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Ozonolysis Fragment Quenching by Nitrate Formation: The Pressure Dependence of Prompt OH Radical Formation

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The gas-phase reaction of ozone with alkenes is known to be a significant source of OH radicals in the troposphere. The pressure dependence of the OH yield in ozone−alkene reactions is both important and controversial; the poor understanding of the pressure-dependent OH yield for different ozone−alkene reactions is a major obstacle to developing an accurate simulation of tropospheric chemistry. Using a high-pressure flow reactor, we have investigated the ozonolysis of a series of alkenes in the presence of NO_2. The four alkenes studied were 2,3-dimethyl-2-butene (TME), *trans*-5-decene, cyclohexene, and α-pinene, which provide significant differences in size (C6 vs C10) and structure (linear vs cyclic) to elucidate the influence of these competing effects on OH formation. OH yields from TME and *trans*-5-decene ozonolysis decrease with increasing pressure, but OH yields from cyclohexene (0.64 ± 0.20) and α-pinene (0.89 ± 0.20) are pressure-independent and consistent with the literature. Acetone production increases relative to TME consumption as pressure increases; this observation, supported by density functional calculations, is consistent with acetone and nitrate radical production from the SCI + NO_2 reaction. Both the pressure dependence of OH formation from the linear alkenes (TME and *trans*-5-decene) and the pressure-independent OH yields observed for cyclohexene and α-pinene can be explained by changes in the extent of collisional stabilization of the carbonyl oxide (Criegee) intermediate with increasing pressure.

1. Introduction

Unsaturated hydrocarbons are profoundly important to global atmospheric chemistry. Fully one-third of the reduced carbon flux to the atmosphere is thought to come through isoprene alone, and other compounds, including ethene, propene, and many terpenes, play a major global role. Unsaturated hydrocarbons are also significant tropospheric pollutants, accounting for approximately 12% of volatile organic compounds (VOCs) in urban air by mass and a much higher fraction of the total input flux.[1]

Atmospheric oxidation of unsaturated hydrocarbons by OH radicals and ozone occurs rapidly, and most unsaturated hydrocarbons have atmospheric lifetimes of a few hours.[2] Oxidation by ozone is of particular interest because this reaction is a known source of HOx.[3,4] OH production from the ozonolysis of alkenes has been observed both directly and indirectly, but the OH yields from particular ozone−alkene reactions remain uncertain. For example, reported OH yields for the reaction of ozone with TME (tetramethyl ethylene; 2,3-dimethyl-2-butene) range from ∼0.4 to ∼1.0 at 760 Torr.[5−7] Additionally, the pressure dependence of OH formation remains unclear.[6,8]

The reaction of ozone with unsaturated hydrocarbons follows the Criegee mechanism,[9] which is shown in Figures 1 and 2. Ozone adds across the double bond (R1) to form an energy-rich primary ozonide, which decomposes (R2) to form a carbonyl species and a vibrationally excited carbonyl oxide (the Criegee intermediate, or CI). The CI subsequently isomerizes to a vinyl hydroperoxide (R3a) before decomposing to form OH (R3b) or undergoes ring closure (R4) to dioxirane. The CI may also be stabilized by collisions with the bath gas.[10−15] Stabilized Criegee intermediates (SCI) may persist long enough in the atmosphere (∼100−500 ms) to react with any number of gas-phase species, including water and NO_2.[12,16] SCI that do not react are believed to thermally decompose along the pathways shown in R3 and R4.[11] Pressure-dependent OH yields arise from increased collisional stabilization of the CI with increases in pressure.

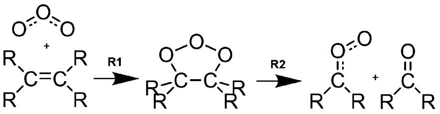

Figure 1. Criegee mechanism: addition of ozone to the alkene to form the primary ozonide (R1) followed by decomposition (R2) to a carbonyl and the carbonyl oxide (Criegee intermediate, CI).

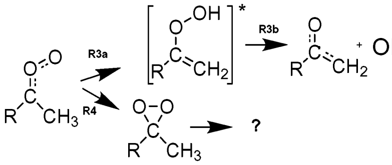

Figure 2. The carbonyl oxide can isomerize (R3a) to a vinyl hydroperoxide that decomposes (R3b) to form OH or can undergo ring closure (R4) to dioxirane.

Early studies of OH production from ozone−alkene reactions relied on the addition of a radical scavenger to the reaction mixture.[17−19] In scavenger studies, OH production is measured either from the formation of a product of the OH-scavenger reaction or from the decrease in scavenger concentration itself. More recently, a tracer method has been used to measure the OH yield in a number of different ozone−alkene reactions,

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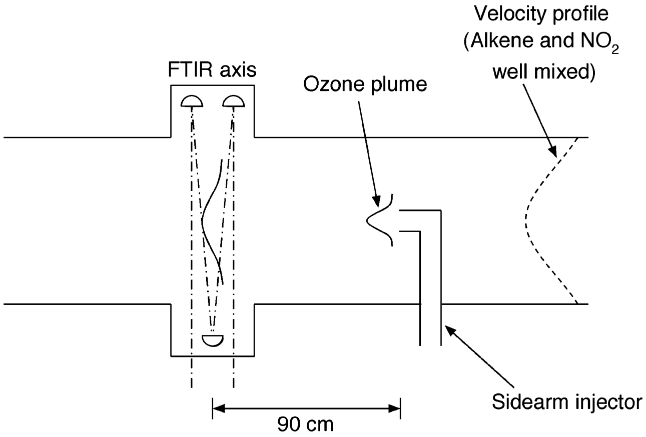

Figure 3. Schematic of the high-pressure flow system used in this study. Alkene and NO_2 are introduced to the flow upstream to ensure a uniform concentration. The reaction is initiated by the introduction of O_3 through the sidearm injector. Products are identified at a fixed axis 90 cm downstream from the injector.

essentially relying on the relative consumption of compounds with different OH reactivities.[6,10,20] Both the scavenger and tracer experiments are typically conducted in environmental chambers with reaction times on the order of minutes or hours. Because of the long reaction times, unwanted secondary chemistry may occur.

