Mechanism of HO\(_x\) Formation in the Gas-Phase Ozone—Alkene Reaction. 1. Direct, Pressure-Dependent Measurements of Prompt OH Yields†

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The gas-phase reaction of ozone with alkenes is known to be a dark source of HO\(_x\) radicals (such as OH, H, and R) in the troposphere, though the reaction mechanism is currently under debate. It is understood that a key intermediate in the reaction is the carbonyl oxide, which is formed with an excess of vibrational energy. The branching ratios of the ozone—alkene reaction products (and thus HO\(_x\) yields) depend critically on the fate of this intermediate: it may undergo unimolecular reaction (forming either OH or dioxirane) or be collisionally stabilized by the bath gas. To investigate this competition between reaction and quenching, we present direct, pressure-dependent measurements of hydroxyl radical (OH) yields for a number of gas-phase ozone—alkene reactions. Experiments are carried out in a high-pressure flow system (HPFS) equipped to detect OH using laser-induced fluorescence (LIF). Hydroxyl radicals are measured in steady state, formed from the ozone—alkene reaction and lost to reaction with the alkene. Short reaction times (usually ~10 ms) ensure negligible interference from secondary and heterogeneous reactions. For all substituted alkenes covered in this study, low-pressure yields are large but decrease rapidly with pressure, resulting in yields at 1 atm which are significantly lower than current recommendations and indicating the important role of collisional stabilization in determining OH yield. The influence of alkene size and degree of substitution on pressure-dependent yield is consistent with the influence of collisional stabilization as well as the accepted reaction mechanism.

Introduction

The gas-phase reaction of ozone and alkenes has received considerable attention in recent years due to its unique potential as a dark source of tropospheric HO\(_x\) radicals. Over the past decade, numerous indirect scavenger studies\(^1\)–\(^8\) have provided strong evidence for significant hydroxyl (OH) radical formation from this class of reaction. Recently our laboratory presented the first direct evidence of prompt OH formation, using laser-induced fluorescence to detect OH in the reaction mixture.\(^9\) The amount of hydroxyl radical formed from such reactions is thought to be important in the atmosphere: it has been shown that measured yields are substantial enough to be a significant, even dominant, contributor of total HO\(_x\) in rural and urban environments.\(^10,11\)

The mechanism by which OH is believed to be formed is shown in Figures 1 and 2. Ozone adds to the alkene (reaction R1) to form a vibrationally excited primary ozonide, which quickly dissociates (R2) into a carbonyl oxide (the Criegee intermediate) and a carbonyl species. If the substituents on either side of the alkene double bond are different, this dissociation has two possible sets of products.

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Figure 1. Criegee mechanism of carbonyl oxide formation: ozone—alkene cycloaddition (R1) and subsequent dissociation (R2) to form the carbonyl oxide.

Figure 2. Unimolecular reaction channels available to the substituted carbonyl oxide: isomerization (R3a) to an excited hydroperoxide, which will quickly dissociate (R3b) to OH or ring closure to form dioxirane (R4).

The vibrationally excited carbonyl oxide may react via further unimolecular reactions or be collisionally stabilized by the bath gas. There are two primary reaction pathways, dissociation to OH (R3) and ring closure to dioxirane (R4),\(^12,13\) as shown in Figure 2 for a substituted carbonyl oxide. OH formation takes place via an excited hydroperoxide intermediate, which is formed via a five-membered transition state. The fate of the
dioxirane, which is also formed with excess vibrational energy, is not clear. If the carbonyl oxide is unsubstituted (that is, the methyl group is replaced by an H), OH will form not via a hydroperoxide but rather in a single concerted step. This step occurs via a four-membered transition state and so has a higher barrier to reaction; accordingly, the degree of substitution is expected to play an important role in OH yield.

