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Barrierless Reactions with Loose Transition States Govern the Yields and Lifetimes of Organic Nitrates Derived from Isoprene

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Abstract

The chemical reaction mechanism of NO addition to two β and δ isoprene hydroxy-peroxy radical isomers is examined in detail using density functional theory, coupled cluster methods and the energy resolved master equation formalism to provide estimates of rate constants and organic nitrate yields. At the M06–2x/aug-cc-pVTZ level, the potential energy surfaces of NO reacting with β -(1,2)-HO-IsopOO $\cdot$ and δ -Z-(1,4)-HO-IsopOO $\cdot$ possess barrierless reactions that produce alkoxy radicals/NO₂ and organic nitrates. The nudged elastic band method was used to discover a loosely bound van der Waals (vdW) complex between NO₂ and the alkoxy radical that is present in both exit reaction channels. Semi-empirical master equation calculations show that the β organic nitrate yield is $8.5 \pm 3.7\%$. Additionally, a relatively low barrier to C-C bond scission was discovered in the β -vdW complex that leads to direct HONO formation in the gas phase with a yield of $3.1 \pm 1.3\%$. The δ isomer produces a looser vdW complex with a smaller dissociation barrier and a larger isomerization barrier giving a $2.4 \pm 0.8\%$ organic nitrate yield that is relatively pressure and temperature insensitive. By considering all these pathways, the first generation NO_x recycling efficiency from isoprene organic nitrates is estimated to be 21% and is expected to increase with decreasing NO_x concentration.

Graphical abstract

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Associated Content

Supporting Information

DFT and NEB calculation details, sensitivity study of kinetic model using MESMER

Introduction

The high temperature oxidation of atmospheric nitrogen from fossil fuel and biomass combustion leads to the production of reactive nitrogen oxide radicals ($\text{NO}_x = \text{NO} + \text{NO}_2$). NO_2 is an EPA designated criteria pollutant that not only exerts detrimental health effects¹ but also gives rise to the production of other criteria pollutants. NO_2 radicals may photolyze in the atmosphere to produce oxygen atoms which combine with oxygen molecules to produce ozone while ozone may react with NO to regenerate NO_2 thereby giving rise to a photochemical cycle. The photochemical cycle is affected by the presence of volatile organic compounds (VOCs) because oxidized organic peroxy radicals may convert NO to NO_2 without consuming ozone.² The imbalance in the cycle therefore generates excess ozone concentrations via NO_2 photolysis. Furthermore, volatile organic species are converted to semi-volatile and low volatility species that may condense on aerosol particles to form secondary organic aerosol (SOA); another tropospheric pollutant.³

However, not all oxidation processes follow this scheme in that some NO reacts with organic peroxy radicals to form organic nitrates also referred to as organonitrates (RONO_2).⁴⁻⁶ This pathway avoids O_3 production although it still yields semivolatile compounds that may contribute to SOA mass where they may be hydrolyzed to produce nitric acid.⁷ Alternatively, organic nitrates may be further oxidized and release NO_x back to the atmosphere. Therefore, organic nitrates serve as a temporary or permanent NO_x sink depending on the relative branching between pathways that recycle NO_x (oxidation and photolysis) and pathways that sequester NO_x (aerosol uptake/hydrolysis, dry and wet deposition) respectively.⁶ As a temporary sink, organic nitrates may harbor NO_x long enough for it to be released in more rural settings where it can react with local emissions.⁸ As NO_x levels have declined over the last several decades,⁹ their loss to organic nitrate formation becomes increasingly important in affecting NO_x lifetimes.⁵ In order to model atmospheric chemistry for regulatory purposes, it is essential to determine all the factors that affect the production, lifetime and fate of this important class of compounds.

Early experimental and computational studies of organic nitrate formation have revealed pressure, temperature and molecular size dependencies.¹⁰⁻¹¹ The pressure and molecular size dependencies have been attributed to the reactivity of vibrationally excited peroxy nitrates (ROONO^*) that were produced subsequent to NO addition to the peroxy radical via an exergonic reaction that releases ~ 20 kcal/mol of energy.¹² Larger peroxy nitrates and higher pressures favor intra- and intermolecular vibrational relaxations respectively that steer the product distribution towards organic nitrates. The temperature dependence has been attributed to the thermal decomposition of the ROONO^* intermediate although the transition states have not been fully characterized.¹³ These reactions are also sensitive to the location of functional groups near the peroxy radical site.¹¹ The presence of a hydroxyl group adjacent to the peroxy radical decreases the yield of organic nitrates by a factor of two.¹⁴ Local interactions therefore modulate organic nitrate reaction kinetics, and it is therefore crucial to scrutinize reactions of different VOC precursors separately and in detail to capture all the relevant chemistry.

Of all the VOCs emitted into the atmosphere, isoprene (2-methyl-1,3-butadiene) is the second most abundant after methane (by the number of molecules emitted)^{15–16} and is highly reactive to OH oxidation. At emission levels of 600 Tg/year,¹⁶ even minor product channels of isoprene oxidation may exert major effects on atmospheric free radical populations and pollutant concentrations. The reactivity of isoprene is due to the presence of two double bonds that are susceptible to attack from atmospheric oxidants such as OH, O₃ and NO₃. Its reaction with OH is particularly fast with a rate constant¹⁰ of $\sim 1.0 \times 10^{-10}$ cm³·molecule⁻¹·s⁻¹ giving rise to a ~ 3 -hour lifetime assuming an atmospheric OH concentration of 10⁶ molecules·cm⁻³. The reaction mechanism quickly bifurcates beyond the first OH addition and each pathway exhibits different susceptibilities to organic nitrate formation.

The hydroxyl radical may attack isoprene by adding at four different sites as shown in Scheme 1. The distribution of hydroxy-isoprene intermediates¹⁷ is correlated with the stability of the radicals generated. 1-HO-Isop· (where the OH added to the first carbon) is the most stable because the radical is both tertiary and allylic, 4-HO-Isop· is secondary and allylic, and 2-HO-Isop·/3-HO-Isop· are the least stable because the radicals are primary and thus represent minor products. Oxygen immediately adds to the carbon-centered radical and gives rise to eight different hydroxy-peroxy isoprene intermediates: four β isomers where the hydroxy and peroxy groups are on neighboring carbons and four δ isomers where the functional groups are separated by four carbons. This addition is reversible¹⁸ even though the equilibrium at 298 K is shifted far towards the peroxy isomers. Interestingly, the reverse reaction where O₂ dissociates exceeds bimolecular rates involving peroxy radical reactions with NO and HO₂ at atmospheric concentrations.¹⁹ This is a direct result of the allylic stabilization afforded to the carbon centered radicals of 1-HO-Isop· and 4-HO-Isop· which lower the barrier to O₂ dissociation. Consequently, the distribution of hydroxy-peroxy isoprene radicals shown in Scheme 1 is governed by the relative thermodynamic stability of the intermediates. Teng *et al.* recently showed that this overwhelmingly favors the β isomers ($\sim 95\%$) under atmospheric conditions and demonstrate their importance in driving the subsequent chemistry.¹⁹ The δ isomers are not completely inconsequential if reactions exist that quickly siphon off the δ peroxy radicals relative to the β isomers. Peeters *et al.* have suggested that intramolecular H atom shifts play an important role in propagating the oxidation of δ hydroxy-peroxy isoprene isomers in low NO_x environments due to a low barrier of abstraction.¹⁸