Using a high-pressure flow system and laser-induced fluorescence OH detection, Donahue et al.[4] reported the first direct observation of OH radical formation from ozonolysis. By combining highly sensitive measurement of OH radicals with low reactant concentrations and short reaction times (1−10 ms), many potential secondary sources of OH formation were excluded in these experiments. The flow systems also facilitated pressure-dependent studies spanning a pressure range of 2−400 Torr, with the upper limit determined by fluorescence quenching. A significant pressure dependence was observed for many acyclic alkenes between 10 and 400 Torr.[8,21]

Our objective is to investigate the pressure-dependent behavior of a series of alkenes and to understand the effects that molecular size and structure have on the production of OH and SCI. Consequently, we have considered four alkenes with differing sizes (C6 and C10) and structures (linear and cyclic). The alkenes used in this study are 2,3-dimethyl-2-butene (TME), cyclohexene, α-pinene, and *trans*-5-decene. As we shall see, this series is sufficient to elucidate the competing roles of size and structure in the generation of OH radicals and SCI. We also aim to expand the useful range of the high-pressure flow system in this context to atmospheric (∼500−760 Torr) to better understand tropospheric OH production from ozone−alkene reactions.

In these experiments, we used a radical scavenger (NO_2) rather than direct OH detection to measure OH yields. The advantage of NO_2 as a scavenger is that it scavenges *all* radical products, including the stabilized Criegee intermediate.[22,23] We are thus able to quench the ozonolysis chemistry effectively at the first stabilized compounds while producing unique tracers of the different pathways. Specifically, OH production appears as nitric acid formation, the extent of ozonolysis is preserved in the alkene consumption, and other organic fragments yield organic nitrates and nitrites.

2. Experimental Section

OH yield experiments are conducted in the Carnegie Mellon University high-pressure flow system (Figure 3), which consists of a stainless steel flow tube, 2 m long and 15 cm in diameter. The flow tube is equipped with an eight-pass White cell coupled to a 0.5-cm^{-1} FTIR (Oriel MIR 8000). The use of midrange FTIR allows for the investigation of pressures ranging from a few Torr to above atmospheric pressure. FTIR shows no loss in the signal-to-noise ratio as pressure changes; this is contrary to LIF measurements, which are subject to quenching and a decrease in signal to noise as pressure increases. Within the reaction zone, which is 90 cm long, species do not have time to diffuse to the wall. This makes the system essentially wall-less. Thus, possible heterogeneous reactions are eliminated.

Nitrogen is used as the carrier gas and is regulated by a 200-slpm flow controller (MKS). Flow velocity is approximated as the bulk flow rate and is typically 20 cm s^{-1}; thus, reaction times are approximately 4−5 s. The pressure of the system may be varied from less than 10 Torr to atmospheric pressure.

Alkene is injected at the beginning of the tube to ensure a uniform concentration. Alkene is introduced into the flow either by evaporating liquid into a stream of nitrogen or by directly mixing gas with the nitrogen carrier. Alkenes used in this study were 2,3-dimethyl-2-butene (98%, Fisher), cyclohexene (97.5%, Fisher), α-pinene (99%, Aldrich), and *trans*-5-decene (99%, Aldrich). Ozone is generated by passing O_2 through a high-voltage ozone generator (Pacific Ozone model L11). At maximum voltage, approximately 8% of the O_2 is converted to O_3. The O_2/O_3 mixture is then sent to the flow tube at a rate of about 5 slpm. The O_3 is present in excess to ensure complete removal of the alkene. NO_2 is added to the system as a radical scavenger. The flow of a 1% NO_2 (in nitrogen) mixture is controlled by a 5000-sccm flow controller (MKS). NO_2 is added in sufficient concentration to scavenge 60−90% of OH radicals produced by the alkene−ozone reaction. The OH−NO_2 reaction produces nitric acid ($HONO_2$), and we use this reaction to quantify the OH yield.[24] NO_2 also sequesters organic peroxy radicals (RO_2), forming peroxy nitrates,[23] and it also reacts with SCI, though the products are unknown. The presence of NO_2 and O_3 in the flow tube leads to the production of nitrate radicals (NO_3), which are also removed by NO_2.

The most likely products of the reaction between NO_2 and SCI fall into two classes. Stable nitrates or nitrites may form from the addition of NO_2 to the SCI in a reaction analogous to the formation of nitrates and peroxynitrates from the reactions of organic peroxy radicals with NO and NO_2. NO_2 may also abstract the terminal oxygen from the SCI, forming a nitrate radical and a carbonyl species. Understanding the product distribution from this SCI scavenging reaction is important in determining the OH yield. The following section of this article discusses the uncertainties and likely products of the NO_2−SCI reaction.

We use reaction modulation spectroscopy,[25,26] a technique that allows us to observe small changes (∼0.01−10%) in reactant and product concentrations. The flow of ozone is modulated on and off (actually upstream and downstream of the detection volume), and data are collected during both the on and off periods. Taking the ratio of the on to the off spectra gives a transmittance spectrum that directly shows any changes in absorption due to ozone modulation. This technique has been used previously to study a number of atmospherically relevant reactions, including reactions involving OH and O_3.[4,8,21,25,27]

Sample results for the reaction of O_3 with TME in the presence of NO_2 at 700 Torr are shown in Figure 4. The production of acetone and $HONO_2$ and the removal of TME are evident. N_2O_5 is produced by the reaction $NO_2 + NO_3$; therefore, the N_2O_5 concentration increases in the presence of