Thus far, most OH yield measurements have relied on the use of a radical scavenger added to the reaction mixture. Most such experiments are performed in environmental chambers, and due to the slow rate of reaction between ozone and alkene, they are carried out over long periods of time, typically several minutes to hours. Thus, unwanted secondary chemistry may interfere. In these studies, OH yield is determined in one of two ways: either from the yield of a product of the OH-scavenger reaction (such as production of cyclohexanone from \( \text{OH} + \text{cyclohexane} \) and cyclohexanol\(^{2,3} \)) or from the decrease in the scavenger concentration.\(^{5,7,8} \) A third tracer technique, in which OH yield is determined by the change in rate of alkene loss when a scavenger is added to the system, has been recently introduced.\(^6 \) In all scavenger studies save one\(^{15} \) (which is believed to have significantly underestimated experimental error\(^ {6,8} \)), the loss of scavenger or formation of products is consistent with production of OH. Yield results from various studies are generally in good agreement; for a comprehensive list of OH yield measurements see Paulson et al.\(^5 \)

Recently we reported the first direct observation of OH radicals from the ozone–alkene reaction.\(^9 \) Radicals were detected using laser-induced fluorescence (LIF) and were measured in steady state, so that no tracer was necessary. In that experiment, OH was detected only 50 ms after reaction initiation, thus minimizing interference by secondary reactions. Formation of OH by secondary reactions could not be entirely ruled out, but prompt formation was suggested by the fact that for one reaction, \([\text{OH}]\) remained linear with \([\text{O}_3]\) down to low ozone concentrations. OH production has since been confirmed using a different spectroscopic technique.\(^{16} \)

While our previous study unequivocally confirmed OH as a product of the ozone–alkene reaction, the pressure range was low (4–6 Torr). In this study we extend the OH yield measurements up to hundreds of Torr, allowing for extrapolation to atmospheric pressures with much less uncertainty. Yields presented here are also considerably more precise than those presented before, and reaction times are significantly shorter, so the influence of secondary reactions is negligible. In addition, in our previous study we reported detecting H atoms by resonance fluorescence (RF); here we have calibrated our RF measurement and therefore present H-atom yields as well.

Our objective is to understand the role of collisional stabilization in OH production, including the influence of substitution on the carbonyl oxide. Consequently, we have selected a series of symmetric alkenes whose reaction pathways are as simple as possible. In all cases only a single carbonyl oxide is produced, though in some cases stereoisomers may play a role. The alkenes in this study are ethene, which produces an unsubstituted carbonyl oxide; \( \text{trans}-2\text{-butene}, \text{trans}-3\text{-hexene}, \) and \( \text{trans}-4\text{-octene} \), which produce monosubstituted carbonyl oxides; and 2,3-dimethyl-2-butene (also called tetramethylethylene, or TME) and 3,4-dimethyl-3-hexene, which produce disubstituted carbonyl oxides. As we shall see, this series is sufficient to elucidate and separate the competing roles of size and substitution on collisional stabilization and OH production.

**Experimental Section**

As reported previously,\(^9 \) we observe radicals in the steady state. OH and H are formed in the ozone–alkene reaction (with yields of \( \alpha \) and \( \beta \), respectively) and are lost to reaction with the alkene:

\[
\text{O}_3 + \text{alkene} \rightarrow \alpha \text{OH} + \beta \text{H} + \text{products} \quad (R5)
\]

\[
\text{OH} + \text{alkene} \rightarrow \text{products} \quad (R6)
\]

\[
\text{H} + \text{alkene} \rightarrow \text{products} \quad (R7)
\]

When reaction R5 is the sole source and reaction R6 the sole sink of OH, the steady-state concentration of OH is

\[
[\text{OH}]_{ss} = \frac{k_{\text{OH}} [\text{O}_3]}{k_{\text{OH}} - k_{\text{OH}}} \quad (1)
\]

where OH concentration is linear with ozone concentration but independent of alkene. Therefore, a yield may be obtained by a single ozone and radical measurement. However, it is more precise to take a derivative approach:

\[
\alpha = \frac{k_{\text{OH}} [\text{OH}]}{k_{\text{O}_3}} \frac{d[\text{OH}]}{d[\text{O}_3]} \quad (2)
\]

We take the latter approach in this study, obtaining yields by measuring steady-state radical concentrations at a number of ozone concentrations. This approach is also useful in that it provides a check on our understanding of the OH chemistry: nonlinearities or nonzero intercepts in \([\text{OH}] vs [\text{O}_3] \) suggest additional chemistry not included in reactions R5 through R7. The H-atom yield \( \beta \) may be found using steady-state equations similar to eqs 1 and 2.

