Isomerization of the Isoprene Hydroxy Nitrates and Formation of Orthonitrite Compounds

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Submitted date: 25/06/2019 • Posted date: 26/06/2019

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Citation information: da Silva, Gabriel (2019): Isomerization of the Isoprene Hydroxy Nitrates and Formation of Orthonitrite Compounds. ChemRxiv. Preprint.

Atmospheric oxidation of isoprene produces significant yields of eight unique nitrate 11 compounds, each with a β - or δ -hydroxy group. These isoprene hydroxy nitrates (ISOPNs) 12 significantly impact upon global NO_x budgets, O₃ levels, and aerosol formation. 13 Uncertainties exist, however, in our understanding of ISOPN chemistry, particularly in their 14 yields from the reaction of isoprene peroxy radicals with NO. This study describes novel 15 isomerization reactions of the ISOPNs, identified through the application of computational 16 chemistry techniques. These reactions produce saturated polycyclic orthonitrite compounds 17 via attack of the R-NO₂ group on the vinyl moiety. For the δ -hydroxy nitrates, low-energy 18 isomerization pathways exist to six-membered ring compounds that are around 5 kcal mol⁻¹ 19 exothermic. These reactions proceed with barriers around 15 kcal mol⁻¹ below the 20 respective peroxy radical + NO reactants and yield orthonitrites that can further isomerize 21 to β -hydroxy ISOPNs. Moreover, the δ -hydroxy nitrates can directly interconvert with their β 22 substituted counterparts via NO₃ group migration, with barriers that are lower yet. It follows 23 that β -hydroxy nitrates may be stabilized in the δ -hydroxy form, and vice versa. Moreover, 24 the lowest-energy pathway for dissociation of the δ -hydroxy ISOPNs is for the formation of 25 β -hydroxy alkoxy radicals, and because of this established branching fractions between the 26 various isoprene peroxy radicals may require re-evaluation. The results presented here also 27 suggest that ISOPNs may be stabilized to some extent in their saturated orthonitrite forms, 28 which has implications for both the total nitrate yield and for their subsequent removal by 29 OH, O₃, and photolysis.

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ABSTRACT

Atmospheric oxidation of isoprene produces significant yields of eight unique nitrate compounds, each with a β - or δ -hydroxy group. These isoprene hydroxy nitrates (ISOPNs) significantly impact upon global NO_x budgets, O_3 levels, and aerosol formation. Uncertainties exist, however, in our understanding of ISOPN chemistry, particularly in their yields from the reaction of isoprene peroxy radicals with NO . This study describes novel isomerization reactions of the ISOPNs, identified through the application of computational chemistry techniques. These reactions produce saturated polycyclic orthonitrite compounds via attack of the R-NO_2 group on the vinyl moiety. For the δ -hydroxy nitrates, low-energy isomerization pathways exist to six-membered ring compounds that are around 5 kcal mol^{-1} exothermic. These reactions proceed with barriers around 15 kcal mol^{-1} below the respective peroxy radical + NO reactants and yield orthonitrites that can further isomerize to β -hydroxy ISOPNs. Moreover, the δ -hydroxy nitrates can directly interconvert with their β substituted counterparts via NO_3 group migration, with barriers that are lower yet. It follows that β -hydroxy nitrates may be stabilized in the δ -hydroxy form, and *vice versa*. Moreover, the lowest-energy pathway for dissociation of the δ -hydroxy ISOPNs is for the formation of β -hydroxy alkoxy radicals, and because of this established branching fractions between the various isoprene peroxy radicals may require re-evaluation. The results presented here also suggest that ISOPNs may be stabilized to some extent in their saturated orthonitrite forms, which has implications for both the total nitrate yield and for their subsequent removal by OH , O_3 , and photolysis.

Introduction

Isoprene hydroxy nitrates (ISOPNs) are produced globally in large quantities through the photochemical oxidation of isoprene. These compounds primarily arise from the sequential addition of $\cdot\text{OH}$ and O_2 to isoprene to produce the isoprene peroxy radicals, which then react with NO to yield stabilized ISOPNs along with the dominant products: isoprene alkoxy radicals + NO_2 .¹ Isoprene is the second most emitted hydrocarbon to Earth's atmosphere² and because of this ISOPNs represent significant NO_x reservoirs as well as chain-terminating free radical sinks.³⁻⁶ Branching between nitrate stabilization vs. chemically activated fragmentation to alkoxy radicals is a key parameter in atmospheric chemical mechanisms, and has been studied extensively for isoprene.⁷ Likewise, the photochemical degradation of ISOPNs is also important, and key atmospheric sinks such as the reaction with OH have been widely investigated.⁸

Despite being intensively studied, there remain significant uncertainties in our understanding of ISOPN chemistry. Total isoprene nitrate yields from peroxy radical + NO chemistry have recently been estimated at 9 %, with uncertainties placing it in the 6 to 14 % range.⁷ Earlier studies report total ISOPN yields anywhere from 4 to 14 %.^{3,4,9-12} When considering the individual ISOPN isomers – of which there are eight – Paulot et al.³ estimated yields of 6.7 % for those with β -hydroxy functionality compared to 24 % for those with δ -hydroxy groups. The source of this variability remains unclear. Furthermore, theoretical attempts to model even the simplest peroxy radical + NO reactions have proven difficult, due to uncertainties involved in the initial peroxy nitrite to nitrate rearrangement, and difficulties in modelling the collisional deactivation of the resultant nitrate vs. fragmentation.¹³⁻¹⁵

In order to gain further insight into the stabilization and fragmentation reactions of the ISOPN isomers, this study investigates their isomerization and decomposition pathways using computational chemistry techniques. Pathways are revealed for isomerization of the isoprene hydroxy nitrates to orthonitrite compounds, as well as for the direct interconversion of select hydroxy nitrates, all proceeding with barriers below the conventional reaction pathways. The chemistry revealed here provides new forms of the ISOPNs that may be collisionally stabilized and also opens up new pathways for the interconversion and decomposition of chemically activated peroxy radical + NO intermediates.

