(2\text{nd gen.}) \approx 1000k_{1,5\text{-H shift}}(\text{first gen.})$. The approximate factor of 100 difference between first- and second-generation 1,5-H shifts is primarily due to the difference in Eckart tunneling factors. First-generation 1,5-H shifts possess Eckart tunneling factors near unity, while they are 161.5 and 90.0 for the second-generation peroxy radicals at 298 K (see Tables S5 and S6). Peeters et al. also observed similar tunneling factors of 102 and 161 for 1,6-H shifts of two first-generation δ -peroxy radicals that are strongly temperature dependent.(9) In both cases, more stable carbon-centered radicals enable tunneling through the distinct barrier. 1,6-H shifts are faster by an approximate factor of 10 relative to second-generation 1,5-H shifts because the barrier heights are about 1 kcal/mol smaller. This trend may lead to the conclusion that only 1,6-H shifts are significant in early-generation isoprene chemistry, yet this is not what is observed from an analysis of product distributions in experimental studies(58) and ultimately affects HO_x recycling.

3.5. HO_x Recycling in Early-Generation Isoprene Chemistry

Challenges remain in modeling the recycling of HO_x species from the oxidation of biogenic compounds. Given the calculations presented here and recent studies,(10) it is possible to make estimates of HO_x recycling in first- and second-generation isoprene chemistry. Table 2 displays estimations for HO_x recycling from first-generation 1,5- and 1,6-H shifts. The initial distribution of OH adducts has been computed before and favors OH addition to the terminal carbons of isoprene.(10) The isomer-specific fraction of the adducts that participate in the 1,6-H shift has recently been estimated by Teng et al. to be 7% for 1-HO-Isop $^{\bullet}$ and 50% for 4-HO-Isop $^{\bullet}$.(12) Furthermore, they determined the specific yield of HPALD from the 1,6-H shift to be 25%. Given these yields, the final yields of HPALDs are the product of all step yields. The 1,5-H shift yields are subsequently calculated by multiplying the remaining OH adduct distribution that did not proceed via 1,6-H shifts with the isomer-specific branching fraction relative to HO_2 addition assuming a concentration of 20 ppt. The branching fractions are obtained by the fractional ratio of the rate constants for the 1,5-H shifts and HO_2 addition reaction. For 1-HO-Isop $^{\bullet}$ and 2-HO-Isop $^{\bullet}$, the branching fraction is given by $1.1/(1.1 + 8.1) = 12\%$, where the 1,5-H shift rate constant is $1.1 \times 10^{-3} \text{ s}^{-1}$ and the HO_2 addition effective first-order rate constant is $8.1 \times 10^{-3} \text{ s}^{-1}$. The branching fraction is different for 3-HO-Isop $^{\bullet}$ and 4-HO-Isop $^{\bullet}$ because the 1,5-H shift rate constant is $2.4 \times 10^{-3} \text{ s}^{-1}$.

The estimated HO_x recycling efficiency is 16%, with the 1,5-H shift reactions being the main contributor. Notably, the 1,5-H shift yield of 11.5% is the same as the $12 \pm 12\%$ MVK/MACR yield determined by Paulot et al. experimentally.(55) Despite the larger rate constants for 1,6-H shifts, the smaller population of δ -peroxy isomers and the meager specific yield of 25% for HPALD inhibits this pathway from being more prominent. However, all of the values in Table 2 harbor significant uncertainties, which can drive the yields up or down. For example, other HO_x recycling reactions may occur from the estimated 75% of the 1,6-H shift products that do not produce HPALDs.(59) The uncertainty in the HO_x recycling efficiency was estimated here by decreasing or increasing specific

yields or branching fractions by a factor of 2. The 1,5- and 1,6-H shift yields are observed to be anticorrelated: if one pathway is suppressed, the other is enhanced because both pathways are competing for peroxy radicals that are rapidly equilibrating with each other. This procedure gave lower and upper values of 10.6 and 27.8% for HO_x recycling. In the atmosphere, the first-generation HO_x recycling will fluctuate substantially based on the HO_2 concentration and the temperature, as evident in Figure 5. Furthermore, there are also other mechanisms giving rise to MVK and MACR that may recycle HO_x in low NO_x isoprene experiments with nonnegligible yields.(14) It is therefore not surprising that this observable is difficult to quantify.