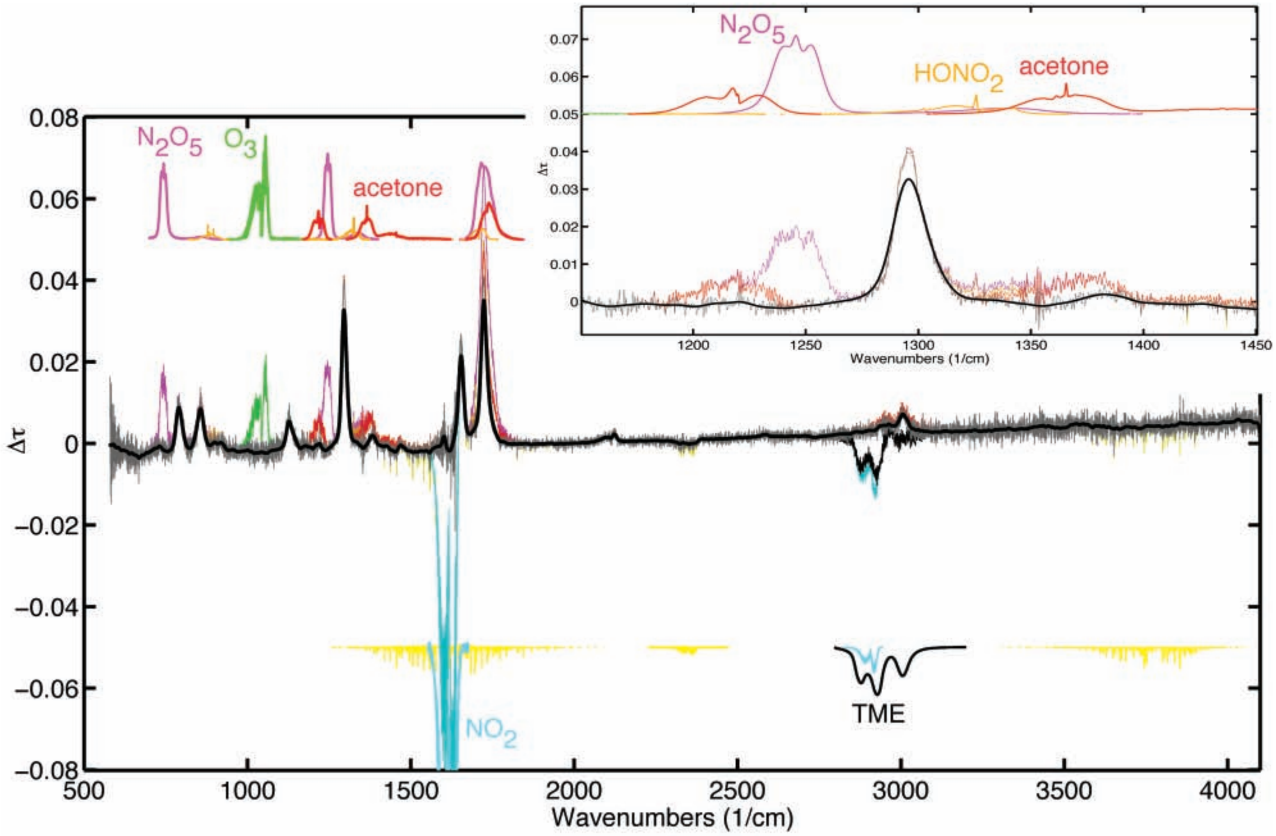

Figure 4. Differential transmittance spectrum of the ozone−TME−NO$_2$ reaction system at 700 Torr. The spectrum is the (average) ratio of spectra taken with ozone flow on and off. Analyzed signals are shown in various colors for products (above the raw data) and reactants (below the raw data). The residual after spectral subtraction is shown at two resolutions: in gray at 1-cm^{-1} resolution and in black at 16-cm^{-1} resolution. The inset shows nitric acid and acetone signals in the 1300-cm^{-1} region, including critical features of acetone at 1225 cm^{-1} and nitric acid at 1325 cm^{-1}.

ozone. The unidentified peaks at 790, 1300, and 1725 cm^{-1} are nitro-oxy peroxynitrates formed from the reaction of TME with NO$_3$ in the presence of NO$_2$.[28] Analysis of the residuals from several experiments shows that these peaks vary together, suggesting that they are all associated with a single species. The peaks at 860 and 1130 cm^{-1} are likely organic nitrates associated with the removal of other organic radicals by NO$_2$.[28]

The concept of this experiment is simple, but there are several complications. We believe the initial reaction is of the form

$$\mathrm{O_3 + alkene \rightarrow carbonyl + \alpha OH + \alpha R\bullet + (1-\alpha)SCI} \tag{R5}$$

indicating that a carbonyl is produced with unit stoicheometry, while the Criegee coproduct either decomposes into OH and a corresponding radical R•, with yield α, or is stabilized. The scavenging processes thus include

$$\mathrm{OH + NO_2 + M \rightarrow HONO_2 + M} \tag{R6}$$

$$\mathrm{R\bullet + NO_2 + O_2 \rightarrow RO_2NO_2} \tag{R7}$$

$$\mathrm{SCI + NO_2 \rightarrow unknown} \tag{R8}$$

If all of the OH reacts with NO$_2$, the yield of OH can be determined by comparing the ratio of nitric acid produced to the alkene consumed:

$$\mathrm{R} = \frac{\Delta[\mathrm{HONO_2}]}{-\Delta[\mathrm{alkene}]} \tag{1}$$

Complications arise when the scavenging of OH is incomplete, causing decreased nitric acid production and increased alkene consumption, and also when nitrate radicals react with the alkene. Also, any H atom production will appear as OH because H will be immediately titrated to OH given the vast excess of NO$_2$. We must account for all of these factors to infer an accurate OH yield. In practice, we correct for the fraction, F (less than 1), of OH radicals that react with NO$_2$ to form HONO$_2$ as well as the fraction, ρ, of alkene removed by ozone. Given these corrections, the pressure-dependent OH yield $\alpha(p)$ is found from eqs 2 and 1:

$$\alpha(p) = \frac{R}{\rho F} \tag{2}$$

Our objective is to observe any pressure dependence in the observed ratio (R) and relate this to the pressure dependence of prompt OH production.However, the pressure dependence of R may result from the pressure dependence of either the yield or the scavenging efficiency, as shown in eq 3; we can solve eq 2 for the observed ratio and differentiate:

$$R = \rho F\alpha \qquad \frac{\partial R}{\partial p} = \rho F\frac{\partial \alpha}{\partial p} + \rho\alpha\frac{\partial F}{\partial p} \tag{3}$$

Equation 3 assumes a constant value for ρ, the fraction of the alkene that reacts with O$_3$. This assumption is consistent with our experimental observations. However, the two terms in this equation could complicate our experiment.