The final distribution of peroxy radicals shown in Scheme 1 provides the framework for resolving later generation product yields derived from the β and δ isomers. This is significant considering that numerous laboratory and field studies have reported a relatively large range of isoprene organic nitrate yields (4–15%).^{20–27} An even larger range of $< 5\% - > 50\%$ has been reported for the NO_x recycling efficiency defined here as the difference between the molar percentage of NO_x that is released versus consumed in the subsequent reactions of RONO₂.^{25, 28} Recent modeling studies have inferred that ozone estimates are keenly sensitive to the NO_x recycling efficiency.^{29–30} Further studies have revealed how intricate this chemistry is given that stark differences in organic nitrate yields have been reported for the β and δ isomers.²⁵ Differences have also been observed to occur in the subsequent chemistry of the isomers. Recent laboratory experiments on several synthesized

isoprene organic nitrates have revealed OH reaction rate constants of $4.2 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ and $1.1 \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ for the β and δ isomers respectively.³¹

In this work, the reactivity of β and δ isomers in high NO_x environments is delineated using computational chemistry methods to understand the nature of their diverging chemical behavior. Because computational chemistry is not hampered by resolution or detection limits, it is ideally suited to investigate all facets of organic nitrate chemistry provided that suitable levels of theory are applied. For example, Butkovskaya *et al.* used density functional theory (DFT) methods to compute the potential energy surface for the reaction of butylperoxy radicals with NO and used a collisional model to explain organic nitrate formation.³² Other computational studies invoking density functional methods and the master equation formalism to describe the vibrationally excited peroxyxynitrite intermediates of isoprene have not identified transition state structures for the exit channels.^{12–13} Without the structures and energies serving as constraints in solving the master equation, they simply become adjustable parameters that may be varied in fitting experimental data. The difficulty in locating these barriers is attributed to the flat nature of the potential energy surface (PES) in this region. To alleviate this challenge, a nudged elastic band (NEB) method was employed³³ to characterize the entire reaction pathway. The stationary and transition states observed in the PES served as input for higher-level calculations. The method was used to identify a vibrationally excited van der Waals (vdW) complex³⁴ between NO_2 and an alkoxy radical that serves as a crucial intermediate prior to the dissociation or isomerization of isoprene peroxyxynitrites. In addition, a loose transition state bridging the vdW complex and RONO_2 reaction pathway was discovered for β and δ hydroxy-peroxy isoprene isomers. Identification of these states enabled the quantification of RONO_2 reaction yields as will be discussed below.

Theoretical Methods

Electronic structure calculations were conducted with the Gaussian 09 electronic structure program.³⁵ Density functional theory (DFT) was almost exclusively employed in molecular geometry optimizations and energy calculations. Only in a few of the cases was the coupled cluster method (CCSD(T)) used to compute a disputed barrier based on structures optimized with DFT methods, and this will be highlighted in the next section. For the DFT calculations, the M06–2x hybrid generalized gradient approximation (GGA) functional was coupled with several basis sets. This functional has been shown to be reliable in computing energies, barrier heights and noncovalent interactions.³⁶ It has also been used recently to explore the PES of related isoprene hydroxy-hydroperoxide reactions.³⁷

Spin unrestricted density functional theory was invoked for all optimizations of stationary and transition states that involved separated radicals such as the van der Waals complex involving NO_2 --- alkoxy radical (vdW₂). Unrestricted density functional theory is an efficient method for describing open shell singlet systems.³⁸ Dibble has also indicated that using spin-restricted wavefunctions for this chemical system may lead to artifacts in the energy calculations.³⁹ However, unrestricted methods introduce spin contamination into the results because α and β electrons are treated separately and the solutions are not

eigenfunctions of the total spin-squared operator (S^2). Despite this, it has been relatively successful in DFT applications and was adopted here.⁴⁰

In a preliminary exploration of the PES of peroxy-NO reactions, the nudged elastic band (NEB) method was employed at the M06-2x/6-311++G** level of theory. This intermediate basis set was found to be large enough to capture important reaction dynamics.⁴¹ The NEB method requires optimized structures for reactants and products (i.e. the ends of the ‘elastic band’) and an initial set of structures or images that interpolate between these limits. The method then conducts a constrained optimization minimizing the NEB force acting on the images to locate the minimum energy path. The NEB force consists of spring forces between neighboring images on the reaction coordinate and the projected perpendicular component of the force on the evolving molecular complex. G09 is used to compute the NEB forces in an algorithm⁴² that determines the minimum energy pathway.^{33, 43} The NEB method was particularly useful for identifying all peroxy-isoprene + NO reaction intermediates and barriers. In the preliminary analysis, all NEB calculations were carried out until the energy gradient was less than 0.0025 Hartrees/Bohr. The reaction intermediates and transition states found on the minimum energy path were then used as starting points in refined calculations at the M06-2x/aug-cc-pVTZ level. Default convergence criteria within the Gaussian program were used to determine convergence and vibrational frequency calculations were used to verify the nature of stationary and transition states. Details of the structural optimizations and vibrational frequency calculations are provided in the Supporting Information.

The electronic structure calculations served as input for kinetic rate calculations using the Master Equation Solver for Multi-Energy well Reactions (MESMER v. 4.0).⁴⁴ Master equation approaches have been invoked in recent years to describe nonequilibrium chemical kinetics for a wide range of chemical reactions including combustion, solution phase and atmospheric chemistry. Recent accounts have detailed the construction and solution of the energy grained master equation.^{45–46} Here, we only briefly highlight the essential facets as a way of describing all input parameters that were used in our kinetic model.