Methods

Stationary points and product sets on the $\text{C}_5\text{O}_4\text{NH}_9$ potential energy surface were optimized at the M06-2X/6-31G(2df,p) level of theory. All structures were confirmed to be stationary points possessing no imaginary frequencies (for minima) or one imaginary frequency corresponding to motion along the reaction coordinate (for transition states). Furthermore,

intrinsic reaction coordinate scans were used to verify transition state connectivity. For instances where multiple conformations exist, both for minima and transition states, only the most stable one is reported. High-level energies were subsequently obtained at the G3X-K level of theory,¹⁶ which uses M06-2X/6-31G(2df,p) structures in a series of single-point wave function theory energy calculations from HF theory through to CCSD(T), with basis sets of incrementally decreasing size. Final G3X-K energies also incorporate an empirical scaling factor, and are expected to be accurate to within around 0.7 kcal mol⁻¹ for barrier height calculations. All reported calculations were carried out within the Gaussian 09 program suite.¹⁷ Coordinates for optimized structures are reported as Supporting Information.

Results and Discussion

There exist eight unique ISOPN isomers that can form from the addition of NO to the isoprene peroxy radicals. These isomers are illustrated in Figure 1, where the naming convention adopted in this study is also introduced. Four ISOPN isomers feature β -OH substituents, with the vinyl group either α (1,2-ISOPN and 4,3-ISOPN) or γ (2,1-ISOPN and 3,4-ISOPN) to the nitrate group. The former arise from “external” OH addition in isoprene whereas the latter arise from “internal” OH addition. The remaining four ISOPN isomers all possess δ -OH substituents, and differ only in position of the methyl group and orientation about the double bond (*i.e.*, *E* or *Z*).

The 1,2-ISOPN and 4,3-ISOPN isomers are formed from what are thought to be the dominant isoprene peroxy radicals,³ and are identical but for placement of the methyl group. Although the yields of these nitrates are relatively low, the importance of their parent peroxy radicals makes them significant ISOPNs. The four δ -OH ISOPNs arise from isoprene peroxy radicals that are predicted to form in lower yields, but account for a significant fraction of the total isoprene nitrates due to their higher individual nitrate yields.³ Finally, the 2,1- and 3,4-ISOPN isomers are the least significant, as they form at low yields from minor (internal OH addition) isoprene peroxy radicals.

This study reveals that all eight ISOPNs can isomerize to polycyclic ring compounds via attack of the R-NO₂ group on the vinyl moiety. The resultant compounds possess an orthonitrite structure, and are referred to here as the isoprene orthonitrites (IONs). Orthonitrites are stable yet little-studied compounds,¹⁸ named after the hypothetical substance sodium orthonitrite, Na₃NO₃.¹⁹ Structures for the IONs are shown in Figure 2, with the transition states leading to their formation depicted in Figure 3. For the ISOPNs in which the nitrate group is located β to the vinyl group, the IONs possess a bridged six-membered ring structure (ION 1 – 4). For the ISOPNs with the nitrate group γ to the vinyl group, the IONs demonstrate a bridged seven-membered ring structure.

Table 1 lists standard enthalpies of formation and entropies for the IONs and ISOPNs, calculated at the G3X-K level of theory. Firstly, we see no major differences between the enthalpies and entropies of the ISOPN isomers. The six-membered IONs (1 – 4) all exhibit enthalpies that are lower than the ISOPNs; on average, they are more stable by *ca.* 4 kcal mol⁻¹. However, these IONs are also consistently lower in entropy, due to loss of internal rotors. The aggregate effect is for these IONs to be lower than the ISOPNs in free energy by around 1 kcal mol⁻¹. The seven-membered IONs (5 – 8) are less-stable than the other orthonitrites by around 3 kcal mol⁻¹ in terms of enthalpy. Accordingly, they are approximately isoenthalpic with the ISOPNs, and are on average about 2 kcal mol⁻¹ higher in terms of free energy.

Theoretical energy diagrams illustrating how the ISOPNs isomerize to the IONs are shown in Figures 4 – 6 and S1 – S5, and are discussed below. These diagrams also include the barrierless dissociation channel to the corresponding alkoxy radical + NO₂, as well as the energy of the peroxy radical (+ NO) from which the ISOPNs are produced.

Figure 4 provides an energy diagram for 1,2-ISOPN. The corresponding diagram for 4,3-ISOPN is included as Figure S1 of the Supporting Information. Formation of 1,2-ISOPN from the RO₂ + NO reaction is around 50 kcal mol⁻¹ exothermic. Dissociation to the RO + NO₂ channel proceeds with a barrier of 41 kcal mol⁻¹ and no adiabatic transition state, placing it 8 kcal mol⁻¹ below the entrance channel energy (11 kcal mol⁻¹ for 4,3-ISOPN). As a result, the dominant fate of chemically activated 1,2-ISOPN produced at around standard temperature and pressure is for dissociation to RO + NO₂, although some collisional deactivation of the nitrate adduct is known to take place. As shown in Figure 4, 1,2-ISOPN can isomerize to two orthonitrite compounds, ION-1 and ION-2, which are stereoisomers of each other. These compounds sit below the isoprene nitrate that they originate from in both enthalpy and free energy, and would therefore dominate the C₅O₄NH₉ population if they were allowed to equilibrate. Indeed, respective equilibrium constants for forming ION-1 and ION-2 from 1,2-ISOPN are 17.6 and 4.3 at 298 K (the values for 4,3-ISOPN yielding ION-3 and ION-4 are 86.2 and 4.9).