To relate the pressure dependence of the observed ratio (R) more directly to the yield (α), we must eliminate any pressure dependence in the factor F; this ensures that any observed change in R is directly related to a change in the OH yield. The

TABLE 1: Alkene and NO_2 Concentrations Used in This Study

alkene	pressure (Torr)	[alkene] (molecule cm^{-3})	$[NO_2]$ (molecule cm^{-3})	$k_{NO_2}[NO_2]$ (s^{-1})	OH yield
TME	100	2.30×10^{14}	2.68×10^{15}	1.07×10^{4}	0.69
	200	1.80×10^{14}	2.14×10^{15}	1.07×10^{4}	0.86
	400	1.25×10^{14}	1.80×10^{15}	1.07×10^{4}	0.50
	700	1.25×10^{14}	1.54×10^{15}	1.07×10^{4}	0.48
	100	2.00×10^{14}	5.35×10^{15}	2.14×10^{4}	0.67
	200	1.80×10^{14}	4.28×10^{15}	2.14×10^{4}	0.81
	200	2.00×10^{14}	4.28×10^{15}	2.14×10^{4}	0.57
	400	1.33×10^{14}	3.56×10^{15}	2.14×10^{4}	0.50
	700	1.40×10^{14}	3.05×10^{15}	2.14×10^{4}	0.34
cyclohexene	100	1.77×10^{14}	2.68×10^{15}	1.07×10^{4}	0.55
	200	1.10×10^{14}	2.14×10^{15}	1.07×10^{4}	0.65
	400	7.57×10^{13}	1.80×10^{15}	1.07×10^{4}	0.72
	700	6.89×10^{13}	1.54×10^{15}	1.07×10^{4}	0.59
	100	1.47×10^{14}	5.35×10^{15}	2.14×10^{4}	0.56
	200	1.11×10^{14}	4.28×10^{15}	2.14×10^{4}	0.77
	200	9.92×10^{13}	4.28×10^{15}	2.14×10^{4}	0.74
	400	8.18×10^{13}	3.56×10^{15}	2.14×10^{4}	0.64
	700	5.58×10^{13}	3.05×10^{15}	2.14×10^{4}	0.65
α-pinene	100	8.65×10^{14}	5.35×10^{15}	2.14×10^{4}	0.81
	100	9.86×10^{14}	5.35×10^{15}	2.14×10^{4}	1.04
	200	6.47×10^{14}	4.28×10^{15}	2.14×10^{4}	0.93
	400	4.48×10^{14}	3.56×10^{15}	2.14×10^{4}	0.91
	700	2.69×10^{14}	3.05×10^{15}	2.14×10^{4}	0.90
	700	3.80×10^{14}	3.05×10^{15}	2.14×10^{4}	0.85
	400	1.48×10^{15}	7.17×10^{15}	4.25×10^{4}	0.83
	700	1.39×10^{15}	6.05×10^{15}	4.25×10^{4}	0.89
trans-5-decene	50	9.00×10^{13}	5.35×10^{15}	1.07×10^{4}	1.13
	100	5.50×10^{13}	2.68×10^{15}	1.07×10^{4}	0.81
	200	5.00×10^{13}	2.14×10^{15}	1.07×10^{4}	0.40
	400	5.25×10^{13}	1.80×10^{15}	1.07×10^{4}	0.00

TABLE 2: Rate Constants Used to Calculate Scavenging Efficiencies

alkene	k_{OH} (cm^3 $molecule^{-1}$ s^{-1})	k_{O_3} (cm^3 $molecule^{-1}$ s^{-1})	k_{NO_3} (cm^3 $molecule^{-1}$ s^{-1})
TME	110×10^{-12}	1130×10^{-18}	5.72×10^{-11}
cyclohexene	67.7×10^{-12}	81.4×10^{-18}	5.9×10^{-13}
α-pinene	53.7×10^{-12}	86.6×10^{-18}	6.16×10^{-12}
trans-5-decene	69×10^{-12a}	140×10^{-18a}	3.90×10^{-13b}

[a] For *trans*-4-octene. [b] For *trans*-2-butene.

scavenging efficiency (F) is defined in eq 4.

$$F = \frac{\int k_{NO_2}[NO_2][OH]\,dt}{\int k_{NO_2}[NO_2][OH]\,dt + \int k_{alkene}[alkene][OH]\,dt} \quad (4)$$

The rate constant for the OH−NO_2 reaction (k_{NO_2}) is pressure-dependent; thus, F may vary with pressure.[24] We eliminate the pressure dependence of F by maintaining a constant initial $k_{NO_2}[NO_2]$. Table 1 details the NO_2 concentrations used in this study to maintain constant values of $k_{NO_2}[NO_2]$.

The scavenging efficiency (F) and the fractional alkene removal by ozone (ρ) are calculated using known kinetic data for each of the alkenes studied. Table 2 presents the values of the rate constants used for calculating the OH yield. All values are from Atkinson.[23] Rate constants for the reactions of *trans*-5-decene with OH, O_3, and NO_3 are not available. In this case, we approximated k_{OH} and k_{O_3} as the values recommended for *trans*-4-octene and k_{NO_3} as the value recommended for *trans*-2-butene.

Kroll et al. observed time-dependent OH yields in ozone−alkene systems due to the thermal decomposition of SCI.[11] Because earlier scavenger studies did not include an SCI scavenger, the yields reported in those studies are a combination of prompt OH formation with that derived from the thermal decomposition of the SCI. Our objective is to scavenge any SCI with NO_2 and thus isolate prompt OH production. Using RRKM/master equation calculations, Kroll et al.[11] determined a first-order decomposition rate for $(CH_3)_2COO$ formed in the ozone−TME reaction of approximately 3 s^{-1} and predicted slower decomposition rates for more highly substituted SCI. SCI are known to react with a number of atmospheric trace species, and Atkinson and Lloyd[22] proposed NO_2 as one such scavenger. Assuming that $k_{SCI-NO_2} \approx 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for the $(CH_3)_2COO-NO_2$ reaction,[22,10] the lifetime of SCI with respect to NO_2 reaction is $\sim 10^{-2}$ s in our system. This lifetime is approximately an order of magnitude less than the thermal lifetime of $(CH_3)_2COO$ (~300 ms).[11] Thus, the presence of NO_2 ensures that our results are not influenced by OH formed from the decomposition of SCI.