The master equation is constructed to describe the time evolution of the rovibrational population density $p_m(E)$ for every isomer m on the potential energy surface. The independent variable for the system is the total rovibrational energy (E), and its inclusion is a consequence of energy fluctuations due to molecular collisions with the bath gas as well as chemical reactions that absorb or release energy. The master equation with the energy expressed as a continuous variable is given by,

$$\begin{aligned} \frac{dp_m(E)}{dt} = & \omega \int_{E_{0m}}^{\infty} P(E|E') p_m(E') dE' - \omega p_m(E) + \sum_{n \neq m}^M k_{mn}(E) p_n(E) - \\ & \sum_{n \neq m}^M k_{nm}(E) p_m(E) - k_{sm}(E) p_m(E) + K_{Rm}^{eq} k_{Rm}(E) \frac{\rho_m(E) e^{-\beta E}}{Q_m(\beta)} n_A p_B - k_{Rm}(E) p_m(E) \end{aligned} \quad (1)$$

Three positive terms on the right hand side correspond to flux into $p_m(E)$ while four negative terms correspond to flux out of $p_m(E)$. The first term represents population gain in $p_m(E)$ via collisional energy transfer at the Lennard-Jones collision frequency (ω) with $P(E|E')$ representing the probability that the collision with bath gas will result in an energy transition from grain E' to grain E for isomer m . The second opposing term represents loss from $p_m(E)$ due to collisions. The third and fourth terms signify gain and loss for $p_m(E)$ due to reactions transferring population from and to isomer n respectively at constant energy E . $k_{nm}(E)$ denotes the microcanonical rate coefficients for population transfer between isomers n and m . Irreversible loss from $p_m(E)$ to products S is characterized by the fifth term. The last two terms describe the bimolecular source term and are applicable when isomer states are populated via bimolecular association reactions. Because the number of states in polyatomic molecules is immense, it is necessary to simplify the phase space by bundling similar energies into grains. For all kinetic calculations described below, a relatively small grainsize of 20 cm^{-1} was selected. By discretizing equation 1 with the application of energy grains, it may be cast in matrix form that is diagonalized to yield a small set of chemically significant eigenvalues (CSEs) and a vast set of internal energy relaxation eigenvalues (IEREs).⁴⁷ The CSEs correspond to experimentally measurable phenomenological rate constants although in some cases they may approach the energy relaxation timescale where direct correspondence is no longer valid.

MESMER takes as input all molecular complex structures (including transition states and bath gas), ground state energies, vibrational frequencies and rotational constants. These data are used by MESMER to compute the energy dependent microcanonical rate constants for all forward and reverse reactions on the PES. For all reactions with well-defined transition states, RRKM theory⁴⁸ was implemented to compute the rate constants. However, two reactions on the PES were barrierless: the entrance channel reaction involving $\text{IsopOO}\cdot + \text{NO}$ to produce the peroxyxynitrite and the exit channel reaction involving the dissociation of a vdW complex involving NO_2 and $\text{IsopO}\cdot$ into separate species. In these cases, MESMER offers the option of computing the $k(E)$ s using an inverse Laplace transform (ILT) technique. The $k(E)$ s may be calculated by using Arrhenius parameters from a fit of the temperature dependent high pressure rate coefficients for association, dissociation and isomerization. Alternatively, a semi-empirical method using the Arrhenius parameters may be used in MESMER to fit phenomenological rate constants that are consistent with experimentally measured rates.³⁷ In this work, the entrance channel Arrhenius pre-exponential factor (A) was set to $3.5 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ for the β isomer and $1.0 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ for the δ isomer so that the MESMER calculations would closely match the experimental rate constant for the $\text{IsopOO}\cdot + \text{NO}$ reaction rate ($8.8 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$).⁴⁹ The exit channel pre-exponential factor was set to $7.6 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ for both $\text{IsopOO}\cdot$ isomers which reflects the association rate of NO_2 with the methoxy radical.⁵⁰

Several other master equation parameters need to be set before launching MESMER calculations. The collision frequency in equation 1 is determined by Lennard-Jones parameters that are provided for the bath gas and all reactive intermediates to take into account pressure dependent energy fluctuations (terms 1 and 2 in equation 1). In this work, N_2 was used as the bath gas with $\epsilon = 91.85 \text{ K}$ and $\sigma = 3.92 \text{ \AA}$.⁵¹ All reactive intermediates were assumed to have the same Lennard-Jones parameters as hexane (a C6 compound

similar in size to isoprene adducts) with $\epsilon = 289.2$ K and $\sigma = 4.37$ Å.⁵² Additionally, an exponential down transition probability model is implemented by MESMER to account for the $P(E|E')$ factor in equation 1.

$$P(E|E') = A(E') \exp(-(E' - E)/\langle \Delta E \rangle_d) \quad (2)$$

In this expression $E' > E$, $A(E')$ is a normalization constant and $\langle E \rangle_d$ is the average energy transferred per collision in the downward direction. Upward transition probabilities are obtained by detailed balance. $\langle E \rangle_d$ values typically range between 100 – 300 cm⁻¹. Barker et al. fitted an average energy transfer parameter of 25 cm⁻¹ for pentyl nitrate yields from NO_x reactions.⁵³ The authors stated that this was likely an unrealistically low value. For this work, a value of 150 cm⁻¹ was selected although sensitivity studies were conducted to see how this value and the parameters mentioned above affect the MESMER results and are detailed in the Supporting Information. The maximum deviation of the variability in the product yields from the sensitivity studies were used as an estimate of the error in the kinetic model.

Once all of the model parameters were input into MESMER, it was used to compute the time dependent species profiles for all products produced including isoprene organic nitrates. The output of the kinetics calculations ultimately provided the temperature and pressure dependent yields of several isoprene organic nitrates and revealed the structural parameters that influence their yields.

Results and Discussion

(I) Isoprene Organic Nitrate Yields

An initial attempt to understand the details of the potential energy surface of hydroxy-peroxy isoprene species reacting with NO was made using the NEB technique which maps a minimum energy pathway for a reaction given optimized reactant and product species. Figure 1 displays two different NEB pathways that start with the reaction of NO with the β -(1,2)-HO-IsopOO· isomer and lead to either the alkoxy radical + NO₂ or the organic nitrate. Both pathways start with the formation of a vdW complex between the two radicals that are held together by a weak hydrogen bond and van der Waals forces, which precedes a very small submerged barrier that leads to the peroxyxynitrite adduct (ROONO). The reaction is exothermic with a large release of energy giving rise to a vibrationally excited peroxyxynitrite species. The pressure dependence of organic nitrate formation is understood to be a function of the internal energy contained in the peroxyxynitrite species.¹² Early investigations of the subsequent reaction of peroxyxynitrites to form organic nitrates led to unreasonably high barriers by assuming that the *trans* conformer of peroxyxynitrite breaks and forms the O-O and O-N bonds respectively in a concerted process.⁵⁴ This has led investigators to conclude that NO₂ initially dissociates from the peroxyxynitrite when it is in the *cis* geometry before the NO₂ twists around to form the O-N bond of the organic nitrate in a two-step process.⁵⁵ The latter stage of both NEB trajectories in Figure 1 show that the dissociation step is common to both alkoxy radical and organic nitrate production. A ~20 kcal/mol barrier to O-O bond dissociation is encountered which then forms a stabilized vdW intermediate where the NO₂

interacts with the alkoxy radical at a distance of 2.64 Å. Significantly, this species is common to both trajectories and its identification here helps to rationalize the behavior of excited peroxyxynitrites as will be discussed below.

At this stage, the vdW complex may fragment completely using 4.2 kcal/mol of energy to generate the alkoxy radical and NO₂ or the NO₂ may rotate so that the nitrogen faces the alkoxy radical to produce the organic nitrate with a concomitant release of energy as discussed by Butkovskaya *et al.*³² The latter process possesses a minute barrier relative to complete vdW dissociation. This is consistent with the results of Zhang and coworkers,¹³ which have indicated that the barrier to organic nitrate formation must be less than alkoxy radical production in order to observe increased alkoxy radical production at higher temperatures. The PES of Figure 1 is also consistent with the conformer dependent PES of HOONO rearrangement by Zhao *et al.*⁵⁵ The NEB trajectories therefore seem to capture most of the relevant energetics and were used as starting points in more demanding DFT calculations.

