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Determination of the Hydroxy Nitrate Yields from the Reaction of C₂–C₆ Alkenes with OH in the Presence of NO

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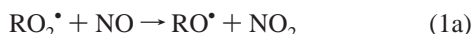
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The yields of hydroxy nitrates from the reaction of selected C₂–C₆ alkenes with OH in the presence of NO were measured at 296 ± 3 K in a 9600 L photochemical smog chamber. Hydroxyl radicals were produced from the photolysis of isopropyl nitrite in the presence of NO. The loss of the alkene was followed using gas chromatography. The hydroxy nitrate products were determined using a combination of capillary chromatography and an organic nitrate specific chemiluminescence detector. The yield of hydroxy nitrates was observed to increase with the size of the precursor alkene as follows: ethene (0.86%), propene (1.5%), 1-butene (2.5%), *cis*-2-butene (3.4%), and 1-hexene (5.5%). Previous studies involving the production of alkyl nitrates from alkanes show a similar trend, but the yields reported here are a factor of 2–3 lower than for the corresponding simple alkylperoxy radical. The impact of a β-hydroxy group on the nitrate yield is examined using an *ab initio* molecular orbital study. It indicates that a hydrogen-bonded peroxy nitrite intermediate is formed, which results in a decrease in D₀(O–O) for the peroxy linkage of about 8 kJ/mol. This would be expected to effectively decrease the organic nitrate yield. The implications of these findings for the organic nitrate path as an atmospheric NO_x removal mechanism are discussed.

Introduction

Ozone production in the troposphere involves an OH-catalyzed oxidation of hydrocarbons in the presence of nitrogen oxides.¹ Although the overall features for this process are well documented, many details remain uncertain, including the role of this process in mediating the ultimate removal of nitrogen oxides from the atmosphere. The major loss process of hydrocarbons emitted into the atmosphere is through the reaction with the OH radical to produce a peroxy radical (RO₂[•]). The peroxy radical can then react with NO in two pathways:



Reaction 1a, which results in tropospheric ozone formation via the subsequent photolysis of NO₂, is the major pathway, while the production of the organic nitrate (RONO₂) in reaction 1b is a relatively minor pathway. However, reaction 1b can significantly impact the production and distribution of tropospheric ozone, since it represents a sink for both the precursor peroxy radicals and NO_x. Thus, the branching ratio of reaction 1a to reaction 1b has an impact on the chain length in the chemistry that produces O₃ and an impact on the distribution and long-range transport of tropospheric NO_x. The yields (*k*_{1b}/(*k*_{1a} + *k*_{1b})) of alkyl nitrates from RO₂ radicals produced from the OH reaction with a number of alkanes have been determined and found to increase with the size of the R group and to increase with increasing pressure and decreasing temperature.²

For the most part, oxidation of alkenes by OH proceeds via addition to one of the double bond carbons, producing a β-hydroxyalkylperoxy radical.³ In contrast to the situation for alkylperoxy radicals, there is very little published data regarding organic nitrate yields for reaction of these radicals with NO. This is in part due to the difficulty in obtaining pure standards, as well as in making measurements of these relatively polar and thus adsorptive species.⁴ The production of β-hydroxyalkyl nitrates is potentially very important because the hydroxy group increases the water solubility,⁵ and thus, the atmospheric lifetimes of these nitrates are much shorter than those of the analogous alkyl nitrates. Because of the wide range of reactive atmospheric alkenes and alkanes that exist and the experimental difficulty in measuring yields, it is desirable to have a firm understanding of the structural features that influence the branching ratio for reaction 1 so that a predictive capability can be developed.