3. SCI Removal by NO_2

Though several potential scavengers of SCI have been discussed in the literature, the products of SCI scavenging reactions are not well constrained by experimental observations. Notably, Fenske et al.[10] observed the formation of a secondary ozonide (SOZ) from the reaction of acetaldehyde with SCI formed from *trans*-2-butene ozonolysis, determining a rate constant on the order of 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for this reaction. Hasson et al.[13,14] observed the formation of hydroxy-

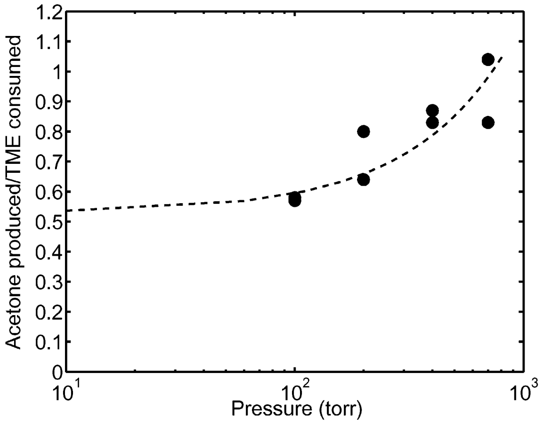

Figure 5. Acetone yield increases with pressure, rising from a low-pressure value of approximately 0.5 (consistent with model results showing that approximately 50% of the TME reacts with ozone, producing acetone, and the remainder reacts with NO_3, producing organic nitrates). The dashed line shows a linear fit to the data. This strong increase is consistent with a reaction of stabilized Criegee intermediates (SCI) with NO_2 to produce NO_3 and acetone. It thus indicates that SCI formation is strongly pressure-dependent.

methyl hydroperoxide from the reaction of water with SCI formed from several different alkenes. Rickard et al.[7] observed enhanced carbonyl production from ozonolysis reactions conducted in the presence of SO_2 and attributed the excess carbonyl to the SCI + SO_2 reaction. The reaction of SCI with NO_2 is not well characterized,[10,22] though we can postulate two likely sets of products—nitrates (or nitrites) from an addition reaction or NO_3 and a carbonyl[22] from the transfer of the terminal oxygen from the SCI to NO_2.

It is critical to the work presented here that NO_2 can scavenge the SCI and that the products of this scavenging reaction differ from the products that would otherwise result from unimpeded reactions of the SCI. Specifically, OH production from the SCI must be inhibited. Given the lack of direct observations of the SCI−NO_2 reaction, we turn to trends in our own data and quantum mechanical calculations to gain insight into the likely products, using the ozonolysis of TME as an example.

The Criegee intermediate is produced in tandem with a carbonyl species, as shown in R2. In the ozonolysis of TME, this carbonyl coproduct is acetone, which is readily identified in the FTIR spectrum. According to the Criegee mechanism, the decomposition of the primary ozonide (R2) should be the sole source of acetone in TME ozonolysis. Thus, the ratio of acetone production to TME consumption should remain constant as the system pressure changes. This assumption comes with the caveat that the fraction of TME removed by ozone remain a constant as pressure changes because TME loss from reaction with NO_3 or OH does not lead to acetone production. The experiments conducted in this study maintained a constant fractional removal of TME by ozone by design.

Figure 5 shows the observed acetone/TME ratio as a function of pressure for the experiments conducted in this study. The ratio clearly increases, by nearly a factor of 2, as pressure increases from 100 to 700 Torr. The low-pressure value of approximately 0.5 is consistent with model results predicting approximately 50% consumption of TME by ozone to form acetone, and the remainder reacts with NO_3, producing organic nitrates. This increase in the acetone/TME ratio can be explained only by acetone production from a reaction other than the TME−ozone reaction.

It is possible that this additional acetone comes from the SCI + NO_2 reaction. To better constrain the likely rate constant and products of this reaction, we have completed a low-level scan of the reaction potential energy surface using density functional theory (B3LYP) and a modes basis set (6-31G(d,p)). To simplify the calculation, we have considered the simpler reaction

$$CH_2OO + NO_2 \rightarrow \text{products}$$

We have considered three possible reaction pathways, initially looking for stable adducts in each case: addition of the NO_2 nitrogen to the terminal oxygen of the carbonyl oxide and addition of either the O or N in NO_2 to the carbon atom. We found that all three addition reactions are effectively barrierless, with transition states lower in energy than the reagents (without zero-point corrections). This is consistent with a very fast SCI + NO_2 reaction and gives us confidence in our previous assumption of the rate constant for the $(CH_3)_2COO-NO_2$ reaction ($k_{SCI-NO_2} \approx 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}). Furthermore, at least two of the pathways lead to carbonyl + nitrate radical products. When NO_2 attacks the terminal oxygen of the SCI, it directly abstracts this oxygen to form the nitrate radical, but when an oxygen of NO_2 adds to the central carbon atom, the resulting intermediate decomposes over a very low barrier into the same products, as shown in Figure 6.

The simplest model of this reaction, using phase space theory, is that each unique interaction of NO_2 with the SCI is equally probable. There are four such interactions here: each oxygen in NO_2 can add to the SCI carbon, and the nitrogen in NO_2 can add to either the SCI carbon or terminal oxygen. Three of these lead to carbonyl + NO_3, so it is reasonable to conclude that these are the major products of this reaction, which is also likely to be quite fast. This is consistent with the increased acetone yield shown in Figure 5. None of the three reaction pathways considered here directly produce OH, and it is therefore reasonable to assume that the SCI + NO_2 reaction is not a significant source of OH radicals.

Although the removal of SCI by NO_2 is a significant source of carbonyl species, this reaction is not a significant source of nitrate radicals in this study. The nitrate radical budget is dominated by formation in the O_3 + NO_2 reaction and removal via reaction with NO_2 or the alkene. The negligible contribution of the SCI + NO_2 reaction to the NO_3 budget ensures that the fractional removal of alkene by O_3 is independent of the extent of SCI formation. Were this not the case, the interpretation of Figure 5 would be more difficult because the ratio of TME removal by O_3 and NO_3 would evolve with CI stabilization. However, we can think of no interpretation of the strong pressure dependence shown in Figure 5 that does not lead to the conclusion that SCI formation is a strong function of pressure in this system.