The barrier heights for isomerization of 1,2-ISOPN to ION-1 and ION-2 are both 35 kcal mol⁻¹, which is over 14 kcal mol⁻¹ below the forming RO₂ + NO energy, and lower than the RO + NO₂ exit channel by more than 6 kcal mol⁻¹ (energetics for the related 4,3-ISOPN isomer are similar, only with slightly higher isomerization barriers). Given the favorable thermodynamics for ION formation, as well as the relatively low isomerization barriers, we hypothesize that the orthonitrite forms will contribute at least some of the stabilized RO₂ + NO adduct yield in the atmosphere for the major external OH addition β -OH peroxy radicals.

There exist four δ -OH peroxy radicals produced from OH, O₂ addition to isoprene, which lead to the *E* and *Z* forms of 1,4-ISOPN and 4,1-ISOPN. Energy diagrams for 1,4-(*E*)-ISOPN and 1,4-(*Z*)-ISOPN are shown in Figures 5 and 6, with the corresponding 4,1-(*E/Z*)-ISOPN

149 diagrams included as Figures S2 and S3. ISOPN formation from the δ -OH peroxy radicals is
150 around 52 – 54 kcal mol⁻¹ exothermic, with dissociation of the ISOPNs to RO + NO₂ requiring
151 around 43 kcal mol⁻¹. The chemically activated RO₂ + NO → RO + NO₂ process therefore
152 occurs with a barrier that is around 10 kcal mol⁻¹ below the reactants. The energetics are
153 similar to the peroxy radical reactions discussed above, and no strong argument could be
154 made for the higher yields observed experimentally. Again, the δ -OH ISOPNs can isomerize
155 to orthonitrites, with barriers of around 35 – 38 kcal mol⁻¹, and these species are predicted
156 to be thermodynamically favoured over the nitrates (298 K equilibrium constants in the
157 range of 0.5 – 173).

158 For the internal addition β -OH ISOPNs (2,1- and 3,4-ISOPN), where the nitrate group is
159 located γ to the vinyl moiety, the available isoprene nitrite isomers (ION-5 through ION-8)
160 are structurally different from those discussed above, and are consistently higher in energy.
161 The energy diagrams for isomerization of these minor ISOPNs are provided as Figures S4 and
162 S5. In both instances the energetics of ISOPN formation via RO₂ + NO and dissociation to RO
163 + NO₂ are similar to the other peroxy radicals, with the isoprene nitrates formed with
164 around 54 kcal mol⁻¹ of excess vibrational energy, and at around 10 kcal mol⁻¹ above the
165 alkoxyl radical exit channel. These ISOPNs can isomerize to two isoprene orthonitrite
166 stereoisomers, with barriers between 32 and 36 kcal mol⁻¹; again this is similar to the
167 preceding cases. However, the ensuing isoprene orthonitrites are either at or above the
168 ISOPN enthalpies (by up to 3 kcal mol⁻¹), and are even higher in terms of free energy
169 (equilibrium constants are ~ 0.1 – 0.0001). As such, the collisional deactivation of 2,1- and
170 3,4-ISOPN as the orthonitrite forms should be less significant than for the other ISOPN
171 isomers, and is likely to be a minor channel at best. The orthonitrite compounds formed
172 from 2,1- and 3,4-ISOPN do, however, show some unique decomposition channels. This is
173 illustrated for ION-6 (2,1-ISOPN) in Figure 7. An intramolecular hydrogen shift, with barrier
174 of 38.5 kcal mol⁻¹ relative to 2,1-ISOPN, can lead to the generation of hydroxyacetone with
175 vinyl nitrite. Moreover, elimination of formaldehyde can also take place, leading to the
176 formation of a hydroxy vinyl nitrite compound with barrier 35.5 kcal mol⁻¹ relative to the
177 nitrate. In 2,1-ISOPN the ION-5 isomer can similarly eliminate formaldehyde but cannot
178 form hydroxyacetone due to the orientation of the hydroxyl group. Analogous mechanisms
179 are also available for ION-7 and ION-8 arising from 3,4-ISOPN. Note that although the
180 internal OH addition isoprene nitrates are themselves almost insignificant (~ 1 % of the total
181 isoprene + OH product yield), the alkoxyl radicals that they generate are thought to be of
182 some importance (~ 8 % in NO_x dominated environments). Significantly, the present work
183 shows that decomposition channels for these nitrates are available below the conventional
184 alkoxyl radical + NO₂ pathways. These reactions all lead to closed-shell products that
185 sequester inorganic nitrogen, and they may need to be incorporated into future chemical
186 mechanisms.

187 The results presented here have broad implications when it comes to assessing the fate of
188 the major isoprene peroxy radicals. Firstly, these peroxy radicals can react with NO and be

189 stabilised to at least some extent as orthonitrites, in addition to the conventionally
190 considered nitrates. Because the IONs are fully saturated, they are likely to be unreactive
191 towards O₃, and considerably less reactive towards OH than their ISOPN counterparts. The
192 structure-activity relationship methods of Atkinson,²⁰ implemented within the AOPWIN
193 (v1.92) code, for instance, predict rate coefficients of 4.5×10⁻¹² cm³ molecule⁻¹ s⁻¹ for ION-
194 1/2 + OH, and 4.7×10⁻¹² cm³ molecule⁻¹ s⁻¹ for ION-3/4 + OH (reaction is dominated by C–H
195 abstraction from the site adjacent to the hydroxyl group). These can be compared to values
196 of around 1.0×10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for the δ -hydroxy ISOPNs + OH and up to 0.6×10⁻¹⁰
197 cm³ molecule⁻¹ s⁻¹ for the β -hydroxy ISOPNs + OH.^{3,19} Moreover, the IONs do not possess the
198 nitrate chromophore, removing a further atmospheric sink (*i.e.*, photolysis). The IONs are
199 also predicted to display significantly different IR spectra from the ISOPNs (Figures S7 and
200 S8), which may allow for the detection in the laboratory or the field.