To date the only published β-hydroxyalkyl nitrate yields are for the following alkenes: propene, 1.6%;⁶ *cis*-2-butene, 3.6%;⁴ isoprene, 4.4%⁷ and 8–13%.⁸

Alkyl and β-hydroxyalkyl nitrate ambient concentrations have been determined in several field studies.^{9–18} The measurement of organic nitrates can provide information about the extent of photochemical processing of an air mass, as well as information regarding the nature of the peroxy radicals responsible for ozone production, if the yields are accurately known.^{15,16,18} Since there are only a few determined yields for β-hydroxy nitrate formation, the impact of the oxidation of alkenes on tropospheric ozone is less certain. In this paper we present a two-pronged analysis of β-hydroxy nitrate production. We have produced new measurement data for the β-hydroxy nitrate yield from the OH-radical oxidation of several alkenes. To aid in interpretation

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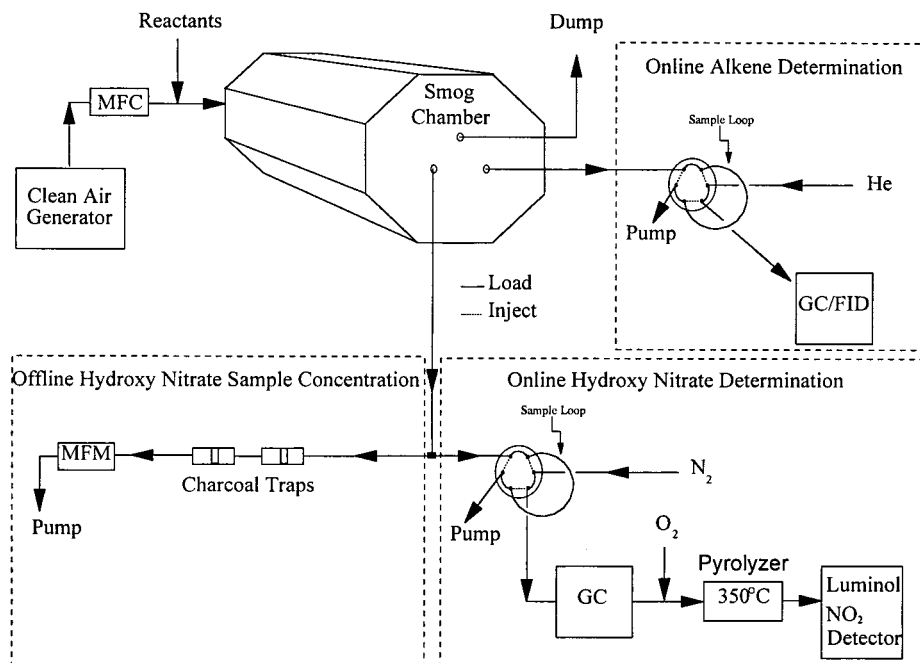


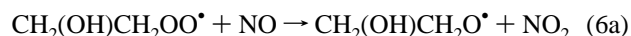
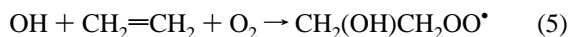
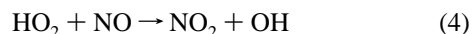
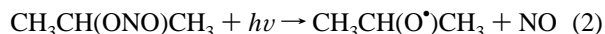
Figure 1. Schematic diagram of the smog chamber and sampling system.

of the structural dependence of this yield, an *ab initio* molecular orbital computational study of the stability of the intermediate peroxy nitrite species was undertaken.

Experimental Section

The oxidations of the alkenes ethene, propene, 1-butene, *cis*-2-butene, and 1-hexene in synthetic air mixtures were separately investigated in a ~9600 L cylindrical Teflon photochemical reaction chamber, shown schematically in Figure 1. The contents of the chamber were irradiated by 310–400 nm radiation from 24 black lamps and mixed using a Teflon fan. Experiments involved irradiating mixtures of isopropyl nitrite (used as the OH source¹⁹), the test alkene, and NO in air, with measurement of both the alkene consumed and organic nitrate produced.