Figure 2 displays the PES of NO + β -(1,2)-HO-IsopOO· at the M062x/aug-cc-pVTZ level of theory. Both *cis* and *trans* conformers relative to the central O-N bond in the –OONO moiety were included in the calculations. The NO may form two vdW complexes in either the *cis* or *trans* arrangement that will lead to the two peroxyxynitrite intermediates. A large barrier for NO₂ dissociation was observed for the *trans* conformer where the transition state (TS₃) structure contained the NO₂ fragment with an intrinsic bond angle of 119.7°. In contrast, the bond angle of NO₂ in TS₄ upon the dissociation of the *cis* conformer is 127.8°. The former bond angle is closer to the ²B₂ excited state of NO₂ (101°) while the latter is closer to the ²A₁ ground state of NO₂ (134°).⁵⁵ Consequently, the high TS₃ barrier is effectively insurmountable so that it does not contribute to organic nitrate formation and the *trans* conformer readily converts to the *cis* conformer before overcoming a much smaller barrier (TS₄).

A stable vdW complex (vdW₂) was identified with an intermolecular distance of 2.67 Å between the alkoxy radical and NO₂. It lies 8.5 kcal/mol higher in energy than the *cis*-peroxyxynitrite intermediate although it is 13.1 kcal/mol more stable than the starting reactant species and still harbors some excess vibrational energy that affects the exit channel branching ratios as will be quantified in the kinetic calculations below. A similar barrier height of ~18 kcal/mol was computed for HOONO – the simplest peroxyxynitrite species although a significantly less stable vdW species (by ~5 kcal/mol) was found using the UCCSD(T)/6–31+G*//UCCSD/6–31+G* method.⁵⁵ Butkovskaya *et al.* identified a vdW adduct for the reaction of HO₂ with NO and found a transition state that links it to HNO₃.³⁸ In more recent work, Butkovskaya *et al.* suggested that a weakly bound adduct leads to both the formation of NO₂ and butyl nitrate although the structure was not optimized.³² The identification of the vdW complex and the transition state leading to the organic nitrate in this study permits the quantification of the isoprene organic nitrate yield because the product distribution is acutely sensitive to the vdW energy relative to the barriers leading to NO₂ and RONO₂.

Interestingly, Figure 2 displays three exit channel reactions: (1) alkoxy radical + NO₂, (2) organic nitrate and (3) a vdW complex involving methyl vinyl ketone, hydrogenated formaldehyde radical and NO₂. We believe that the latter pathway has not been considered in conventional reaction mechanisms involving isoprene and NO_x. Barker *et al.*⁵³ and Lohr *et al.*⁵⁶ have discussed the formation of HONO albeit from the direct decomposition of organic nitrates and concluded that the pathway is not important due to high barriers. The alternative pathway was included here because the barrier to C₁–C₂ bond scission in vdW₂ was only 3.2 kcal/mol. The NO₂ in the vdW₂ complex plays somewhat of a stabilizing role for TS₆ because without it the barrier was 1.4 kcal/mol higher using the NEB method at the M06–2x/6–311++G** level. In essence, this step occurs after the NO₂ has departed from the alkoxy radical, but the calculations here show that to a certain extent it may occur before. The barrier to NO₂ reorientation to form the β-organic nitrate is only 0.4 kcal/mol, and complete vdW₂ dissociation requires 4.2 kcal/mol.

The mechanistic sequence is depicted in Scheme 2. The reaction scheme also displays the subsequent reactions of channels 1 and 3. Channel 1 produces the expected methyl vinyl ketone from β-(1,2)-HO-IsopO· decomposition and also yields the hydrogenated formaldehyde radical that immediately reacts with O₂ to produce formaldehyde and HO₂. Similarly, vdW₃ also produces methyl vinyl ketone after C–C bond scission but because the vdW complex has not fragmented, the hydrogenated formaldehyde radical immediately reacts with the NO₂ radical in a barrierless radical recombination reaction to produce HONO (see Figure S1 in Supporting Information). At the M06–2x/aug-cc-pVDZ level, the reaction releases 52 kcal/mol of energy and is irreversible. This new source of HONO may at least partly explain recent studies that have not been able to account for larger than expected HONO measurements.^{57–58} This mechanism may also conceivably occur for other unsaturated VOCs in NO_x environments where a carbon-carbon double bond is effectively broken to yield two carbonyls and the attacking hydroxyl radical effectively combines with NO.

The optimized structures of all exit channel species are shown in Figure 3. The dissociation of vdW₂ to the alkoxy radical and NO₂ in channel 1 is barrierless and as such no definitive structure for the transition state was identified. Variational transition state theory⁵⁹ may be implemented in this case to find the dividing position between reactant and product species that minimizes the dissociation rate constant. The transition state will necessarily involve a loose complex with a relatively large intermolecular distance > 2.67 Å. The transition state for organic nitrate formation in channel 2 also involves loose intermolecular interactions between NO₂ and the alkoxy radical with an intermolecular distance of 2.62 Å. In TS₅, NO₂ rotates about the axis generally defined by the two oxygens in NO₂ before it forms the O–N bond to produce an organic nitrate. It is these loose interactions that crucially determine the branching ratio between all exit channels. Other local interactions such as the neighboring hydrogen bond also play a vital role in affecting the exit channel rates. The hydrogen bond is also present in vdW₃ and helps to hold the complex together during the dissociation of the C₁–C₂ bond. The feasibility of HONO production may be seen in the structure of vdW₃ which contains a weak hydrogen bond between two radicals: NO₂ and hydrogenated formaldehyde. A barrierless biradical reaction where the hydrogen atom transfers to NO₂ gives rise to stable closed shell species and a concomitant release of 52 kcal/mol of energy.

The differences in the three reaction paths shown in Figure 3 are stark, each with different implications on atmospheric free radical and pollutant concentrations. All three channels produce oxygenated carbon species. The organic nitrate is largest in size and contains nitrogen and oxygen atoms that polarize the molecule making it less volatile than methyl vinyl ketone (from channels 1 and 3). This makes it more likely to give rise to species that condense onto aerosol particles, which is a regulated tropospheric pollutant. However, methacrolein and methyl vinyl ketone are produced in much larger quantities in NO_x environments from the two dominant β -peroxy isoprene isomers (see Scheme 1) although further oxidation gives rise to species such as methyl glyoxal which can participate in aqueous phase aerosol chemistry.⁶⁰ Each pathway also converts NO into three different species: NO_2 , organic nitrate and HONO. NO_2 may photolyze in the atmosphere and produce ozone, another regulated tropospheric pollutant and oxidant. Organic nitrate at least temporarily sequesters the NO_x some of which ends up in the particle phase and may be hydrolyzed to yield nitric acid.⁶¹ Further gas phase oxidation of the organic nitrate may either retain or release NO_2 . The branching ratio of these pathways is of considerable interest because the extent of NO_x recycling affects ozone estimates in atmospheric models, and its value is highly uncertain.