201 Secondly, and potentially of most significance, the present work discloses that the major β -
202 OH isoprene nitrates can interchange with their δ -OH isomers; this process is illustrated in
203 Figure 8 for the 1,4 and 1,2 isomers (a corresponding diagram for the 4,1 and 4,2 isomers is
204 provided as Figure S6). In addition to being able to isomerize via the common orthonitrites,
205 direct NO₂ migration reactions are available with even lower barriers (see Figure 9 for
206 transition state structures). These isomerization reactions are predicted to require barriers
207 more than 10 kcal mol⁻¹ below the alkoxyl radical + NO₂ dissociation thresholds, and result
208 in scrambling of the δ and β substituted isoprene hydroxy nitrates. One consequence is that
209 the β -OH peroxy radicals may actually react with NO to produce δ -OH nitrates (and *vice*
210 *versa*). This leads us to hypothesize a new mechanism for the much higher individual yields
211 of δ vs. β substituted hydroxy nitrates observed in the photochemical oxidation of isoprene.
212 Conversely, the δ -OH isoprene peroxy radicals may react with NO to produce β -OH
213 substituted alkoxyl radicals (+ NO₂). Indeed, Figure 8 illustrates that this would be the
214 lowest-energy decomposition pathway for these energized nitrate intermediates. A non-
215 negligible yield of β -OH alkoxyl radicals from the δ -OH peroxy radicals would require us to
216 re-evaluate the initial branching fractions for O₂ addition to the isoprene–OH adducts, which
217 have been assigned mainly on the basis of these alkoxyl radical products under NO_x
218 dominant conditions. If δ -OH peroxy radical yields are higher than currently thought this
219 would also revise down the fitted yields of δ -OH nitrates. Revised branching fractions for the
220 isoprene peroxy radicals would have significant implications for isoprene chemistry under
221 NO_x-deficient conditions, where hydroperoxide formation and peroxy radical isomerization
222 becomes important. In particular, higher δ -OH peroxy radical yields would provide
223 increased opportunities for HPALD formation, which can lead to cascading OH radical
224 generation.^{22–24} Despite recent advances, our description of isoprene chemistry in remote
225 environments is still lacking, particularly with respect to OH radical regeneration,^{25–28} and
226 this new chemistry could provide a further mechanism to help bridge this gap.

228 **Supporting Information Available:** Coordinates for optimized structures. Energy diagrams
229 and reaction schemes for ISOPN isomers not included in the manuscript.

230
231 **Acknowledgements:** This work was supported by the Australian Research Council (ARC)
232 through the Future Fellowship (FT130101304) scheme.
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TABLES

Table 1. Standard enthalpies of formation at 0 K ($\Delta_f H^\circ_0$) and 298 K ($\Delta_f H^\circ_{298}$) and entropies (S°_{298}) for the isoprene hydroxy nitrates (ISOPNs) and isoprene orthonitrites (IONs). Enthalpies in kcal mol⁻¹ and entropies in cal mol⁻¹ K⁻¹, calculated at the G3X-K level of theory.

	$\Delta_f H^\circ_0$	$\Delta_f H^\circ_{298}$	S°_{298}
1,2-ISOPN	-54.1	-62.6	98.6
2,1-ISOPN	-57.1	-65.7	99.4
3,4-ISOPN	-55.6	-64.1	101.7
4,3-ISOPN	-55.3	-63.7	101.2
1,4-(<i>E</i>)-ISOPN	-55.0	-63.3	103.2
1,4-(<i>Z</i>)-ISOPN	-54.7	-63.2	99.5
4,1-(<i>E</i>)-ISOPN	-53.4	-61.5	106.0
4,1-(<i>Z</i>)-ISOPN	-54.2	-62.7	99.7
ION-1	-57.4	-67.1	89.2
ION-2	-56.4	-66.0	90.1
ION-3	-59.6	-69.2	90.4
ION-4	-58.1	-67.5	91.6
ION-5	-55.3	-65.0	88.5
ION-6	-54.0	-63.7	88.1
ION-7	-54.9	-64.5	88.9
ION-8	-55.7	-65.4	88.7

FIGURES

Figure 1. The isoprene hydroxy nitrate (ISOPN) isomers and naming convention.

Figure 2. Optimized structures for the isoprene orthonitrite (ION) isomers, calculated at the M06-2X/6-31G(2df,p) level of theory.

Figure 3. Optimized transition state structures for isomerization of the isoprene hydroxy nitrates to orthonitrites, calculated at the M06-2X/6-31G(2df,p) level of theory. Displacement vectors for imaginary frequencies are indicated.

Figure 4. Potential energy diagram for isomerization of 1,2-ISOPN to the isoprene orthonitrites ION-1 and ION-2. The initiating peroxy radical + NO energy (dashed line) is included for reference. Energies are 0 K enthalpies in kcal mol⁻¹ at the G3X-K level of theory.

Figure 5. Potential energy diagram for isomerization of 1,4-(*E*)-ISOPN to the isoprene orthonitrite ION-3. The initiating peroxy radical + NO energy (dashed line) is included for reference. Energies are 0 K enthalpies in kcal mol⁻¹ at the G3X-K level of theory.

Figure 6. Potential energy diagram for isomerization of 4,1-(Z)-ISOPN to the isoprene orthonitrite ION-4. The initiating peroxy radical + NO energy (dashed line) is included for reference. Energies are 0 K enthalpies in kcal mol⁻¹ at the G3X-K level of theory.

Figure 7. Reaction scheme for the decomposition of the isoprene orthonitrite ION-6, formed from 2,1-ISOPN. Energies are 0 K enthalpies in kcal mol⁻¹ at the G3X-K level of theory.

Figure 8. Reaction scheme for interconversion of the isoprene hydroxy nitrates 1,2-ISOPN, 1,4-(*E*)-ISOPN, and 1,4-(*Z*)-ISOPN and decomposition to the corresponding alkoxy radicals. Energies are 0 K enthalpies in kcal mol⁻¹ at the G3X-K level of theory, relative to 1,2-ISOPN.

Figure 9. Optimized transition state structures for NO_2 migration in 1,2-ISOPN to 1,4-(*E*)-ISOPN (left) and 1,4-(*E*)-ISOPN (right), calculated at the M06-2X/6-31G(2df,p) level of theory. Displacement vectors for imaginary frequencies are indicated.