The HO_x recycling efficiency is more difficult to quantify for second-generation isoprene oxidation chemistry because there are eight Isop-OOH isomers and the yields of higher oxygenated species are uncertain. Once Isop-OOH is formed, further oxidation gives rise to IEPOX and OH at 70–80% yields, with a 13% yield being attributed to non-IEPOX pathways from OH addition.(10) In the case of the latter, O_2 addition followed by isomerization will likely comprise a majority of the products due to the favorable kinetics of second-generation 1,5-H shifts. When both of these reaction yields are combined, second-generation OH recycling likely surpasses 80%. This is not a surprising result because as more oxygen is added to a VOC there are more sites from which to break hydroperoxy groups to release OH or sites from which to abstract labile hydrogens to yield HO_2 . Even the further oxidation of IEPOX will recycle more HO_x species because further OH abstractions at carbon sites lead to (a) peroxy radicals that may carry out additional isomerization reactions leading to OH/ HO_2 release and/or (b) the release of fragmentation products like the hydrogenated formaldehyde radical, which reacts with O_2 to yield HO_2 .(60) By considering these additional pathways that recycle HO_x , it may be possible to account for recent experimental results suggesting a larger than expected atmospheric oxidizing capacity in isoprene-rich environments.(61) These results may help to close the modeling gap that typically underestimates HO_x concentrations in pristine environments.

4. Conclusions

A computational protocol was implemented to obtain the PESs of atmospherically relevant chemical reactions involving isoprene. This computational approach has been previously used to successfully study the reaction of methacryloylperoxynitrate (MPAN) with the hydroxyl radical.(62) The NEB method has the advantage that it can identify the transition states and wells along the reaction energy profile and explicitly see which transition states are connected to which wells. The IDM not only has the advantage of requiring knowledge of the gradient (and not the Hessian) but it is well-suited for optimizing transition states in which the transition state is a complex such as we have in this study. The combination of the M06–2X exchange–correlation functional with the maug-cc-pVTZ basis set provided a very good estimate for the rate constants and branching ratio of OH addition to isoprene. However, it gave rise to low 1,5-H transfer rates, particularly in the second-generation oxidation chemistry. Consequently, several DFT methods were averaged to conclusively show that first-generation 1,5-H shifts are relevant and play an important role in recycling OH. 1,5-H shifts in later-generation chemistry that abstract at carbon sites bonded to hydroxy groups are more readily accessible because tunneling becomes pertinent and makes

the H transfers able to proceed more rapidly than HO₂ additions to peroxy radicals. Because of this, later-generation isoprene chemistry is responsible for recycling HO_x species to a considerable extent after enough sites have been oxidized. The results impact our understanding of HO_x recycling and PM growth due to the production of HOMs and may be used to improve atmospheric air quality models.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Zero-point energy-corrected M06-2X/maug-cc-pVTZ PESs of (a) OH addition to isoprene at carbon sites 1 and 4 and (b) OH addition to the dominant β -hydroxy-hydroperoxy-isoprene isomer.

Figure 2. Structures of the vdW complexes for (a) isoprene +OH addition and (b) β -(1,2)-HO-Isop-OOH+OH addition reaction. Interatomic distances are shown in Angstroms (green text).

Figure 3.
PES of isoprene oxidation leading to *anti*-MVK (blue)/MACR (red). The barrier for the 1,5-H shift is TS₃.

Figure 4. Reaction barriers for second-generation 1,5-H shifts in two different Isop(OH)₂-(OOH)-OO• isomers computed using M06-2x/maug-cc-pVTZ.

Figure 5.

Temperature-dependent plots of the 1,5-H shift rate constant for (a) (1,2)-HO-Isop-OO• and (b) (4,3)-HO-Isop-OO•. The error bars represent a ± 1 kcal/mol uncertainty in the barrier height of the H transfer. Recent calculations by Peeters et al. in 2014,(9) da Silva et al. in 2010,(15) and Peeters et al. in 2009(13) are also displayed along with the effective first-order rate constant of HO₂ addition assuming 20 and 40 ppt concentrations.(58)

Figure 6.

Uncertainty calculations for the temperature-dependent 1,5-H shift rate constants for (1,2)-HO-Isop-OO*. Relative to the base calculation, the H shift barrier and alkoxy intermediate were lowered by 1 kcal/mol and increased by 1 kcal/mol, the intermediate was lowered by 1 kcal/mol only, and two sequential reactions were considered (1,5-H shift and C–C bond dissociation) where the alkoxy intermediate was lowered by 8 kcal/mol and the C–C bond dissociation barrier was increased by 1 kcal/mol (see the text).