For the above equations to hold, a number of experimental conditions must be met. The first is that the radicals must be observed in the steady state. Since the alkene serves as the radical sink and thus controls the approach to steady state, this condition can be met by using a high concentration of alkene. In addition, it is necessary that the above reactions (R5–R7) completely describe the chemistry of OH and H in the system. Even in a simple \( \text{N}_2/\text{O}_2/\text{O} \) environment, there exist numerous additional sources and sinks of OH, including

\[
\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 \quad (R8)
\]

\[
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad (R9)
\]

\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad (R10)
\]

\[
\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \quad (11)
\]

All of these may be safely neglected so long as all OH and H radicals react with alkene only. Thus, for this study large alkene concentrations and small ozone concentrations are required.

However, this does not necessarily eliminate all interferences from secondary chemistry. Sources of OH (or H) that are independent of \([\text{O}_3] \), such as bimolecular reactions of stabilized intermediates, may still exist. Thus there is the additional requirement that radicals formed via reaction R5 only be formed from unimolecular decomposition of the vibrationally excited intermediates (via reactions 1–4) and not by intermediate bimolecular channels; this may be accomplished by making the experimental time scale as small as possible.

Flow systems, in which experimental time scales are controlled by flow velocity, are well-suited for such measurements. The high-pressure flow system (HPFS) used in this study was
lyzed. Here major features of the system necessary for yield are
 studied by varying the voltage through the oxygen; at maximum
 pressure, flow velocities are typically smaller (down to 1 m/s).

 Controller but by the valve to the vacuum pump, so that at higher
 pressures, flows. Thus the UV cell is placed near the end of
 the tube; this requires that by the time alkene is injected into
 the flow, the ozone profile has stopped evolving, so that the
 [O₃] in the reaction zone equals that further downstream. In
 other words, the ozone must be of uniform radial concentration;
 using the UV cell we have verified that in the reaction zone
 this is the case, over a wide range of experimental conditions.

 Alkene is injected into the center of the flow via a quartz
 injector, located 2.4 m downstream of the beginning of the tube.
 As mentioned above, high alkene concentrations are generally
desired; however, care is taken that flow through the alkene
 injector is not so high as to interfere with the flat ozone profile
 (see ref 19). Alkenes used in this study were ethene (99.5+/-%,
 Matheson); trans-2-butene, 2,3-dimethyl-2-butene, trans-3-
 hexene (all 99+/-%, Aldrich); 3,4-dimethyl-3-hexene (99+/-% cis/
 trans, Chemsampco); and trans-4-octene (90+/-%, Aldrich). We
do not measure alkene concentration directly, but it may be
 estimated on the basis of flows through calibrated flow
 controllers; a typical alkene concentration in the flow tube is
 10¹⁵–10¹⁶ molecules/cm³.

 Hydroxyl radicals are detected using laser-induced fluorescence
 (LIF), 5–10 cm (corresponding to 5–10 ms) downstream of the
 alkene injector. While at this point the alkene is a plume,
 the alkene is well-mixed within the very small volume of the
 LIF measurement. LIF detection of OH is discussed in ref 23,
 and its adaptation for the HPFS is described in ref 18. A
 frequency-doubled, tunable dye laser pumps the A²Σ⁺ (ν = 1)
 ← X²Π (v = 0) transition in OH (at 282.2 nm). Some of the
 excited OH fluoresces back to the ground state, but most is
 collisionally stabilized to the ν = 0 state and then fluoresces or
 is collisionally stabilized to the ground state. This red-shifted
 fluorescence at 309 nm is measured using a PMT (Hamamatsu)
 placed normal to the laser beam. A photodiode placed at the
 end of the beam monitors average UV laser power. The PMT
 signal, corrected for undercounting and scaled by average
 power, yields a signal which is proportional to OH number
 density. The LIF axis used in this experiment is more sensitive
 than previous HPFS designs, due to better optical filters (Omega
 Optical) as well as a wider solid angle.