TOC Image

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SUPPORTING INFORMATION

Isomerization of the Isoprene Hydroxy Nitrates and Formation of Orthonitrite Compounds

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Figure S1. Potential energy diagram for isomerization of 4,3-ISOPN to the isoprene orthonitrites ION-3 and ION-4. The initiating peroxy radical + NO energy (dashed line) is included for reference. Energies are 0 K enthalpies in kcal mol⁻¹ at the G3X-K level of theory.

Figure S2. Potential energy diagram for isomerization of 4,1-(*E*)-ISOPN to the isoprene orthonitrite ION-1. The initiating peroxy radical + NO energy (dashed line) is included for reference. Energies are 0 K enthalpies in kcal mol⁻¹ at the G3X-K level of theory.

Figure S3. Potential energy diagram for isomerization of 4,1-(Z)-ISOPN to the isoprene orthonitrite ION-2. The initiating peroxy radical + NO energy (dashed line) is included for reference. Energies are 0 K enthalpies in kcal mol⁻¹ at the G3X-K level of theory.

Figure S4. Potential energy diagram for isomerization of 2,1-ISOPN to the isoprene orthonitrites ION-5 and ION-6. The initiating peroxy radical + NO energy (dashed line) is included for reference. Energies are 0 K enthalpies in kcal mol⁻¹ at the G3X-K level of theory.

Figure S5. Potential energy diagram for isomerization of 3,4-ISOPN to the isoprene orthonitrites ION-7 and ION-8. The initiating peroxy radical + NO energy (dashed line) is included for reference. Energies are 0 K enthalpies in kcal mol⁻¹ at the G3X-K level of theory.

Figure S6. Reaction scheme for the decomposition of the isoprene orthonitrite ION-6, formed from 2,1-ISOPN. Energies are 0 K enthalpies in kcal mol⁻¹ at the G3X-K level of theory.

Figure S7. Predicted IR spectra for the isoprene nitrates (ISOPNs), at the M06-2X/6-31G(2df,p) level of theory.

Figure S8. Predicted IR spectra for the isoprene orthonitrites (IONs), at the M06-2X/6-31G(2df,p) level of theory.

Cartesian coordinates (in Å)

1,2-ISOPN

C	0.50111	1.28427	-0.84545
C	0.64527	-0.01268	-0.00333
O	-0.44594	-0.97163	-0.25230
O	0.03818	2.40523	-0.15753
N	-1.73291	-0.59170	-0.01543
O	-2.51687	-1.47860	-0.14048
O	-1.96001	0.55779	0.27822
H	-0.10207	1.04453	-1.73373
H	-0.87712	2.23601	0.08057
C	1.79439	-0.80425	-0.58089
H	1.64756	-1.09934	-1.61773
C	2.91914	-1.10509	0.04690
H	3.10056	-0.82908	1.07926
H	3.71127	-1.64272	-0.46007
H	1.50550	1.54249	-1.19229
C	0.77180	0.26432	1.48176
H	0.92210	-0.66962	2.02634
H	1.62388	0.92611	1.65014
H	-0.11438	0.77183	1.85835

1,4-(E)-ISOPN

C	-0.39527	0.92761	-0.64471
C	0.87022	1.46351	-0.05826
H	0.86536	1.48959	1.03041
H	1.08918	2.46475	-0.43720
C	-1.45036	0.47783	0.03245
O	1.42170	-0.80108	0.96503
N	2.15734	-0.51828	0.05904
O	2.01968	0.72431	-0.51990
O	3.02991	-1.16651	-0.42938
C	-2.66853	-0.00591	-0.71882
H	-3.54081	0.59246	-0.43201
H	-2.51896	0.11953	-1.79968
O	-2.99895	-1.33791	-0.38816
H	-2.24305	-1.88737	-0.61332
C	-1.56468	0.38672	1.52682
H	-2.18450	1.20488	1.90972
H	-2.06938	-0.54688	1.78561
H	-0.59918	0.41059	2.03013
H	-0.42693	0.93135	-1.73253

1,4-(Z)-ISOPN

C	0.58022	-1.39422	0.13121
C	-0.56593	-1.23778	1.09099
H	-0.25594	-1.18568	2.13687
H	-1.30438	-2.03124	0.97914
C	1.53588	-0.47803	-0.02206
O	-1.97978	1.33278	-0.62051
N	-1.80279	0.18730	-0.32210
O	-1.21454	0.04370	0.91652
O	-2.06853	-0.80351	-0.93521
C	1.59183	0.79782	0.79417
H	1.06599	0.68459	1.74947
H	2.63931	1.02302	1.02213
O	1.10628	1.90087	0.06183
H	0.14455	1.84654	0.04027
C	2.59303	-0.58552	-1.07906
H	2.45189	-1.45928	-1.71684
H	2.57072	0.31654	-1.69861
H	3.58799	-0.63715	-0.62444
H	0.56164	-2.27272	-0.50584

2,1-ISOPN

C	-2.36377	-0.55263	-0.21816
H	-2.46681	-1.63259	-0.30382
C	-3.38292	0.25008	-0.47724
H	-3.27825	1.32394	-0.38604
H	-4.34635	-0.14477	-0.77703
C	-0.99391	-0.08022	0.21025
C	-0.03120	-0.43266	-0.95053
H	-0.38150	-1.31754	-1.48391
H	0.03161	0.41178	-1.63987
O	1.28927	-0.86069	-0.56574
O	-1.07598	1.30830	0.40902
N	2.13687	0.12311	-0.13760
O	3.23108	-0.26854	0.11333
O	1.70759	1.24871	-0.06178
H	-0.18282	1.63878	0.53943
C	-0.57977	-0.79588	1.49959
H	-0.50203	-1.87627	1.35233
H	0.38873	-0.42920	1.85245
H	-1.32695	-0.59033	2.26754