A number of studies have suggested that the β and δ hydroxy-peroxy isoprene isomers exhibit distinctly different organic nitrate yields. Giacomelli *et al.* determined that the δ isomer yields are favored over the β isomers by a factor of 2.6.¹⁴ They argued that this factor consists of two distinct components. The first component comes from the fact that alkane derived organic nitrates have a factor of 2 higher yield than alkenes.¹¹ O'Brien *et al.* concluded that organic nitrates are produced in lower yields for the β isomers because the neighboring hydrogen bond weakens the O-O bond by 8–9 kJ/mol and this leads to the alkoxy radical instead.¹¹ However, the computed pathway shown in Scheme 2 disputes this notion because the O-O bond has to break for the organic nitrate to form as well. The second component derives from the fact that adding atoms (in this case –OH) relative to an alkane with the same number of carbon atoms increases the organic nitrate yield by a factor of 1.3 because the internal energy present in the preceding peroxy intermediate may dissipate more readily with a larger number of vibrational modes. This component however should be present for both β and δ isomers and should therefore not be applied to the δ isomers only. Paulot *et al.*²⁵ also reported that the δ isoprene organic nitrates were ~3.5 times more favorable than the β isomers using Carter's parametrization⁶² and the factor of 2 from O'Brien *et al.*¹¹ Of considerable interest and one of the motivating factors of this inquiry is rationalizing the different reactivity of isoprene isomers based on molecular structure and dynamics because the insight may possibly extend to other volatile organic compounds emitted in the atmosphere.

The uncertainty in the relative branching ratio and the causes for it were investigated here by computing the PES for the δ -Z-(1,4)-HO-IsopOO· isomer. Figure 4 displays the detailed PES for the δ -Z-(1,4)-HO-IsopOO· + NO reaction. It should be noted that the zero-point corrected energy of δ -Z-(1,4)-HO-IsopOO· is calculated to be 1.8 kcal/mol greater than β -(1,2)-HO-IsopOO·. This is consistent with the expected thermodynamic distribution of IsopOO· isomers, which heavily favors the β isomers.¹⁹ The PES of δ -Z-(1,4)-HO-IsopOO· + NO looks very similar to the β isomer with subtle but important differences. Once again,

essentially barrierless reactions of NO addition to the peroxy radical precede the formation of the peroxyxynitrite intermediates. Both *cis* and *trans* conformers may interconvert although only the *cis* conformer has a low enough barrier to produce alkoxy radicals or organic nitrates. The TS₅ energy relative to vdW₂ is larger for the δ -Z isomer than the β isomer while the dissociation energy for vdW₂ is less. The results suggest that the organic nitrate yield for the δ -Z isomer may be less than the β isomer in direct contrast to recent studies. Another major difference is that there is no path to HONO production for the δ -Z isomer because any single C-C bond dissociation along the backbone would produce an unstable alkenyl radical. The predicted reaction scheme is summarized in Scheme 3.

In order to confirm the supposition that the δ -Z isomer has a smaller organonitrate yield relative to the β isomer, kinetic calculations using MESMER were employed. Initial master equation modeling using the PESs shown in Figures 2 and 4 for the two peroxy isomers exhibited no temperature or pressure dependence for the organic nitrate yields. Given that numerous experimental and computational studies of this reaction have shown temperature and pressure sensitivities, a careful inspection of the PESs was warranted. One of the possible reasons for the pressure and temperature insensitivity is that TS₄ is too large in both PESs and would require that most of the internal energy of the excited peroxyxynitrite intermediate be expended in surmounting TS₄ thereby rendering vdW₂ unexcited. However, vdW₂ needs to be vibrationally excited in order to observe a pressure and temperature dependence because that is where the chemical mechanism branches off into the three exit channels. Further evidence that the calculated TS₄ barrier may be too high is provided by Arenas *et al.*⁶³ who applied second order multiconfigurational perturbation theory (CASPT2) to the dissociation of methylperoxy nitrite and observed no exit barrier even though DFT methods predicted an extra energy exit barrier greater than 10 kcal/mol. As a first rudimentary approximation to multiconfigurational interactions, we applied the coupled cluster CCSD(T) method using the maug-cc-pVTZ basis set to DFT derived structures and observed that the TS₄ barriers were indeed lowered although only by 1.2 kcal/mol for each isomer. The T1 diagnostic⁶⁴ was computed to be 0.037 using the CCSD method for TS₄ which also confirmed that multireference electron correlation procedures are necessary to properly describe O-O bond dissociation in organic peroxyxynitrites. For the purposes of kinetic modeling, TS₄ was lowered by 5.2 kcal/mol so that it was equivalent to the alkoxy radical + NO₂ exit channel energy. The adjusted PES for the β isomer is shown in Figure 5. This sole adjustment immediately gave rise to pressure and temperature dependent organic nitrate yields for the β isomer.

Figure 6 displays the computed microcanonical rate constants ($k(E)$) for the formation of vdW₂, IsopO₂ + NO₂, organic nitrate and vdW₃ for β -(1,2)-HO-IsopOONO dissociation. The formation of the peroxyxynitrite gives rise to an excited Boltzmann distribution that is schematically illustrated in the figure. The dissociation of the peroxyxynitrite to yield vdW₂ (yellow curve) has rates that are more than an order of magnitude slower than the atmospheric collision rate. This implies that some of the excited internal energy of the peroxyxynitrite will be expended in atmospheric collisions before producing vdW₂. All of the energy is not lost, however, because that would imply that the organic nitrate yields would become comparable or greater than alkoxy radical yields in the low energy limit where there is a crossover of the microcanonical rate constants. Based on typical reported organic nitrate

yields for isoprene and an assumed pressure dependence, Figure 6 suggests that vdW_2 still has $\sim 10\text{--}15$ kcal/mol of excess energy. Under such circumstances, the application of the energy grained master equation approach is essential because canonical transition state theory cannot account for nonequilibrium reaction kinetics.

Figures 7a and b encapsulate the reaction dynamics of β -(1,2)-HO-IsopOO $\cdot$ and δ -Z-(1,4)-HO-IsopOO $\cdot$. Three sets of curves each computed at three different temperatures are present in Figure 7a depicting the product yields of the three exit channels for the β isomer. A pressure dependence is observed to occur for pressures greater than 100 torr. At 1 atm, the organic nitrate yield is $8.5 \pm 3.7\%$ at 298 K and increases with increasing pressure as expected given the low barrier to organic nitrate formation relative to vdW_2 dissociation. The organic nitrate yield also decreases with increasing temperature because at higher temperatures, the vdW_2 complex is less stable and more susceptible to dissociation. This yield is virtually identical to measurements obtained during the recent SOAS field campaign.²⁷ The computed pressure dependence also closely tracks several independent experimental studies. At 100, 445 and 745 torr the isoprene organic yields were measured to be 7, 8 and 13% by Patchen *et al.*,²³ Sprengnether *et al.*²² and Teng *et al.*¹⁹ respectively. The computed values at the same pressures are 6.0, 7.5 and 8.5% respectively (see Figure 7a). The master equation calculations therefore do not predict as strong a pressure dependence to the organic nitrate yield with a plateau being reached at pressures greater than 10,000 torr.