In the case of ethene as the test alkene, the following reactions occur:



Here, the OH radicals are generated in reactions 2–4 and the product β -hydroxy nitrate (nitrooxy ethanol) is produced in reaction 6b. Alkene concentrations were monitored using an HP 5890 series II gas chromatograph equipped with a flame ionization detector. Injection was achieved using a six-port valve and 0.8 cm³ sample loop, and separation was achieved using a 30 m megabore HP Al₂O₃ column. The β -hydroxy nitrates (with the exception of the ethene and one of the 1-hexene experiments) were quantified using a Varian 3300 GC

containing a 30 m megabore HP-1701 column and equipped with a six-port valve and a 0.5 cm³ sample loop for direct gas-phase sampling and injection. Detection of organic nitrates was accomplished using a nitrate-specific detector.¹⁹ The nitrate detector functions by thermally decomposing the chromatographically separated organic nitrates, which quantitatively converts them to NO₂, which is then detected using a luminol-based NO₂ detector.¹⁹ Calibration of the entire nitrate detection system was performed using both standard samples containing known concentrations of the target β -hydroxy nitrate in Teflon bags and using a flowing mixture of isopropyl nitrate in N₂ from a standard 10.2 ppm cylinder (Matheson gas), diluted to low concentrations with laboratory-generated clean air. Isopropyl nitrate calibration is more convenient and, since all organic nitrates are detected with identical instrumental sensitivity,¹⁹ acts as a satisfactory surrogate calibration standard.

Experiments were typically conducted with initial concentrations from 75 to 200 ppm of alkene, 200–500 ppm of NO, and 75 ppm of isopropyl nitrite. The alkenes (with the exception of 1-hexene) and the NO were added into the chamber using calibrated Tylan mass flow controllers. Care was taken to limit the amount of NO₂ added to the chamber, since it can interfere in the determination of the branching ratio by promoting the production of organic nitrate via alkoxy radical reaction with NO₂. Therefore, the NO was added in a large excess of N₂ to minimize the reaction of NO with O₂, which is second order in NO. The isopropyl nitrite (and 1-hexene) was added by injecting the liquid into a stream of clean air entering the chamber. The contents of the chamber were allowed to mix (with the lights off) for a period of at least 1 h before initial concentrations/blanks were determined. The lamps were then turned on for irradiation periods ranging from 30 s to 20 min, depending on the initial reactant concentrations. Determination of the alkene and β -hydroxy nitrate concentrations was undertaken while the lights were switched off. This procedure was repeated up to 10 times for each experiment. Because the time required for the chromatographic separation of the nitrate products was much longer than that for the reactant alkene, replicate alkene determinations were performed to decrease the measurement uncertainty so that small conversions (~5% per

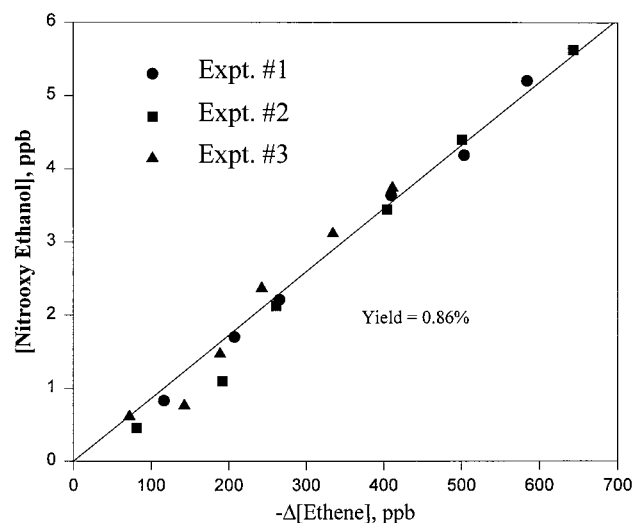
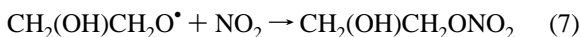


Figure 2. Yield of hydroxy nitrates from OH reaction with ethene.

photolysis period) for the reactant hydrocarbon could be used. Because air was removed from the chamber for analysis, up to 5 L min⁻¹ (~3%/h) of clean air was added to maintain the chamber at atmospheric pressure.