4. Results

Measured OH yields for the ozonolysis of TME, *trans*-5-decene, cyclohexene, and α-pinene are plotted versus pressure in Figure 7. Experiments were typically performed at two different values of $k_{NO_2}[NO_2]$, usually differing by a factor of 2 for each pressure sampled (Table 1). In all cases, there is no significant dependence of the OH yield on $k_{NO_2}[NO_2]$. Ideally, the total correction factor $1/(\rho F)$ would be kept low, below 1.5, to minimize the propagation of error from this correction. In practice, the relative OH, O_3, and NO_3 rate constants are more favorable sometimes than others. Consequently, the magnitude of the total correction factor varied from ~1.5 for TME to ~7 for α-pinene. Only at the lowest $k_{NO_2}[NO_2]$ for α-pinene (not shown), where the correction factor reached 15, did the

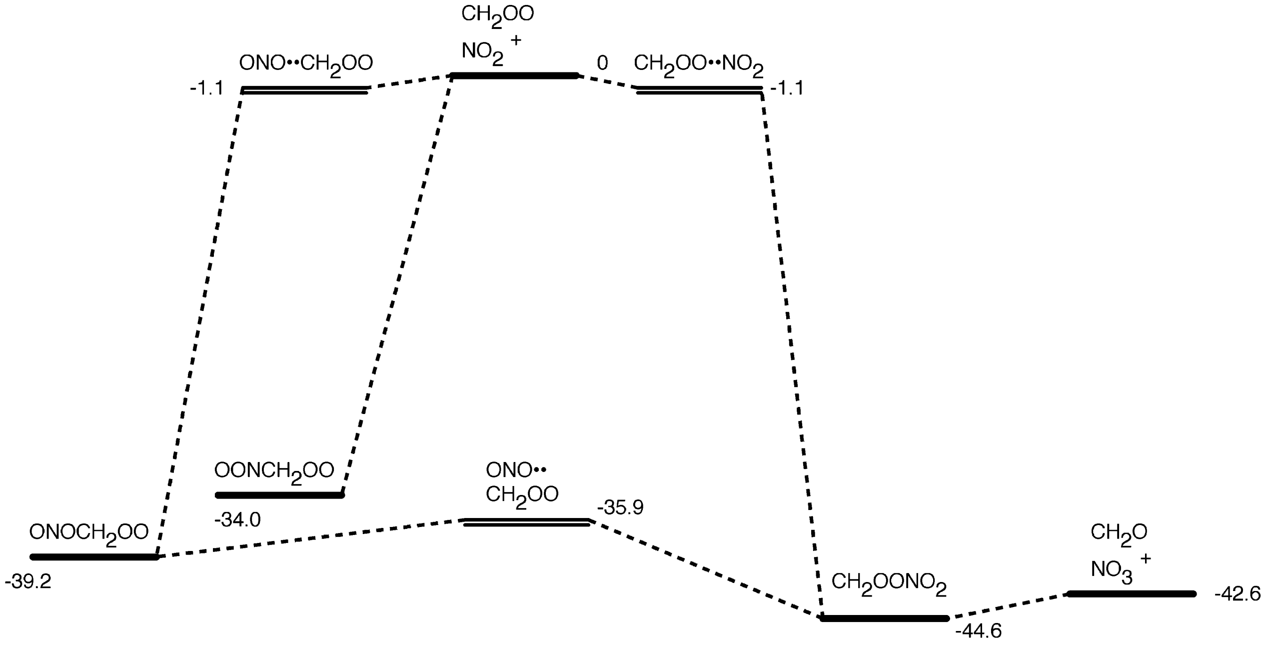

Figure 6. Potential energy surface for the reaction $CH_2OO + NO_2 \rightarrow$ products computed at the B3LYP/6-31G(d,p) level of theory. Energies are in kcal/mol relative to the reactants ($CH_2OO + NO_2$) shown at center top. No zero-point energies have been added. Transition states are indicated with a double horizontal line, and stable species with a single thick line. All of the reactions are essentially barrierless. $NO_3 + CH_2O$ is produced in two ways: directly by O atom abstraction from CH_2OO and indirectly via a nitrite intermediate. Given two identical pathways for the ONO−CH_2OO reaction (leftmost), roughly three-fourths of the reactive flux is likely to yield $NO_3 + CH_2O$.

correction clearly break down. We are thus confident of the other values.

The OH yield for TME (Figure 7) decreases with increasing pressure over the entire sampled range (100−700 Torr). The yield decreases from approximately 0.70 at 100 Torr to 0.35 at 700 Torr. The agreement between the data taken at different values of $k_{NO_2}[NO_2]$ shows that the calculated OH yield does not depend on the efficiency of OH removal by NO_2. The consistency between the two data sets is also further proof that the reaction mixture contains sufficient NO_2 to scavenge all SCI. Failure to scavenge all SCI would result in OH yields that change with NO_2 concentration because the decomposition of SCI produces OH.

Trans-5-Decene, which like TME is a straight-chain alkene, also displays a pressure-dependent OH yield (Figure 7). The absolute value of the yield is uncertain because of uncertainties in k_{OH}, k_{O_3}, and k_{NO_3}, which are not available for this alkene. Solely on the basis of the appearance of the Figure, it seems likely that the reported yields are systematically high by at least a factor of 2, but independent verification will require additional rate constant data. According to the Criegee mechanism, each CI that isomerizes to a vinyl hydroperoxide can produce a single OH radical.[9] This imposes a maximum OH yield of unity for any given alkene. The nitric acid signal at 400 Torr was indistinguishable from the noise in the spectrum, but the OH yield may be as high as 0.40 at this pressure. The key result, however, is that this alkene shows a strong pressure dependence in OH yield over the sampled pressure range (50−400 Torr).

The OH yields from the ozonolysis of cyclohexene and α-pinene are pressure-independent. Experimental results are plotted in Figure 7, along with the average yield for the sampled pressure range. We determined an OH yield of 0.64 ± 0.20 for cyclohexene and 0.89 ± 0.20 for α-pinene. The relative rate constants for the reactions of α-pinene with O_3, OH, and NO_3 favor the use of higher NO_2 concentrations for this alkene. At $k_{NO_2}[NO_2] = 1.07 \times 10^4$, the correction factor for calculating the OH yield reaches 15. Increasing the NO_2 concentration reduces the correction factor to a more reasonable value.

5. Discussion

5.1. Relation to Other Laboratory Experiments. Our experimental results show that OH is formed in the reaction of ozone with the selected alkenes. We observed pressure-dependent OH formation for TME and *trans*-5-decene and pressure-independent OH formation from α-pinene and cyclohexene, which both contain endocyclic double bonds. The pressure-dependent OH yield from TME ozonolysis is qualitatively consistent with the findings of Kroll et al.[21] The pressure-dependent results are well described by increased formation of SCI at higher pressure. The current results extend the range of pressure-dependent measurements to ∼1 atm of pressure.