Figure 7. Temperature-dependent plots of the 1,5-H shift rate constant for (a) (1,4)-(HO)₂-(2)-HOO-Isop-(3)-OO• and (b) (1,4)-(HO)₂-(3)-HOO-Isop-(2)-OO•. The error bars represent a ± 1 kcal/mol uncertainty in the barrier height of the H transfer. The effective first-order rate constants of HO₂ addition assuming that 20 and 40 ppt concentrations are also included.(58)

Scheme 1.

First-Generation Isoprene Peroxy Radical Reactions in Low NO_x Conditions: (a) HO_2 Addition, (b) 1,5-H Shift^a, and (c) 1,6-H Shift^a

^aMVK denotes methyl vinyl ketone and HPALD denotes hydroperoxy aldehyde. Reactions (b) and (c) regenerate HO_x species.

Scheme 2.

Second-Generation Isoprene Peroxy Radical Reactions in Low NO_x Conditions: (a) HO₂ Addition and (b) 1,5-H Shift Producing a Carbon-Centered Radical Leading to Several HOMs^a

^aAll 1,5-H shifts may recycle either OH or HO₂.

Scheme 3.

Reaction Scheme for the Generation of MVK and MACR in the Anti Geometry from the Oxidation of Isoprene^a

^aThe 1,5-H shift occurs in the fifth step in both mechanisms.

Table 1.

Zero-Point-Corrected Reaction Barriers and Energies for Two Different (a) First- and (b) Second-Generation 1,5-H Shift Reactions of Isoprene-Derived Peroxy Radicals Using Several Computational Methods^a

a)

1st Generation:

Method	$\Delta E_{\text{ZPE}}^{\ddagger}$ (kcal/mol)	ΔE_{RXN} (kcal/mol)	$\Delta E_{\text{ZPE}}^{\ddagger}$ (kcal/mol)	ΔE_{RXN} (kcal/mol)
M06-2X	21.3	20.9	20.4	19.9
MN15	19.7	19.7	19.0	18.7
wB97X-D	21.0	21.1	20.5	20.2
CBS-QB3	21.2	20.2	20.5	19.5
Average:	20.8	20.5	20.1	19.6

b)

2nd Generation:

Method	$\Delta E_{\text{ZPE}}^{\ddagger}$ (kcal/mol)	ΔE_{RXN} (kcal/mol)	$\Delta E_{\text{ZPE}}^{\ddagger}$ (kcal/mol)	ΔE_{RXN} (kcal/mol)
M06-2X	21.7	7.7	19.8	9.5
MN15	19.9	5.8	18.4	8.1
wB97X-D	20.8	9.8	20.4	11.7
CBS-QB3	19.4	8.1	19.0	9.7
Average:	20.5	7.9	19.4	9.8

^aThe average of the methods is indicated and was used in subsequent rate constant calculations.

Table 2.Yields from First-Generation Reactions of Isoprene with OH that Recycle HO_x

Reactions					Total Yield	
OH addition ^a	67.0%	2.0%	2.0%	29.0%	100.0%	
1,6-H shift ^b	4.7%	-	-	14.5%	19.2%	
HPALD formation ^c	1.2%	-	-	3.6%	4.8%	<-- HO ₂ recycling
1,5-H shift ^d	7.5%	0.2%	0.5%	3.3%	11.5%	<-- OH recycling
Total HO_x recycling:					16.3%	

^a OH addition yields are given in Wennberg et al.(10)^b 1,6-H shift yields are a product of the OH addition yield and 7 and 50% for the C1 and C4 isomers, respectively.(12)^c HPALD formation yields are a product of the 1,6-H shift yield and the 25% specific HPALD yield from the 1,6-H shift reaction.(12)^d 1,5-H shift yields are a product of the difference between the OH addition and 1,6-H shift yields and the branching fraction between the 1,5-H shift reaction and HO₂ addition reaction assuming a concentration of 20 ppt. The branching fraction for isomers 1 and 2 is 1.1/(1.1 + 8.1) = 12.0%, and the branching fraction for isomers 3 and 4 is 2.4/(2.4 + 8.1) = 22.9%