One possible source of systematic error is that the hydroxy alkoxy radical produced in reaction 6a could react, under high NO₂ concentrations, to also produce the β-hydroxy nitrate, as shown in reaction 7 for the ethene system:



This problem would be more severe for peroxy radicals that have smaller branching ratios for reaction 1b so that reaction 7 would make a larger contribution to the observed organic nitrate concentration. To minimize the NO₂ concentration and therefore the possible effects of this interfering reaction, the experiments involving ethene (and an experiment with 1-hexene for comparison) were conducted at significantly lower initial reactant concentrations. At these lower concentrations the analytical method used for the quantitation of the β-hydroxy nitrate products required sample concentration. In this case the β-hydroxy nitrate products were quantified by concentrating a 1–2 L sample of chamber air on 5 mg of activated charcoal.²⁰ These charcoal traps were extracted with 100 μL of a 50:50 mixture of acetone and benzene, and a 5 μL aliquot of this extract was directly injected into the GC with the specific nitrate detector. In this case calibration was conducted using known concentration liquid standards.

The β-hydroxy nitrates needed for calibration and for retention time determination were synthesized in the laboratory using previously described synthesis procedures.⁴ The isopropyl nitrite was synthesized according to the procedure described by Noyes.²¹ Ethene, propene, 1-butene, and *cis*-2-butene were obtained from Matheson, and 1-hexene was acquired from Aldrich. These reagents all had quoted purities of 99% and were used without further purification.

All ab initio molecular orbital calculations were performed using the GAUSSIAN 94 program.²² Geometry optimizations were carried out for all structures using Schlegel's method²³ to better than 0.001 Å for bond lengths and 0.01° for angles. Optimizations were performed with second-order Møller–Plesset (MP2) perturbation theory^{23,24} and with the Becke's nonlocal three-parameter exchange with the Lee–Yang–Parr correlation functional (B3LYP) density functional method.²⁵ The energies were refined using the G2MP2 method.²⁶ Harmonic

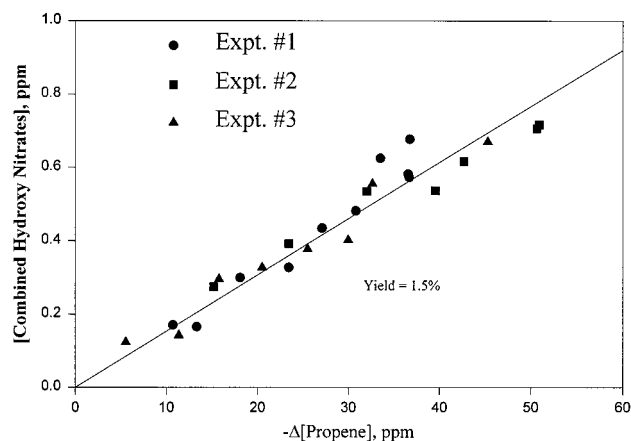


Figure 3. Yield of hydroxy nitrates from OH reaction with propene.

vibrational frequency calculations were performed on each optimized geometry to verify that it was a minimum-energy structure.

Results and Discussion

The alkene and product mixing ratios were corrected for dilution flow of clean air entering the chamber (0–5 L/min) and the β-hydroxy nitrates for secondary removal by the OH radical,²⁷ using OH radical reaction rate coefficients calculated using the method described in Kwok and Atkinson.²⁸ In the worst case for secondary consumption, the correction factor was determined to be 1.05. The yield of β-hydroxy nitrates (HN) from the precursor alkene (i.e., $k_{1b}/(k_{1a} + k_{1b})$) is determined as follows. Assuming that OH attack on the alkene produces exclusively an RO₂ radical by addition (this could cause as much as a ~10% error for 1-hexene³) and that this radical is lost by reaction with NO, we can write