A separate study by Fenske et al.[6] reported a pressure-independent OH yield from the TME−ozone reaction. However, this study did not use any sort of scavenger to remove SCI from the system. Our results are consistent with the argument presented by Kroll et al.; for these linear alkenes, SCI decomposition leads to OH radical formation.[11] It is important to separate these yields because the SCI is vulnerable to scavenging; however, the extent of SCI scavenging in the atmosphere remains unclear.

Kroll et al.[11] proposed that the stabilized $(CH_3)_2COO$ formed in TME ozonolysis has a thermal lifetime of 300 ms. Previous flow system studies by Kroll et al.[8,21] and Donahue et al.[4] used laser-induced fluorescence to directly observe OH approximately 10 ms after the initiation of the ozonolysis reaction. The short reaction times eliminated SCI decomposition as an OH source. In this study, the SCI lifetime with respect to NO_2 scavenging is approximately 10 ms. The reaction of NO_2 with SCI severely limits OH production from SCI decomposition and allows the observance of a pressure-dependent OH yield for linear alkenes. The tracer studies of Fenske et al.[6,29] and others[7,20,30,31] do not employ a scavenger, making unimolecular decomposition the primary sink for SCI. The results of these

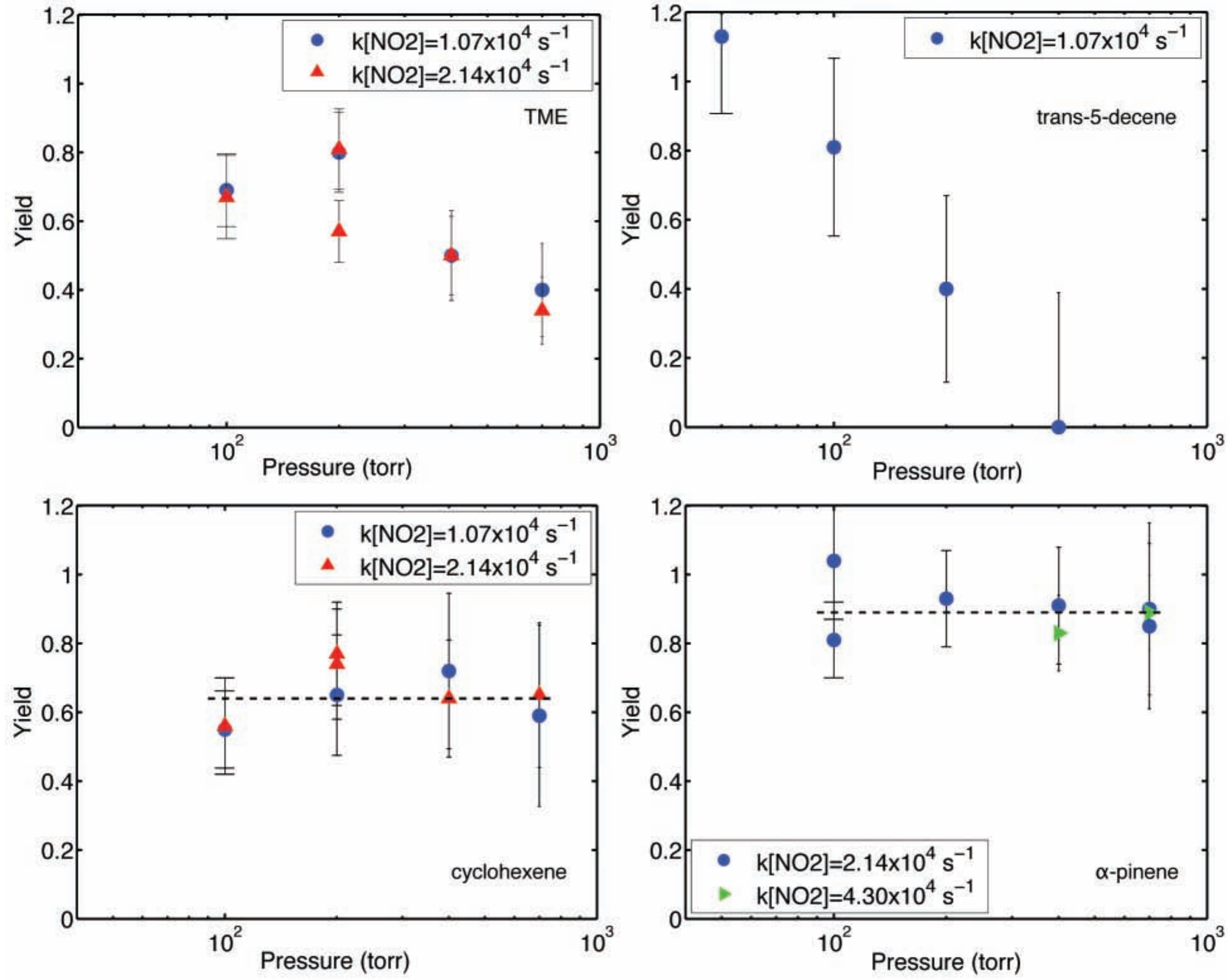

Figure 7. OH yields from the ozonolysis of 2,3-dimethyl-2-butene (TME), *trans*-5-decene, cyclohexene, and α-pinene vs pressure. Error bars show the precision of the spectral recovery for nitric acid and the alkene. TME and *trans*-5-decene show a strong pressure dependence, but cyclohexene and α-pinene show large OH yields with no pressure dependence. This is consistent with the collisional stabilization of modestly excited Criegee intermediates produced when a primary ozonide (POZ) fragments following ozonolysis of a linear alkene but no stabilization of the extremely (and uniformly) excited solitary intermediate produced after ozonolysis of endocyclic alkenes.

tracer studies are therefore influenced by OH produced via SCI decomposition.