 To measure the H-atom yield, we replace the LIF detection
 axis with a resonance fluorescence (RF) detection axis. Measure-
 ment of H atoms in the HPFS is described in detail in ref 17.
 A sealed lamp consisting of UH₃ in Ne is heated and subjected
to an rf plasma, sending Lyman-α (121.6 nm) light into the
 tube, again normal to the flow. H atoms in the flow absorb the
 Lyman-α light, and a PMT perpendicular to the lamp monitors
 the subsequent fluorescence; the fluorescence signal is then
 scaled by the lamp power, measured by a photodiode opposite
 the lamp.

 Both the LIF and RF have been calibrated by titrating NO₂
 in an excess of H atoms:

 \[ \text{NO}_2 + \text{H} \rightarrow \text{OH} + \text{NO} \]  \hspace{1cm} (R12)

 Trace amounts (10⁸–10¹¹/cm³) of NO₂ in the HPFS are
 maintained in an advective steady state through the addition of
 a standard NO₂/He mixture, determined to be 36.4 ppm NO₂
 by FTIR spectroscopy. The NO₂ is well-mixed by the time it
 pressure in the cell to obtain [O₃] in the tube. In a separate
 HPFS, we have compared concentrations obtained using this
 technique with FTIR measurements; concentrations agree to
 within a few percent over a wide range of pressures.

 Since this is a bulk sampling technique, measurements cannot
 be made from within the reaction zone without the risk of
 interfering with the radical concentrations, spectroscopic mea-
surements, or flows. Thus the UV cell is placed near the end
 of the tube; this requires that by the time alkene is injected into
 the flow, the ozone profile has stopped evolving, so that the
 [O₃] in the reaction zone equals that further downstream. In
 other words, the ozone must be of uniform radial concentration;
 using the UV cell we have verified that in the reaction zone
 this is the case, over a wide range of experimental conditions.
reaches the reaction zone, and its concentration is calculated on the basis of the measured flows. Our H-atom source, described elsewhere,\textsuperscript{17} is essentially a H\textsubscript{2}/He/Ar mixture sent through a microwave plasma and injected as a plume into the center of the flow through a quartz injector. We verify that NO\textsubscript{2} is titrated by changing [H] within the plume and finding no change in LIF signal. Calibrations are performed by modulating NO\textsubscript{2} flow (and thus concentration); the calculated NO\textsubscript{2} concentration is equal to loss of H and formation of OH, so we may correlate our change in RF and LIF signals with concentration.

Calibrations have been performed over a range of pressures (5–50 Torr). At high pressures both the RF and LIF calibrations vary with pressure inversely, as expected, since in both cases collisional quenching competes with fluorescence from the excited state. The full pressure dependence of the LIF measurement is understood, and the rates of the individual processes (collisional stabilization vs fluorescence of the excited OH) are known (see ref 23). Our LIF calibration data fit this known pressure dependence well. We have some reason to question the accuracy of our calibration (see Results below), but precision is very high (\(\approx 10\%\)), and the measured pressure dependences of the yields are reliable. Soon we plan to more accurately calibrate our LIF system by measuring the N\textsubscript{2} Raman shift at 302 nm.\textsuperscript{23}

Before a yield measurement is made, a test is done in which ozone and alkene are both injected into the system and alkene flow is modulated. By eq 1, steady-state radical concentration should be independent of alkene concentration, so if the LIF (or RF) signal does not change with a change in alkene flow, the radical is assumed to be in steady state and the yield measurement is performed.

Yield measurements are performed by sending a constant flow of alkene into the reaction zone and modulating ozone on and off at various concentrations. During the “off” cycle the O\textsubscript{2}/O\textsubscript{3} flow is diverted downstream of the UV cell, while background LIF (or RF) and UV signals are taken. In a typical run, this is repeated for four to six ozone concentrations, spanning [O\textsubscript{3}] by at least a factor of 3 and often a factor of 10 or more. A yield measurement for a given alkene and pressure takes between 10 and 45 min.