$$-d[\text{alkene}]/dt = k_1[\text{RO}_2^\bullet][\text{NO}]$$

and

$$d[\text{HN}]/dt = k_{1b}[\text{RO}_2^\bullet][\text{NO}]$$

Therefore, $\Delta[\text{HN}]/(-\Delta[\text{alkene}]) = k_{1b}/k_1$. In Figure 2 we have plotted the results of all three ethene experiments as $\Delta[\text{nitrooxy ethanol}]$ vs $\Delta[\text{ethene}]$. The best-fit linear regression slope, forced through zero, gives a β-hydroxy nitrate yield of $(8.6 \pm 0.04) \times 10^{-3}$ (0.86%), where the stated uncertainty is the 95% confidence interval for the slope. For the larger 1-alkenes, the OH radical can add to either carbon of the double bond, leading to the formation of two different β-hydroxy nitrates. In Figure 3 we present the sum of the two organic nitrate concentrations, 2-nitrooxy propanol and 1-nitrooxy-2-propanol, plotted against $-\Delta[\text{propene}]$ for three separate propene experiments; the slope then gives the overall yield of β-hydroxy nitrates from the OH reaction with propene as $(1.5 \pm 0.1) \times 10^{-2}$. The individual isomeric organic nitrate product yields (which are equal to $\alpha k_{1b}/(k_{1a} + k_{1b})$, where α is the fraction of the OH–propene reactions that produce the appropriate precursor peroxy radical) for production of 2-nitrooxy propanol and for 1-nitrooxy-2-propanol were found to be $(8.5 \pm 0.08) \times 10^{-3}$ and $(6.7 \pm 0.10) \times 10^{-3}$, respectively. The difference in yields between the isomers reflects a combination of the preferential tendency for OH addition to the terminal carbon atom³ and the difference in branching ratios of the primary and secondary peroxy radicals in reaction 1.² For propene it has been estimated that OH adds

TABLE 1: Initial Conditions and Product Yields for Each Experiment

test alkene	initial [alkene], ppm	approx initial [NO], ppm	approx initial [isopropyl nitrite], ppm	hydroxy nitrate product	% yield ($\pm 95\%$ CI)	previous studies
ethene no. 1 ^a	2.3	2.3	25	nitrooxy ethanol	0.86 ± 0.04	
ethene no. 2 ^a	2	2.1	25	nitrooxy ethanol	0.85 ± 0.07	
ethene no. 3 ^a	2.1	2.2	25	nitrooxy ethanol	0.89 ± 0.11	
overall ethene				nitrooxy ethanol	0.86 ± 0.03	
propene no. 1	80	200	75	1-nitrooxy-2-propanol	0.64 ± 0.07	
				2-nitrooxy-1-propanol	1.0 ± 0.1	
				combined	1.6 ± 0.1	1.6 ⁶
propene no. 2	100	400	75	1-nitrooxy-2-propanol	0.57 ± 0.04	
				2-nitrooxy-1-propanol	0.88 ± 0.07	
				combined	1.5 ± 0.1	1.6 ⁶
propene no. 3	120	300	75	1-nitrooxy-2-propanol	0.67 ± 0.10	
				2-nitrooxy-1-propanol	0.85 ± 0.08	
				combined	1.5 ± 0.1	1.6 ⁶
overall propene				1-nitrooxy-2-propanol	0.62 ± 0.04	
				2-nitrooxy-1-propanol	0.92 ± 0.05	
				combined	1.5 ± 0.1	1.6 ⁶
1-butene no. 1	230	500	75	1-nitrooxy-2-butanol	1.0 ± 0.1	
				2-nitrooxy-1-butanol	1.4 ± 0.3	
				combined	2.4 ± 0.4	
1-butene no. 2	210	500	75	1-nitrooxy-2-butanol	1.1 ± 0.1	
				2-nitrooxy-1-butanol	1.5 ± 0.2	
				combined	2.6 ± 0.2	
1-butene no. 3	230	500	75	1-nitrooxy-2-butanol	1.3 ± 0.3	
				2-nitrooxy-1-butanol	1.5 ± 0.1	
				combined	2.8 ± 0.3	
overall 1-butene				1-nitrooxy-2-butanol	1.1 ± 0.1	
				2-nitrooxy-1-butanol	1.4 ± 0.1	
				combined	2.5 ± 0.2	
cis-2-butene	75	500	75	2-nitrooxy-3-butanol	3.4 ± 0.5	3.6 ⁴
1-hexene no. 1	165	500	75	1-nitrooxy-2-hexanol	2.3 ± 0.9	
				2-nitrooxy-1-hexanol	3.1 ± 1.1	
				combined	5.4 ± 1.9	
1-hexene no. 2	100	500	75	1-nitrooxy-2-hexanol	1.6 ± 0.7	
				2-nitrooxy-1-hexanol	4.3 ± 1.1	
				combined	5.9 ± 1.0	
1-hexene no. 3 ^a	1.9	2.5	25	1-nitrooxy-2-hexanol	0.82 ± 0.35	
				2-nitrooxy-1-hexanol	6.2 ± 1.1	
				combined	7.0 ± 1.4	
overall 1-hexene				1-nitrooxy-2-hexanol	2.3 ± 0.5	
				2-nitrooxy-1-hexanol	3.2 ± 0.7	
				combined	5.5 ± 1.0	