4,1-(E)-ISOPN

C	0.63773	0.76214	-0.29197
C	-0.69187	1.10138	-0.90629
H	-0.85495	0.58978	-1.85496
H	-0.79654	2.18108	-1.04751
C	1.44582	-0.09537	-0.91252
O	-1.55082	-1.28636	-0.64113
N	-2.09699	-0.51862	0.10136
O	-1.78453	0.82185	-0.00954
O	-2.90825	-0.73693	0.94655
C	2.80601	-0.52742	-0.41752
H	3.19907	-1.30854	-1.08099
H	3.51073	0.31029	-0.45994
O	2.80927	-0.96277	0.92736
H	2.08905	-1.59107	1.02774
H	1.10298	-0.54304	-1.84238
C	0.94805	1.47607	0.99355
H	1.89364	1.14810	1.42018
H	0.97844	2.55811	0.82244
H	0.15663	1.29853	1.72849

3,4-ISOPN

C	2.15578	-0.16645	-0.11247
C	3.11057	0.65199	0.30703
H	2.90190	1.69452	0.50858
H	4.12779	0.30026	0.43980
C	0.73013	0.31026	-0.27814
C	-0.12845	-0.24274	0.88329
H	0.38225	-1.03664	1.42858
H	-0.37091	0.57134	1.56970
O	-1.32823	-0.91516	0.46527
O	0.70692	1.70857	-0.31497
N	-2.30343	-0.09736	-0.04042
O	-3.29149	-0.67614	-0.35962
O	-2.07224	1.08553	-0.10446
H	-0.21441	1.97710	-0.37362
H	0.32723	-0.12651	-1.20862
C	2.38667	-1.61097	-0.45281
H	3.40101	-1.91914	-0.19627
H	1.68643	-2.27407	0.06792
H	2.23476	-1.78032	-1.52431

4,1-(Z)-ISOPN

C	1.32619	-0.57656	0.05720
C	0.35679	-0.82988	1.19062
H	0.70900	-0.44219	2.14907
H	0.13213	-1.89241	1.29796
C	1.58000	0.66321	-0.35867
O	-2.40091	0.29802	-0.44684
N	-1.58224	-0.50337	-0.10538
O	-0.87251	-0.10000	1.00664
O	-1.32133	-1.56880	-0.58200
C	1.02878	1.93275	0.24529
H	0.77610	1.77767	1.30216
H	1.80762	2.70041	0.21239
O	-0.06444	2.45883	-0.47297
H	-0.84270	1.93090	-0.26802
H	2.22722	0.79140	-1.22343
C	1.92604	-1.80179	-0.56818
H	2.60781	-1.53756	-1.37755
H	2.48611	-2.38379	0.17213
H	1.13912	-2.45165	-0.96321

4,3-ISOPN

C	0.22687	1.39797	-0.72622
C	0.41426	0.23098	0.26962
O	-0.44893	-0.89726	-0.04000
O	-0.39101	2.51693	-0.16233
N	-1.78749	-0.68505	0.12741
O	-2.45578	-1.63776	-0.12005
O	-2.14786	0.40406	0.50330
H	-0.30429	1.01618	-1.61181
H	-1.27210	2.24727	0.11176
C	1.79925	-0.35956	0.22046
C	2.61044	-0.23326	1.26215
H	2.28952	0.24492	2.18082
H	3.63036	-0.60000	1.22711
H	1.21497	1.73226	-1.05449
H	0.17692	0.58945	1.27395
C	2.19295	-1.02496	-1.06794
H	3.23457	-1.34649	-1.03712
H	1.56182	-1.89686	-1.25938
H	2.06675	-0.34612	-1.91846

ION-1

C	-0.66173	0.15478	1.03285
H	-0.50999	0.27135	2.10303
C	-1.88075	0.81655	0.41157
H	-1.73401	1.86048	0.13469
H	-2.76816	0.70865	1.04038
C	0.56153	0.36254	0.13347
C	1.81212	-0.29671	0.71980
H	2.24316	0.34968	1.49164
H	1.52707	-1.25205	1.17993
O	0.15657	-0.45371	-1.00112
O	2.78917	-0.46733	-0.27225
N	-1.08255	-1.03681	-0.66510
O	-2.02640	0.01223	-0.77038
O	-0.96923	-1.20776	0.70869
H	2.37603	-0.98961	-0.96869
C	0.84482	1.77590	-0.34086
H	0.06502	2.12463	-1.01891
H	0.92516	2.46092	0.50830
H	1.79678	1.77780	-0.87506

ION-2

C	0.74587	0.42395	0.95320
H	0.75041	0.99056	1.88012
C	1.47141	-0.90961	0.93260
H	0.89861	-1.75470	1.31399
H	2.43612	-0.84624	1.44335
C	-0.59700	0.33284	0.21028
C	-1.37055	1.63900	0.27143
H	-1.78538	1.78926	1.27218
H	-0.71068	2.47124	0.02176
O	-0.10112	0.15173	-1.14660
N	1.30158	0.17843	-1.07555
O	1.67517	-1.05766	-0.48045
O	1.52442	1.08982	-0.05242
C	-1.48167	-0.87270	0.51826
H	-0.89996	-1.79421	0.39805
H	-1.85046	-0.82029	1.54812
O	-2.60873	-0.88620	-0.32073
H	-2.27907	-0.95414	-1.22299
H	-2.19694	1.60713	-0.43886

ION-3

C	-0.61603	0.73662	-0.05390
C	-1.78690	0.12366	-0.82270
H	-1.61997	0.08903	-1.90188
H	-2.73333	0.62353	-0.59650
C	0.65535	0.04179	-0.54635
C	1.95318	0.53424	0.07244
H	2.23809	1.49722	-0.36304
H	1.79704	0.67176	1.15242
O	0.41944	-1.29677	-0.06134
O	2.99272	-0.36825	-0.19601
N	-0.78556	-1.25460	0.68339
O	-1.80922	-1.20392	-0.28167
O	-0.78178	0.03436	1.19068
H	2.69485	-1.22720	0.12204
H	0.72767	0.01075	-1.63788
C	-0.60131	2.22752	0.13320
H	-0.46496	2.72389	-0.83057
H	-1.54716	2.55968	0.56550
H	0.21169	2.52724	0.79684