Surprisingly, a $3.1 \pm 1.3\%$ yield of vdW_3 was observed at 1 atm indicating that this channel should not be ignored in reaction mechanisms. The yield likely represents an upper bound for HONO production via first generation isoprene/ NO_x chemistry because vdW_3 may dissociate before HONO is produced by hydrogen atom transfer. However, the binding energy of vdW_3 is 9.6 kcal/mol at the M062x/aug-cc-pVDZ level of theory which is large enough to inhibit dissociation before barrierless hydrogen atom transfer occurs to produce HONO. The yield does not exhibit a large pressure or temperature variation under atmospheric conditions of interest. The error estimates provided for all yields were determined by conducting sensitivity studies on uncertain parameters within the kinetics calculations (see Supporting Information).

Figure 7b presents the results of the kinetic simulations for the δ -Z isomer. Even with a lowered TS_4 barrier, the organic nitrate yield is not pressure or temperature dependent. The organic nitrate yield is calculated to be $2.4 \pm 0.8\%$ at 1 atm. It appears that having a smaller dissociation energy and a larger isomerization barrier overwhelmingly lead to large alkoxy radical yields that are insensitive to the energy state of vdW_2 complex. In this limit, the microcanonical exit channel rate constants do not vary with energy to a great extent. As mentioned above, these results seemingly contradict predictions of elevated δ organic nitrate yields. One plausible explanation is that different geometric isomers (δ -Z vs. δ -E) exhibit diverging reaction dynamics whereby the yield of δ -E organic nitrates is considerably larger than for the δ -Z isomer. The source of this divergence is likely the proximity of the hydroxyl group to the alkoxy radical. As shown in Figure 8, the distances between the hydroxyl and alkoxy groups for β -(1,2)-HO-IsopO $\cdot$ and δ -Z-(1,4)-HO-IsopO $\cdot$ in vdW_2 are 2.45 Å and 2.24 Å respectively while it is 5.53 Å for δ -E-(1,4)-HO-IsopO $\cdot$. The hydroxyl group may possibly act as a tether via a hydrogen bond to NO_2 thereby preventing it from reorienting to form the

organic nitrate in the cases of the β and δ -Z isomers. While this may partly be the case for the β isomer where the H---O intermolecular hydrogen bond distance is 2.35 Å, it is less likely for the δ -Z isomer where the intermolecular distance is 2.95 Å. Another more likely possibility is that the hydroxyl group may hydrogen bond with the alkoxy radical for the β and δ -Z isomers and thereby shield it from attack by NO₂. This seems to explain why the yields for the δ -Z isomer were so low because its structure has a relatively strong intramolecular hydrogen bond which renders the NO₂ more labile.

The divergent reaction dynamics for the δ -E and δ -Z geometric isomers were captured by the M06-2x functional, and the exit channel PESs are shown in Figure 9. Even though the isomerization barriers leading to organic nitrates are small (< 1.0 kcal/mol), the computational results predict that the δ -E isomer should produce more organic nitrate because it has a smaller isomerization barrier and a larger vdW₂ dissociation energy. Kinetics calculations confirm this albeit with a modified PES for δ -E-(1,4)-HO-IsopOO $\cdot$. Although a detailed calculation of the entire PES for the δ -E isomer was not undertaken here, the segment of the PES shown in Figure 9 was combined with the NO addition reaction to δ -Z-(1,4)-HO-IsopOO $\cdot$ in a MESMER calculation. It is assumed that the NO addition kinetics do not affect the branching ratio of the exit channels which are determined primarily by the energetics of the exit channels. Under this approximation, the organic nitrate yield for δ -E-(1,4)-HO-IsopOO $\cdot$ was $19.4 \pm 6.4\%$. This yield is approximately a factor of two larger than the β isomer yield, which one would expect to occur if a similar sized alkane was being oxidized.¹¹ In this instance, δ -E-(1,4)-HO-IsopOO $\cdot$ is effectively behaving like an alkane because the hydroxyl group is structurally prohibited from closely interacting with the alkoxy radical like it can in the β and δ -Z isomers. Local interactions therefore play a crucial role in affecting the loose transition states observed in isoprene/NO_x chemistry.

(II) Isoprene Organic Nitrate Lifetimes

First generation yields from NO_x reactions represent a significant step to modeling their impact on air quality. However, subsequent reactions of organic nitrates (chemical or photochemical) and physical processes (aerosol adsorption, deposition) continue to affect NO_x, ozone and particulate matter concentrations. The relative importance of each of the processes continue to be debated, and it is therefore important to look at each process in detail separately. In this section, the reactivity of OH with organic nitrates is examined to determine all of the relevant pathways and rates.

Recently, the rate constants of OH with several isoprene derived organic nitrates were experimentally measured by Lee *et al.*³¹ The δ -E and -Z organic nitrate isomers had OH rate constants of 1.1×10^{-10} cm³·molecule⁻¹·s⁻¹ while a β isomer had a rate constant of 4.2×10^{-11} cm³·molecule⁻¹·s⁻¹. This would give rise to organic nitrate lifetimes of 2.5 and 6.6 hours respectively. OH may specifically react with organic nitrates via addition to any present double bonds or it may extract labile hydrogen atoms. In the case of isoprene, the rate of addition far exceeds the abstraction of hydrogens from either the methyl group or the olefin sites. The branching ratio changes upon oxidation because the α hydrogen atoms at the hydroxyl site are more susceptible to extraction while a subsequent addition becomes less favorable if the radical produced is not stabilized by resonance or the presence of

electron donating groups. Furthermore, the effect of multiple functional groups on the branching between addition and abstraction reactions for different isomers is an important topic of interest.

In order to explore OH addition versus abstraction pathways for isoprene derived organic nitrates, it was necessary to initially compute the barriers of OH addition to the δ -Z and β isomers so that the results may be compared with the experimentally measured rates for validation purposes. Figures 10a and b display the energetics of OH addition to δ -Z-(1,4)-HO-IsopONO₂ and β -(1,2)-HO-IsopONO₂ respectively. A hydrogen bonded vdW complex initially forms in both cases between the OH and organic nitrate with over 5 kcal/mol stabilization energy. Each complex then passes over a small barrier that is still lower in energy relative to the reactants before forming the adduct.

The vdW complexes and TSs for these reactions are within approximately 1 kcal/mol of each other. While errors in DFT calculations may exceed this value (as in the ~5 kcal/mol of excess barrier energy computed for the O-O dissociation of the β isoprene peroxyxynitrite discussed above), the reactions shown in Figure 10 involve similar reactants and products, and any errors in the DFT calculations are likely to be systematic in nature rendering comparisons more reliable. Furthermore, the computed PESs of the OH reactions are expected to have errors significantly smaller than 5 kcal/mol.⁶⁵ A kinetic analysis using the above PESs will therefore provide an estimate of the relative importance of the addition versus abstraction OH reaction pathways for isoprene organic nitrates.