Because of the reduced sensitivity of LIF and RF at high pressures (>50 Torr), higher concentrations of ozone, and therefore alkene, are often used. Also in these cases, as well as at low pressures (<3 Torr), velocity can be slower as well. Therefore it is possible that a significant fraction of the ozone will have reacted between the reaction zone and the UV cell. To compensate for this, we measure ozone concentrations without alkene and use these values for calculating the yield; this correction is generally of the order of a few percent and is never higher than 15%.

Results

A typical run, for TME at 10 Torr, is shown in Figure 4. Ozone is held at five different concentrations, and the resulting OH signal is proportional to ozone concentration. The detection of OH is unequivocal; detuning the laser reveals the 3:1 doublet characteristic of the OH transition. Laser-generation of OH, by photolysis of O\textsubscript{3} to O(1\textsuperscript{D}) followed by H-atom abstraction, is a potential problem, but our experimental design greatly minimizes this interference. We draw on the proven design of the NASA ER2 HO\textsubscript{x} instrument,\textsuperscript{23} using very high laser pulse repetition rates to keep the peak laser power (and thus secondary production) low. Two separate tests have established that none of the OH observed is laser-generated. First, measured OH yield is independent of laser power, suggesting that no two-photon processes (namely ozone photodissociation and subsequent OH detection) are occurring. Second, negligible LIF signal is observed when a large amount of isobutane is added to the ozone in the system. Isobutane has a tertiary hydrogen and thus is expected to be significantly more susceptible to H-atom abstraction than any of the alkenes used in this study. We thus conclude that laser-generated OH does not interfere with our experiment.

Plotting [OH] vs [O\textsubscript{3}] shows an extremely tight correlation, as predicted by the steady-state expression (eq 2). The yield, as
determined by the slope of the line multiplied by $k_{OH}/k_{O3}$, is 1.86. The measured yield above unity is probably not real but instead caused by errors in $k_{OH}$, $k_{O3}$, or the LIF calibration, all of which scale the raw data. Such errors do not affect the precision of the measurements, nor do they significantly affect the reported pressure dependence of the yields: as mentioned above, the pressure dependence of LIF sensitivity is well-constrained. Uncertainties in the pressure dependences of the rate constants ($k_{OH}$, $k_{O3}$) may be a factor, but there is little evidence that those rates are significantly pressure-dependent. An important exception is the reaction of OH with ethene, but the pressure dependence of that reaction is well-characterized.24

We have found that [OH] remains linear with [O3] as low as $10^{11}$ molecules O3/cm3. This demonstrates that the OH is indeed a prompt product of the reaction and is not formed by secondary processes: the lifetime of a species which reacts at the collision rate ($k = 3 \times 10^{-10}$ cm3 molecule$^{-1}$ s$^{-1}$) with ozone or a reaction product (with concentration of $\leq 10^{11}$ molecules/cm3) is 33 ms, longer than the time scale of the experiment. Furthermore, bimolecular rate constants for carbonyl oxides are believed to be much slower than the collision rate; secondary reactions with ozone or reaction products are thus not significant in this experiment. Our alkene concentration ($10^{15} - 10^{16}$/cm3) is much higher than [O3], so secondary reactions with the alkene are at least possible on the time scale of our experiment. However, this is unlikely to lead to any interference, as there are few alkene reactions that could produce OH; those that might (such as reactions with HO2, or carbonyl oxide + alkene cycloadditions) have high barriers and thus long time scales well beyond that of our experiment. We also cannot completely rule out bimolecular reactions with O2, which is present in higher concentrations than O3; however, by varying [O2] we see no change in the measured yield.

Table 1 presents the values of the rate constants used for determining yield; $k_{OH}$ and $k_{O3}$ are from the recommendations in ref 24 and $k_{H}$ are from ref 17. Rates are in molecules/cm3/s; “na” indicates no value is available. *Pressure-dependent rate constant, from ref 24. + Pressure-dependent rate constant, from ref 17.