^a Charcoal sampling; see text.

65% to the terminal C atom and 35% to C-2. Given these numbers, the calculated branching ratios of the secondary and the primary β -hydroxy nitrates are 0.013 and 0.019, respectively.

For the β -hydroxy nitrates produced from 1-butene, *cis*-2-butene, and 1-hexene, we were also able to determine the individual product yields. The initial conditions, the yield of β -hydroxy nitrates from the precursor alkene, and the yields determined from previous studies (where available) are summarized in Table 1 for all alkenes studied. For alkenes other than propene, we cannot reliably estimate the relative production of the two β -hydroxyperoxy radicals. Thus, the total organic nitrate yields in Table 1 then represent the number average branching ratio for the two β -hydroxyalkylperoxy radical precursors in the case of propene, 1-butene, and 1-hexene. Including possible systematic errors, we estimate an absolute uncertainty for each determination of $\pm 25\%$ of the reported yield.

The results of this study indicate that the β -hydroxy nitrate yields from the reaction of β -hydroxy peroxy radicals with NO increase as a function of the size of the alkene, similar to the observations reported for alkylperoxy radicals² (i.e., from OH + alkanes). A plot of the total hydroxy nitrate yield vs the size of the corresponding hydrocarbon (including the yield from isoprene⁷) is plotted in Figure 4, along with the calculated total organic nitrate yields resulting from OH radical reaction with

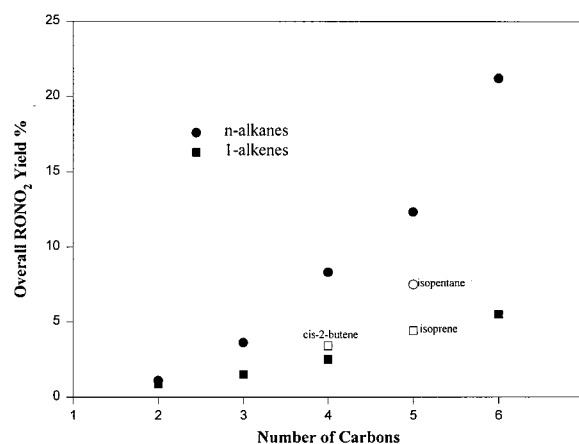


Figure 4. Overall organic nitrate yields for *n*-alkanes and 1-alkenes as a function of size.

the corresponding size *n*-alkane (calculated from information in Carter and Atkinson² and Kwok and Atkinson²⁸), for comparison. As shown in Figure 4, the yields of β -hydroxy nitrates from the β -hydroxyperoxy radicals is significantly lower than those from the corresponding unsubstituted peroxyalkyl radicals, indicating that the presence of a β -hydroxy group has a substantial negative effect on the yield of organic nitrates.