ION-4

C	0.76911	0.67142	-0.04862
C	1.09537	-0.01813	1.26988
H	0.39698	0.19663	2.08010
H	2.11951	0.20358	1.58654
C	-0.66855	0.32054	-0.45300
O	-0.53254	-1.08510	-0.74276
N	0.82454	-1.40418	-0.52663
O	0.98954	-1.39374	0.88407
O	1.46454	-0.24185	-0.91950
C	-1.78582	0.49829	0.55802
H	-1.56558	-0.09332	1.45617
H	-1.87404	1.55146	0.84592
O	-3.01604	0.12271	-0.00662
H	-2.93401	-0.80137	-0.26319
C	1.22051	2.09015	-0.24179
H	0.67111	2.75382	0.43030
H	2.28678	2.18226	-0.02667
H	1.03704	2.40781	-1.26997
H	-0.93738	0.83868	-1.38133

ION-5

C	-0.04219	0.67634	0.76190
H	0.30084	1.23057	1.63472
C	-1.06175	1.43859	-0.09382
H	-0.65496	1.81366	-1.03270
H	-1.51925	2.25820	0.46282
C	1.16616	0.05937	0.03189
C	0.64809	-1.30133	-0.46038
H	1.20948	-1.66495	-1.32564
H	0.72144	-2.02683	0.35528
O	-0.68175	-1.17229	-0.92413
N	-1.60563	-0.75484	0.11445
O	-2.07957	0.46351	-0.34252
O	-0.85308	-0.41181	1.22472
O	2.14955	-0.10579	1.03452
H	2.91886	-0.52647	0.64043
C	1.69781	0.90755	-1.11517
H	1.86698	1.94167	-0.80256
H	2.65312	0.49375	-1.45441
H	1.01302	0.89227	-1.96632

ION-6

C	-0.01455	0.72881	0.70045
H	0.31761	1.37173	1.51587
C	-1.07390	1.38544	-0.20106
H	-0.70280	1.54694	-1.21165
H	-1.46617	2.31063	0.22084
C	1.16120	0.08736	-0.05586
C	0.60696	-1.26084	-0.54831
H	1.09177	-1.54836	-1.48532
H	0.78433	-2.04325	0.19776
O	-0.76596	-1.17686	-0.86911
O	1.49446	0.95530	-1.11946
N	-1.59721	-0.76141	0.24295
O	-2.14039	0.42753	-0.19092
O	-0.74779	-0.36227	1.26985
H	2.29407	0.62633	-1.53899
C	2.35157	-0.12952	0.86862
H	3.12748	-0.72166	0.37076
H	2.77885	0.83495	1.15319
H	2.04510	-0.66450	1.77095

ION-7

C	-0.31094	0.71972	0.03871
C	0.87570	1.04503	0.97327
H	0.77729	0.57008	1.95270
H	1.02206	2.11978	1.09355
C	-1.09242	-0.50976	0.53604
C	-0.30017	-1.72073	0.02546
H	-0.46438	-2.61321	0.63347
H	-0.62224	-1.91936	-1.00267
O	1.09146	-1.49051	0.09524
N	1.52352	-0.34411	-0.67927
O	2.00956	0.53093	0.27870
O	0.39262	0.29641	-1.14693
C	-1.17807	1.90662	-0.31228
H	-1.91470	1.62451	-1.06352
H	-1.71275	2.25325	0.57542
H	-0.55171	2.71499	-0.69413
O	-2.39111	-0.48859	-0.00470
H	-2.85427	-1.28041	0.27983
H	-1.12878	-0.49218	1.63451

ION-8

C	0.49343	-0.65892	-0.18118
C	-0.21501	-0.90739	1.16826
H	0.07728	-0.17771	1.92216
H	-0.05595	-1.92294	1.53363
C	1.09854	0.75212	-0.26713
C	-0.07124	1.69055	-0.58168
H	0.10429	2.68588	-0.16424
H	-0.19806	1.77896	-1.66605
O	-1.26934	1.25730	0.02898
O	1.75413	1.01977	0.94964
N	-1.66224	-0.08596	-0.34739
O	-1.60231	-0.78339	0.84179
O	-0.62575	-0.63492	-1.08625
H	1.81116	0.78075	-1.10499
H	2.20284	1.86542	0.87956
C	1.45290	-1.74877	-0.59658
H	1.78885	-1.58810	-1.62354
H	2.32509	-1.72838	0.06201
H	0.97466	-2.72783	-0.53030

TS1			
C	1.75128	-0.27552	0.77560
C	0.57253	0.44897	0.12600
O	0.06100	-0.47937	-0.97221
N	-1.12060	-0.99345	-0.50174
O	-2.10271	-0.26486	-0.77666
O	-1.00761	-1.36555	0.67630
H	2.25073	0.41242	1.46627
C	-0.58009	0.62043	1.05838
H	-0.46761	0.39280	2.11048
C	-1.75068	1.14789	0.52168
H	-2.64246	1.20752	1.13386
H	-1.70750	1.83008	-0.31662
O	2.70040	-0.66529	-0.17976
H	2.24160	-1.24630	-0.79552
H	1.36904	-1.12955	1.34687
C	1.02841	1.68268	-0.63814
H	1.42208	2.42522	0.05930
H	1.82741	1.39357	-1.32224
H	0.21352	2.12228	-1.21273