Table 1: Rate Constants for Reactions of Alkenes with O3, OH, and H*

<table>
<thead>
<tr>
<th>alkene</th>
<th>$k_{O3}/(10^{-17})$</th>
<th>$k_{OH}/(10^{-12})$</th>
<th>$k_{H}/(10^{-12})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethene</td>
<td>0.159(±0.048)</td>
<td>p-dep$^b$</td>
<td>p-dep$^b$</td>
</tr>
<tr>
<td>trans-2-butene</td>
<td>19(±6.7)</td>
<td>64.0(±12.8)</td>
<td>0.825(±0.006)</td>
</tr>
<tr>
<td>TME</td>
<td>113(±40)</td>
<td>110(±22)</td>
<td>1.34(±0.010)</td>
</tr>
<tr>
<td>trans-4-octene</td>
<td>13(±1.5)</td>
<td>69(±17)</td>
<td>na</td>
</tr>
<tr>
<td>3,4-dimethyl-3-hexene</td>
<td>37</td>
<td>na</td>
<td>1.05(±0.006)</td>
</tr>
</tbody>
</table>

* Values for $k_{OH}$ and $k_{O3}$ are from ref 1 and $k_{H}$ are from ref 17. Rates are in molecules/cm3/s; “na” indicates no value is available. + Pressure-dependent rate constant, from ref 24. $^+$ Pressure-dependent rate constant, from ref 17.

Figure 5. OH yields versus pressure (in Torr) for the six alkenes covered in this study. Data are fit to an empirical function which duplicates master equation results well; yields may be greater than 1 due to uncertainties in $k_{OH}$, $k_{O3}$, and LIF calibration (see text).
folds master equation results well (we discuss our use of the
master equation in a separate paper25). For the fit, data points
are weighted by their respective uncertainties.

Measurements of OH yields for ethene above 10 Torr were
not made due to very low precision: when pressure is increased,
not only does LIF sensitivity decrease but the OH—ethene rate
constant (k_\text{OH}) increases, decreasing the steady-state concentra-
tion of OH.

Due to the poor signal-to-noise ratio, H-atom yields are
determined at low pressures: 10 Torr for the substituted alkenes
and 5 Torr for ethene. Results are presented in Table 3. For all
alkenes, yields are small but nonzero; in general, yield decreases
with size and degree of substitution.

Discussion

For the reaction of ozone with all the alkenes studied, OH is
found to be produced promptly. In all cases save ethene, yields
are found to be highly pressure-dependent, indicating competi-
tion between collisional stabilization and dissociation of a
vibrationally excited intermediate, presumably the carbonyl
oxide. This conclusion is supported by the fact that the data
are generally fit well by our empirical function; one notable
exception is the high-pressure TME data.

Given the competition between stabilization and dissociation,
we would expect that the larger alkenes (those with more
vibrational modes) would exhibit the greatest pressure depen-
dence, as they are the most susceptible to collisional stabiliza-
tion. Within the series of alkenes studied, this effect seems to
be weak but existent: trans-2-butene, for example, certainly
exhibits a weaker pressure dependence than trans-4-octene.
Yields from larger alkenes (including many species which are
important in the troposphere) are expected to be even more
strongly pressure-dependent.

As is to be expected, OH yield is closely related to degree of
alkene substitution. TME is found to have the highest yields,
consistent with the reaction mechanism shown in Figure 2, in
which OH is formed via the hydroperoxide channel. On the
other hand, ethene is found to have the lowest yields, consistent
with isomerization to dioxirane dominating over dissociation
to OH. The three disubstituted alkenes (trans-2-butene, trans-
3-hexene, and trans-4-octene) may react by either mechanism,
and correspondingly their OH yields are intermediate.

However, while the degree of substitution may control
absolute yields, it does not seem to have a significant influence
on the pressure dependences of such yields. The degree of
substitution affects not only which reaction pathways are
available but also the stability of the carbonyl oxide, since alkyl
groups serve to stabilize the electron-poor carbon. For two
alkenes with the same number of vibrational modes but different
degree of substitution (for example, TME and trans-3-hexene),
the observed pressure dependences are not drastically different,
even though the disubstituted carbonyl oxide (from TME) is
significantly more stable than the monosubstituted one. This
suggests that only the excess energy of the ozonide—which is
not expected to vary much from reaction to reaction—determines
the vibrational energy content of the carbonyl oxide.