TABLE 2: Computational Study Results for $D_0(\text{O}-\text{O})$ for Organic Peroxy Nitrite Intermediates

level of theory	D_0 (kJ/mol)		
	$\text{CH}_3\text{CH}_2\text{O}-\text{ONO}$ cis-perplanar	$\text{HOCH}_2\text{CH}_2\text{O}-\text{ONO}$ complex (p'p'-cis)	$\text{HOCH}_2\text{CH}_2\text{O}-\text{ONO}$ cis-perplanar
MP2/6-31G(d)	67.8	56.0	61.5
B3LYP/6-31G(d)	45.2	34.7	43.9
G2MP2	71.1	68.6	78.2

Because much of the reactive hydrocarbon emitted into the earth's atmosphere is believed to be in the form of isoprene and terpenes, i.e., alkenes, it is critically important to understand the relationship between molecular structure and the organic nitrate yields so that a predictive capability can be established. To gain insight into the influence of the presence of an $-\text{OH}$ group on the carbon atom β to the peroxy group on the ultimate organic nitrate yield, we conducted an ab initio molecular orbital computational study. The reaction of organic peroxy radicals with NO proceeds through an energy-rich peroxy nitrite intermediate,²⁹ which then rapidly either rearranges to form the organic nitrate via reaction 9b or undergoes O–O bond scission, i.e., reaction 9a:



That reaction 8 is not reversible is indicated by the fact that k_8 is not pressure-dependent, while k_{9b}/k_9 increases with pressure.³ The competition between reactions 9a and 9b depends on the distribution of internal energy among the available vibrational modes in the peroxy nitrite, as well as the impact of any structural features on the strength of the O–O bond. The latter is conveniently studied through application of an ab initio molecular orbital study. Here, we applied the MP2/6-31G(d) and B3LYP/6-31G(d) levels of theory to a study of ethylperoxy nitrite and 2-hydroxyethylperoxy nitrite, i.e., the ROONO intermediates produced from OH radical oxidation of ethane and ethene, respectively. Because of the observation of the impact of the β -hydroxy group on the organic nitrate yields, it was of particular interest to calculate the bond dissociation energy for the peroxy nitrite O–O bond. To refine the energetics for these systems, G2MP2 energies were calculated. The results are shown in Table 2 for the three levels of theory used in our study, i.e., MP2/6-31G(d), B3LYP/6-31G(d), and G2MP2. For ethylperoxy nitrite, the most stable conformation is the cis-perplanar species. The MP2 and G2MP2 results indicate a consistent estimated $D_0(\text{O}-\text{O})$ of 67.8–71.1 kJ/mol, which is consistent with literature estimates for $\text{HO}-\text{ONO}$ and other $\text{RO}-\text{ONO}$ species.³⁰ For the hydroxyethylperoxy nitrite species, we considered two stable conformations. There is a cis-perplanar conformation, for which the $D_0(\text{O}-\text{O})$ values are comparable or somewhat smaller than for the simple ethylperoxy nitrite. However, we find that there is also a p'p'-cis hydrogen-bonded complex that, as shown from the data in Table 2, is stabilized relative to the cis-perplanar conformation by ~ 8 –9 kJ/mol, relative to the non-hydrogen-bonded form. This geometry facilitates an internal hydrogen bond from the hydroxy group to one of the peroxy group oxygen atoms, as shown in Figure 5. The H-bonding interaction then weakens the O–O bond by ~ 8 –9 kJ/mol, i.e., in comparison to the $D_0(\text{O}-\text{O})$ value for the ethylperoxy nitrite species. The expected impact of this weakened bond would be to increase the rate of reaction 9a at