TS2			
C	-1.26008	1.67591	0.32602
C	-0.61147	0.30587	0.33025
O	-0.05709	0.04994	-1.07149
N	1.30275	0.15241	-0.95910
O	1.84409	-0.93803	-0.65110
O	1.62243	1.14621	-0.29110
H	-1.67637	1.88771	1.31522
C	0.57150	0.20340	1.23179
H	0.80408	1.01623	1.90631
C	1.30440	-0.98248	1.20711
H	2.22220	-1.04840	1.77937
H	0.82592	-1.92609	0.98444
H	-0.52142	2.43677	0.07495
C	-1.65349	-0.81085	0.46450
H	-2.21662	-0.65476	1.38904
H	-1.15544	-1.78523	0.52581
O	-2.57882	-0.77510	-0.58820
H	-2.08022	-0.90132	-1.40196
H	-2.07135	1.69295	-0.40235

TS3			
C	1.92715	0.47690	0.11153
C	0.64935	0.09808	-0.61059
O	0.31611	-1.31225	-0.19505
N	-0.83566	-1.20398	0.55615
O	-1.86489	-1.29485	-0.14132
O	-0.76206	-0.25894	1.35271
H	2.26520	1.46036	-0.23093
C	-0.56164	0.93366	-0.33857
C	-1.70020	0.48883	-1.00888
H	-2.65121	0.98237	-0.84196
H	-1.60105	-0.06604	-1.93339
O	2.94791	-0.44001	-0.18045
H	2.62630	-1.30484	0.09356
H	0.83525	-0.02338	-1.68117
H	1.72137	0.53497	1.18821
C	-0.48535	2.25266	0.37497
H	-0.08103	3.02380	-0.28886
H	-1.48494	2.56635	0.68139
H	0.14734	2.20191	1.26216

TS4			
C	-0.46778	0.54757	-0.76470
O	-0.45405	-0.92457	-1.01185
N	0.69043	-1.39201	-0.38900
O	0.49770	-1.66602	0.81368
O	1.66202	-0.68346	-0.67500
C	0.59169	0.84964	0.25538
C	0.45180	0.22073	1.49019
H	1.24865	0.32445	2.21984
H	-0.52884	-0.03673	1.86286
C	-1.93321	0.81533	-0.40456
H	-2.52899	0.66338	-1.31571
H	-2.04869	1.85905	-0.10009
O	-2.39492	0.01005	0.64411
H	-2.15625	-0.89621	0.41450
C	1.58948	1.93888	-0.00987
H	1.95239	1.90169	-1.03866
H	1.13503	2.92114	0.15775
H	2.44089	1.84603	0.66703
H	-0.22494	1.04033	-1.71080

TS5

C	-0.09344	0.93448	-0.33785
C	-1.55640	0.92991	-0.62925
H	-1.78217	0.95542	-1.69628
H	-2.09193	1.71610	-0.09605
C	0.61154	-0.07187	-1.00575
C	2.04834	-0.40606	-0.70728
H	2.27969	-1.37386	-1.17226
O	-0.35168	-1.64761	-0.19102
N	-1.13339	-0.98698	0.52581
O	-2.12948	-0.38486	-0.19516
O	-0.62934	-0.20755	1.34802
H	2.71203	0.33970	-1.16304
O	2.32053	-0.41811	0.66950
H	1.56506	-0.83825	1.09930
C	0.53635	2.06895	0.41882
H	0.71899	2.91151	-0.25671
H	-0.12362	2.41151	1.21788
H	1.48656	1.75606	0.85013
H	0.21044	-0.43672	-1.94653

TS6

C	0.75845	0.85270	0.10835
C	1.02557	0.00482	1.31049
H	0.43250	0.26488	2.18822
H	2.08732	-0.02132	1.56057
C	-0.56416	0.84675	-0.35013
O	-0.65654	-1.11765	-0.79875
N	0.48394	-1.41517	-0.38271
O	0.56940	-1.37219	0.99848
O	1.44297	-0.83859	-0.90567
C	-1.78560	0.71959	0.53557
H	-1.57367	0.06559	1.38920
H	-2.02967	1.71569	0.92396
O	-2.91447	0.29512	-0.17649
H	-2.71873	-0.59316	-0.49017
H	-0.76552	1.35479	-1.29183
C	1.80560	1.78948	-0.41793
H	1.58705	2.05785	-1.45350
H	1.82613	2.71342	0.16910
H	2.79706	1.33488	-0.37527

TS7

C	-0.09667	0.05121	1.13424
H	0.31064	-0.66782	1.83055
C	-1.52896	0.41264	1.15042
H	-1.72740	1.48061	1.23759
H	-2.10012	-0.15161	1.88589
C	0.71753	0.66282	0.16894
C	2.10403	0.09555	-0.03232
H	2.38555	0.26677	-1.08176
O	-0.25665	-0.03705	-1.39718
N	-1.14201	-0.70135	-0.80718
O	-2.08605	0.09375	-0.21484
O	-0.74857	-1.58866	-0.03215
C	0.53913	2.09667	-0.26657
H	-0.51142	2.37474	-0.34089
H	1.03847	2.76095	0.44594
H	2.81586	0.65515	0.58763
O	2.20482	-1.25052	0.33183
H	1.47181	-1.71149	-0.09574
H	0.99193	2.24856	-1.24849

TS8

C	0.53669	0.70083	1.04439
H	0.84284	1.68030	1.38624
C	1.41755	-0.47340	1.26023
H	0.97515	-1.28322	1.83957
H	2.38647	-0.19267	1.67148
C	-0.70699	0.49768	0.43003
C	-1.52182	1.68768	0.01435
H	-0.87865	2.52317	-0.26292
H	-2.15525	1.41886	-0.83139
O	0.03713	-0.22781	-1.27901
N	1.25697	-0.15178	-0.98877
O	1.63658	-1.11018	-0.07692
O	1.68372	0.96465	-0.66840
C	-1.50772	-0.77716	0.65442
H	-0.83779	-1.62165	0.84670
H	-2.13034	-0.62525	1.54471
O	-2.39262	-1.05304	-0.39579
H	-1.84529	-1.23449	-1.16684
H	-2.18063	1.99469	0.83426

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