Johnson et al.[33] investigated the effects of several SCI scavengers on OH production from the ozonolysis of 2-methyl-2-butene in a series of tracer experiments. OH production was shown to be independent of tracer concentration, and upper limits (in cm^3 $molecule^{-1}$ s^{-1}) for the bimolecular scavenger−SCI rate constant were determined for H_2O (1×10^{-16}), SO_2 (4×10^{-15}), butanone (2×10^{-14}), and acetic acid (1×10^{-14}). These upper limits are considerably slower than the acetaldehyde−SCI rate constant determined by Fenske et al. (1×10^{-12} cm^3 $molecule^{-1}$ s^{-1})[10] and the NO_2−SCI rate constant assumed in this work (1×10^{-13} cm^3 $molecule^{-1}$ s^{-1}).[10,22] Clearly, NO_2 is a more efficient SCI scavenger than the species considered by Johnson et al.[33] The fast NO_2−SCI reaction allows us to separate prompt OH formation from OH formed via thermal decomposition of SCI.

The pressure-dependent OH yield from *trans*-5-decene ozonolysis is reported here for the first time. OH formation in the reaction of *trans*-5-decene with ozone is consistent with the trend observed in a series of homologous alkenes. OH yields from the reaction of ozone with *trans*-2-butene, *trans*-3-hexene, and *trans*-4-octene were all previously observed to be pressure-dependent.[8] The pressure dependence for *trans*-5-decene is more pronounced than for TME. Nitric acid formation (and therefore OH production) is undetectable at pressures of 400 Torr and above. This indicates that there is greater collisional stabilization of the five carbon CI formed in the ozonolysis reaction.

TABLE 3: OH Yields from Cycloalkenes

alkene	pressure (Torr)	OH yield	ref
cyclohexene	400−700	0.64 ± 0.20	this work
	760	0.54 ± 0.13	29
	760	0.54 ± 0.08	32
	760	0.68, +0.34−0.22	18
α-pinene	400−700	0.89 ± 0.20	this work
	760	0.85	17
		0.76 ± 0.11	19
		0.70 ± 0.17	20
		0.83	7
		0.91 ± 0.23	34

Table 3 presents a summary of OH yield measurements for cyclohexene and α-pinene. Our results compare well with findings from a number of other scavenger studies conducted at atmospheric pressure. The pressure independence of the OH yield from cyclic alkenes was also discussed in recent work from this research group.[35]

The pressure-independent OH yields from cyclohexene and α-pinene indicate that SCI formation in these systems is also independent of pressure. This pressure independence arises from the allocation of energy upon the decomposition of the high-energy primary ozonide. Using master equation calculations, Kroll et al.[11] showed that CIs from linear alkenes are formed with a statistical distribution of energies. The work proposes that some CIs are actually formed cold, without sufficient energy to generate OH promptly.

Alkenes with endocyclic double bonds behave differently. Decomposition of the primary ozonide results in a single species that is "tethered" by a carbon chain. This carbonyl-CI contains all of the reaction energy; the energy distribution for the formation of this CI is essentially a δ function. This makes CI formed from cyclic alkenes difficult to stabilize without going to very high pressures or very large carbon numbers.[35]

A tracer study by Fenske et al.[6] observed a pressure-independent OH yield for cyclopentene ozonolysis. Our results for cyclic alkenes agree well because of the low yields of SCI for these cyclic species. The OH yields for both cyclopentene and cyclohexene are truly pressure-independent, and SCI formation is of minor importance at all sampled pressures. The tracer results are therefore not influenced by SCI decomposition and reflect an accurate measure of the OH yield.

5.2. Atmospheric Implications. These results show clearly that a large fraction of Criegee intermediates are collisionally stabilized at atmospheric pressure. Our experimental procedure is completely independent of the laser-induced fluorescence measurements reported by Kroll and one of the current authors (N.M.D.)[4,8,21] but yields a consistent result. Specifically, a large fraction of Criegee intermediates with three or more carbons (starting with the $(CH_3)_2COO$ intermediate produced from TME ozonolysis) are collisionally stabilized in the atmosphere and thus exist for at least a short time as SCI. It appears that, at least under conditions typical of most chamber experiments, the syn-SCIs thought to exhibit large OH yields subsequently decompose before bimolecular reactions can scavenge them.[6,7,13] However, we need to proceed with great caution before assuming that this conclusion applies to the atmosphere as a whole. Specifically, all competitive bimolecular reactions will have very low barriers and a correspondingly modest temperature dependence (as in the NO_2 + SCI case explored in this work). The unimolecular pathways, on the other hand, all have very substantial barriers and a correspondingly large temperature dependence. Consequently, we expect a very strong temperature dependence to the branching ratio of any competition, with the bimolecular pathway being favored at low temperatures. It is imperative that the temperature dependence of this competition be fully explored before broad conclusions about the atmospheric role of stabilized Criegee intermediates are drawn.

6. Conclusions

We have observed OH production from ozone−alkene reactions over a wide range of pressure using NO_2 as a radical scavenger. The scavenger is unique in that it removes both OH radicals and SCI from the reaction mixture, allowing for the quantification of the pressure dependence of the OH yield. The linear alkenes used in this study (TME and *trans*-5-decene) exhibited pressure-dependent OH yields consistent with theory and previous experimental observations. The OH yields from cyclohexene and α-pinene, both alkenes with an endocyclic double bond, were pressure-independent and consistent with previous studies. The behavior of all species considered in this study can be explained by the formation of SCI. For linear species, SCI production increases as the pressure increases, leading to reduced OH formation. Cyclic species produce only small amounts of SCI at the sampled pressures and therefore exhibit a pressure-independent OH yield.

Experimental and computational evidence shows that the reaction of NO_2 with any SCI produced in our experiments produces NO_3 and a carbonyl species in high yield. This influences the interpretation of data based on carbonyl production (as opposed to alkene consumption) and also demonstrates a facile SCI scavenging reaction.

This work illustrates the importance of separating prompt OH formation from OH formed via SCI decomposition. The use of an SCI scavenger such as NO_2 is one way to remove SCI from the system. Failure to account for SCI decomposition leads to an overestimation of the OH yield for species that exhibit pressure-dependent behavior. Using the tracer method to determine OH yields from ozone−alkene reactions is therefore inaccurate when applied to systems that display pressure-dependent OH yields.

The atmospheric implications of these findings remain uncertain. It is clear, however, that a substantial fraction of Criegee intermediates capable of generating OH radicals go through a collisionally stabilized state before continuing on to produce those OH radicals. They are thus vulnerable to removal by sufficiently aggressive scavengers, with possible significance to atmospheric radical production.

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