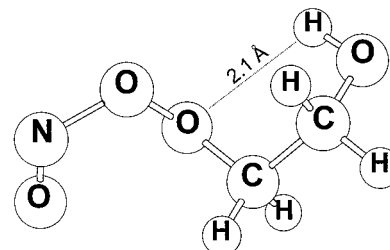


Figure 5. Structure of the p'p'-cis hydrogen-bonded hydroxyethylperoxy nitrite.

the expense of reaction 9b, accounting for the relatively smaller observed β -hydroxy nitrate yields, as discussed for Figure 4.

We note that the rearrangement of the nitrite to a nitrate can be considered to occur through a three-centered transition state. To examine this, we consider HOONO as a model for the rearrangement chemistry. The transition state for the rearrangement of HOONO to HONO₂ has been found to be ~ 250 kJ mol⁻¹ higher in energy than HOONO.^{31–33} The O–O bond dissociation energy in this species^{34,30} is ~ 84 kJ mol⁻¹. It is very unlikely that transformation occurs via a three-centered concerted mechanism in HOONO. If we assume as a first approximation that the transition state for the rearrangement of ROONO (where R = CH_3CH_2 and $\text{CH}_2(\text{OH})\text{CH}_2$) is compatible with that for HOONO, even though we expect the geometry of the three-centered transition state to be more hindered by the substituents on the carbon chain, the O–O bond dissociation values for the ROONO's (as shown in Table 2) are well below the isomerization barrier. The rearrangement for ROONO most likely goes through O–O bond fission followed by $\text{RO} + \text{NO}_2$ recombination.

The observed significant yields of organic nitrates from alkene oxidation impacts on the expected role of organic nitrate formation in the atmosphere. As discussed in Chen et al.,⁷ even though the organic nitrate yield for OH reaction with isoprene is relatively small at 4.4%, the impact of isoprene nitrate formation is that an estimated 7% of NO emitted in the eastern U.S. in the summer is removed from the atmosphere in the form of the isoprene nitrates. The second major source of alkenes to the atmosphere is the terpenes, which are emitted at an annual rate of about $2/3$ that of isoprene.³⁵ We would therefore expect the production of terpene-derived nitrates to have a similar, if not larger, role as NO_x sinks. The recently reported organic nitrate yield of 17% from the OH reaction with α -pinene (Nozière et al.³⁶) is quite high compared to analogous β -hydroxy nitrate yield measurements and indicates that our understanding of the structural features that determine the magnitude of organic nitrate yields may be incomplete. This reaction produces a β -hydroxyperoxy nitrite intermediate, which, on the basis of this work, would have been expected to have a smaller yield than that reported.

Conclusions

Although the yields of β -hydroxy nitrates from alkenes were found to be lower than those for the alkyl nitrates derived from similar-size alkanes, β -hydroxy nitrates have a shorter atmo-

spheric lifetime and their production may represent a more efficient mechanism for removing NO_x from the atmosphere. This idea has recently been discussed in a modeling study by Horowitz et al.,³⁷ who find that a significant fraction of nitrogen emitted in the U.S. is exported from North America in the form of isoprene nitrates. Through the combination of the yields determined in this study and field measurements of β -hydroxy nitrates, computer modeling studies can better address the question of the impact of organic nitrate formation on the production of ozone and long-range transport of NO_x. The production of hydroxy nitrates could be an important process for forest environments and in urban areas, where the yields for the relatively larger biogenic or urban hydrocarbons (e.g., terpenes or aromatics) may be such that the production of hydroxy nitrates represents an important mechanism for the removal of atmospheric nitrogen. Thus, further work is clearly necessary with regard to the mechanisms and yields for organic nitrate formation from biogenic alkenes and aromatic hydrocarbons to assess their importance as NO_x removal processes in urban and forested environments.

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