The barrierless addition displayed in Figures 10a and b may be kinetically analyzed by dividing the reaction into two elementary steps: (1) reversible formation of the vdW complex and (2) irreversible C-O bond formation in the vdW complex to form the adduct. These steps may be described by three elementary rate constants: k_1 for vdW formation from reactants, k_{-1} for vdW dissociation back to reactants and k_2 for vdW conversion to the adduct. A steady state kinetic analysis of the overall process produces an overall rate constant $k_{total} = k_1 k_2 / (k_{-1} + k_2)$.⁶⁶ This canonical description of OH reactions is markedly different from the microcanonical rate constants computed to account for the peroxyxynitrite chemistry conveyed in the previous section. In the latter case, the peroxyxynitrite intermediate and vdW complex possess lots of internal energy (10 – 20 kcal/mol) before confronting essentially barrierless exit channels which warrant the use of the energy grained master equation formalism. On the other hand, the OH addition/abstraction reactions initially lead to a relatively shallow well with a vdW complex that is not too distant from thermal equilibrium. The total canonical rate constant may then be computed using a combination of variational and standard transition state theory (TST) for k_1 and k_2 respectively.

Further approximations to the total canonical rate constant may be made in order to compare the three reactions shown in Figure 10. k_{total} is not that sensitive to the depth of the vdW complex because to a first approximation both k_{-1} and k_2 are similarly scaled and these effects cancel in the factor $k_2 / (k_{-1} + k_2)$. The total rate is mostly sensitive to the energy of the transition state (TS), and the ratio of the rate constants for the reactions in Figures 10a and b was computed by assuming that the energy difference between the TSs account for the majority of the difference in rates. In this limit, the computed ratio of the rate constants is

simply the Boltzmann factor involving the energy difference between the TSs. A value of 2.3 is obtained for an energy difference of 0.5 kcal/mol at 298 K in favor of the δ -Z isomer with a range of 1.0 – 5.4 for an error of ± 0.5 kcal/mol in the barrier height. The experimental value derived from the rate constants measured by Lee *et al.* is 2.6.³¹ It should be noted that the β isomer computed here is the predominant (1,2) isomer while the experiments were carried out with the β -(4,3) organic nitrate. The difference in rates between these isomers is not known although if the exit barrier TS correlates with the stability of the radical products, then the OH addition rate constant would be expected to be larger for the (4,3) isomer because a tertiary carbon centered radical is produced.

Because the computational rate constant ratio method worked well in predicting an experimentally measured OH rate constant ratio, it was used to predict the ratio of the rates of OH addition and abstraction for β -(1,2)-HO-IsopONO₂. Figure 10c displays the PES of the OH hydrogen atom abstraction from β -(1,2)-HO-IsopONO₂ at the hydroxyl site (α carbon). The exit channel TS is 0.7 kcal/mol higher for the abstraction reaction which gives a rate constant ratio of 3.2 in favor of addition with a range of 1.4 – 7.6 for an error of ± 0.5 kcal/mol in the barrier height. The abstraction pathway is therefore not negligible here and plays a relatively larger role in the oxidation chemistry than is thought to occur in low NO_x oxidation pathways.³⁷ If the total OH reaction rate constant for the β organic nitrate is measured to be $4.2 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, then the calculated ratio gives an abstraction rate constant of $1.0 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ and an addition rate constant of $3.2 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$. These values are shown in Scheme 4. The prevalence of the abstraction pathway opens the door for other subsequent chemistry to occur which affects the NO_x recycling efficiency and the production of ozone.

(III) NO_x Recycling Efficiency

Current atmospheric modeling studies of NO_x environments frequently cite the uncertainty of the NO_x recycling efficiency as one of the major obstacles for accurately predicting ozone concentrations.²⁹ The NO_x recycling efficiency is defined here as the number of moles of NO_x recycled minus the number of moles of NO consumed for a given set of reactions.^{25, 31} NO_x may be recycled from organic compounds that have already incorporated it (such as aliphatic or peroxyacyl nitrates) via reactions with atmospheric oxidants. The focus here is on OH reactions with isoprene derived organic nitrates because it potentially leads to substantial recycling of the NO_x that was originally sequestered. Because β -(1,2)-HO-IsopONO₂ is by far the dominant organic nitrate isomer produced, its chemistry was explored in detail.

As deduced in the previous section, OH addition and abstraction reactions may affect the release of NO_x from organic nitrates. OH addition is the major channel that leads to the formation of an alkoxy-organic nitrate in a NO_x environment. Specifically, OH initially adds to the remaining double bond in β -(1,2)-HO-IsopONO₂, followed by O₂ and NO addition which then releases NO₂ and the alkoxy-organic nitrate as the major product. This alkoxy-organic nitrate may fragment at two sites (C₂–C₃ or C₃–C₄) to yield stable products and smaller radicals. The reaction scheme and energetics are displayed in Figure 11. The data clearly show that the dominant products result from C₃–C₄ scission. This is significant given

that the major product of the oxidation of β -(1,2)-HO-IsopONO₂, is a methacrolein based organic nitrate that retains NO_x. In this case, NO_x may then be transported further from its source before it is released or adsorbed onto aerosol particles. These results agree with the recent study by Lee *et al.* who indicated that an analogous methyl vinyl ketone nitrate compound is the primary product of the oxidation of β -(4,3)-HO-IsopONO₂.³¹

The oxidation chemistry of β -(1,2)-HO-IsopONO₂ is summarized in Scheme 5. It has an 8.5% yield after NO addition to the corresponding peroxy radical. It may react further via OH addition or hydrogen atom abstraction with 77 and 23 % yields respectively based on the computed ratio of the rate constants (see Scheme 4). The carbon centered radicals generated in both channels may expel NO₂ and produce two different epoxides: an isoprene derived epoxy-diol (IEPOX)⁶⁷ and an unsaturated epoxy-ol.³⁷ Elrod and coworkers have determined the yield to be 16% for IEPOX⁷ and this value was also assumed for the unsaturated epoxy-ol. In a NO_x environment, the remaining carbon centered radicals react with O₂ and NO to yield either dinitrates or the fragmentation products. The dinitrate yields in each channel were assumed to be double the original organic nitrate yield. This is reasonable given that the organic nitrate alkoxy radical --- NO₂ vdW complex has more atoms than the original alkoxy radical --- NO₂ vdW complex and therefore possesses more vibrational modes to dissipate excess internal energy to favorably yield dinitrates. The fragmentation of the alkoxy radicals predominantly yields the methacrolein based organic nitrate in the addition channel and produces methyl vinyl ketone in the abstraction channel. The latter channel also provides an early generation source of formic acid that has been observed in experimental chamber experiments.²⁵