In addition, we present the first direct measurements of
H-atom yields from gas-phase ozonolysis. The H yields are
extremely small (<1%) for the fully substituted alkenes (TME
and 3,4-dimethyl-3-hexene), which is consistent with the
hydroperoxide channel being the dominant reaction mechanism.
For ethene, H yield is larger (at low pressures at least), on the
order of a few percent. This suggests an alternate reaction
mechanism; one possible source is the “hot acid” channel,26 in
which the dioxirane isomerizes to highly excited formalic acid,
via a dioxymethane intermediate. This acid can then dissociate
to one of many sets of products, including H atoms; the observed
H may also arise from the dissociation of HCO. For the
disubstituted alkenes, H yields are small but not insignificant,
ranging from 4.5% for trans-2-butene to 0.7% for trans-4-
ocetc. This too may be from dissociation of the “hot acid,” to
form H + RCO_2. However, the observed H may be formed
instead via the hydroperoxide channel (reaction R6b): the
resulting HCOOCR_2 fragment may further dissociate, to a ketene
and an H atom.

Table 2 presents a summary of OH indirect yield measure-
ments, made at 1 atm. With the exception of ethene, extrapolat-
on of the data in this study to 1 atm suggests OH yields
significantly lower than those determined in most scavenger
studies. Recently, the Paulson laboratory has determined ethene
OH yields to be pressure-dependent, with significantly higher
yields at pressures below 100 Torr.27 Because of the limited
pressure range of our measurements, as well as the large error
carried in our calculations, we cannot rule out the possibility of
a pressure dependence. However, the same study reports no
pressure dependence for trans-2-butene, trans-3-hexene, or
TME.27 In sharp contrast with the results of this work.

It is of course extremely important to understand the source
of this discrepancy. An obvious candidate is the different method
of OH detection: direct, spectroscopic detection versus indirect,
scavenger-based measurements. But this is unlikely to introduce
any major errors, as the measurements in scavenger studies are
most certainly of OH and not some other oxidant. Thus the
difference likely lies in an additional source of OH, not present
in our system but present in the scavenger studies.

This additional source may arise from generation of OH via
secondary chemistry in the scavenger studies that could not
occur within the time scale of our experiments. OH has been
suggested as a possible product of the reaction of carbonyl oxide
with carbonyls28 or water.29,30 In addition, RO_2 chemistry is
highly uncertain and may also be an OH source, via either
unimolecular or bimolecular channels. Still, there is little
evidence that any of these potential sources could produce
enough OH to account for the large differences in yields
measured in this study and in scavenger studies.
In another paper\textsuperscript{25} in this series, we present an alternate explanation for this discrepancy, using the time-dependent master equation. We show that the carbonyl oxide, assuming it does not undergo fast bimolecular reactions, may dissociate to OH thermally on the time scales of the scavenger studies, but not of our experiments.

**Conclusions**

We have presented spectroscopic measurements of OH yields from the gas-phase ozone–alkene reaction for a series of simple, symmetric alkenes over a wide range of pressures. These constitute the first direct gas-phase OH measurements from this class of reaction at pressures above a few Torr. In all cases we observe prompt OH formation, and in all cases (save ethene) the yield is pressure-dependent. This is consistent with a competition between unimolecular reaction and collisional stabilization of the vibrationally excited carbonyl oxide intermediate. As expected, the larger alkenes exhibit a greater pressure dependence, but this effect is not particularly strong. The relationship between yield and degree of substitution is more pronounced, suggesting our understanding of the reaction mechanism (reactions R1–R4) is qualitatively accurate, even if the branching ratios are not well constrained. In another paper\textsuperscript{25} we use statistical-dynamical calculations to estimate these branching ratios, further constraining the reaction mechanisms. Yields of H atoms were also measured directly for the first time, and may be understood in terms of the “hot acid” channel, available only for ethene and disubstituted alkenes. Finally, for the substituted alkenes, our measured yields, extrapolated to 1 atm, are considerably lower than those determined by scavenger studies; this point, too, will be addressed in the companion paper.

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**References and Notes**