All of the yields expressed in green font in Scheme 5 recycle NO_x from β -(1,2)-HO-IsopONO₂ while the red font denotes pathways where NO is consumed. The large yield of the methacrolein based organic nitrate (grey font) is neutral with regards to NO_x recycling because NO_x is both consumed and released in the form of NO and NO₂ respectively. The NO_x recycling efficiency as determined from Scheme 5 is 21%. This value is lower than that reported by Paulot *et al.* (45%)²⁵ while greater than the value determined by Lee *et al.* (−8%).³¹ The former study did not take into account the production of dinitrates for this isomer, which exerts a large negative contribution to the NO_x recycling efficiency. The latter study did not include the positive contribution from isoprene epoxides.⁷ The NO_x recycling efficiency is expected to be dependent on the concentration of NO. This effect may manifest itself during the transport of first generation organic nitrates to areas with low NO concentrations. Instead of producing alkoxy organic nitrate radicals and dinitrates in high NO_x environments, peroxy radicals will produce nitrated hydroperoxides via reaction with HO₂ and/or nitrated aldehydes/alcohols via reaction with other organic peroxy radicals or intramolecular rearrangements.¹⁸ The lack of dinitrate formation drives the NO_x recycling efficiency higher. All of these reactions and transport effects are crucial to understand in order to model the atmosphere more accurately for regulatory purposes.

Conclusions

NO_x is a significant air pollutant that may give rise to other pollutants via a complex chain of chemical reactions. The reaction of NO with peroxy radicals is one of the pillars of

atmospheric chemistry because it describes the evolution of NO_x. In this work, the reaction of NO with several isoprene derived peroxy radicals was investigated in detail using a combination of DFT methods and kinetic modeling. The results have shown that organic nitrate yields are sensitive to local interactions because structural and geometric isomers possess different reaction dynamics. The yields of β -(1,2)-HO-IsopONO₂, δ -Z-(1,4)-HO-IsopONO₂ and δ -E-(1,4)-HO-IsopONO₂ were 8.5%, 2.9% and 19.4% respectively and depend on the absence or presence of a neighboring hydrogen bond between a hydroxyl group and the alkoxy radical. An unexpected pathway to HONO production was discovered for the NO_x reaction with β -(1,2)-HO-IsopOO· giving rise to a non-negligible yield of 3.1%. The lifetime of β -(1,2)-HO-IsopONO₂ (the predominant isoprene derived organic nitrate) is affected by OH addition and abstraction mechanistic pathways. The rate of OH addition to β -(1,2)-HO-IsopONO₂ was estimated to be $3.2 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ while the rate was $1.0 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ for OH hydrogen atom abstraction. By considering all these pathways, the first generation NO_x recycling efficiency from isoprene organic nitrates was found to be 21% and is expected to increase with decreasing NO_x concentration.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Potential energy surface (PES) for the addition of NO to the β -(1,2)-HO-IsopOO $\cdot$ isomer. Two different trajectories with 47 total images (structures) were computed using the nudged elastic band (NEB) method at the M06-2x/6-311++G** level. Two dominant products arise: alkoxy radicals + NO₂ and an organic nitrate.

Figure 2.
Zero-point energy corrected PES for the addition of NO to the β -(1,2)-HO-IsopOO $\cdot$ isomer computed at the M06-2x/aug-cc-pVTZ level.

Figure 3. Optimized stationary and transition states for all exit channel reactions involving the β -(1,2)-HO-IsopO $\cdot$ --- NO $_2$ vdW complex.

Figure 4.
Zero-point energy corrected PES for the addition of NO to the δ -Z-(1,4)-HO-IsopOO· isomer computed at the M06-2x/aug-cc-pVTZ level.

Figure 5. Revised PES for the dissociation of the β -(1,2)-HO-*cis*-IsopOONO intermediate. TS_4 was lowered to be equivalent to the alkoxy radical + NO_2 dissociation products in order to achieve pressure dependent rate constants in the kinetic modeling (see text).

Figure 6. Microcanonical rate constants for the formation of vdW_2 (β -(1,2)-HO-IsopO $\cdot$ --- NO_2), IsopO $\cdot$ + NO_2 , β -(1,2)-HO-IsopONO $_2$ (organic nitrate) and vdW_3 (MVK --- HC $\cdot$ HOH --- NO_2). A schematic Boltzmann distribution of the excited β -(1,2)-HO-cis-IsopOONO population is given along with the atmospheric collision rate for reference.

Figure 7.

Temperature and pressure dependent product yields for all exit channels for (a) β -(1,2)-HO-IsopOO· + NO and (b) δ -Z-(1,4)-HO-IsopOO· + NO.

Figure 8.

Optimized structures for three different vdW alkoxy radical/NO $_2$ isomeric complexes derived from isoprene. A weak internal hydrogen bond between the hydroxyl and alkoxy groups is present only in the β -(1,2)-HO-IsopO $\cdot$ --- NO $_2$ and δ -Z-(1,4)-HO-IsopO $\cdot$ --- NO $_2$ complexes.

Figure 9.
Zero-point energy corrected PES of the exit channels for two δ vdW complexes: δ -E-(1,4)-HO-IsopO $\cdot$ --- NO $_2$ and δ -Z-(1,4)-HO-IsopO $\cdot$ --- NO $_2$.

Figure 10. Zero-point energy corrected PESs of (a) OH addition to δ -Z-(1,4)-HO-IsopONO₂, (b) OH addition to β -(1,2)-HO-IsopONO₂ and (c) OH abstraction of β -(1,2)-HO-IsopONO₂.

Figure 11. PES profile of the fate of an alkoxy-organic nitrate produced from OH/O₂/NO addition to β -(1,2)-HO-IsopONO₂. Dissociation of the C₃-C₄ bond is preferable and leads to the retention of NO_x.

Scheme 1. Reaction scheme for the addition of $\cdot\text{OH}$ followed by O_2 to isoprene with relative yields.

Scheme 2. Reaction scheme for the addition of NO to β -(1,2)-HO-IsopOO $\cdot$.

Scheme 3.

Reaction scheme for the addition of NO to $\delta\text{-Z-(1,4)-HO-IsopOO}\cdot$.

(a) δ -Z-(1,4)-HO-IsopONO₂ + $\cdot$ OH addition **(b) β -(1,2)-HO-IsopONO₂ + $\cdot$ OH addition** **(c) β -(1,2)-HO-IsopONO₂ + $\cdot$ OH abstraction** **Scheme 4.**

Experimental¹⁹ and calculated rate constants for OH addition and abstraction reactions with two organic nitrates: δ -Z-(1,4)-HO-IsopONO₂ and β -(1,2)-HO-IsopONO₂.

Scheme 5.

Reaction scheme showing the yields and fate of the prominent β -(1,2)-HO-IsopONO₂ organic nitrate. The green yields denote pathways that recycle NO_x, red pathways signify the consumption of NO_x and the grey yield is neutral in that the original NO is retained although another one was consumed to produce the methacrolein derived organic nitrate.