

Direct observation of OH production from the ozonolysis of olefins

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Abstract. Ozone olefin reactions may be a significant source of OH in the urban atmosphere, but current evidence for OH production is indirect and contested. We report the first direct observation of OH radicals from the reaction of ozone with a series of olefins (ethene, isoprene, trans-2-butene and 2,3 dimethyl-2-butene) in 4-6 torr of nitrogen. Using LIF to directly observe the steady-state of OH produced by the initial ozone-olefin reaction and subsequently destroyed by the OH-olefin reaction, we are able to establish OH yields broadly consistent with indirect values. The identification of the OH is unequivocal, and there is no indication that it is produced by a secondary process. To support these observations, we present a complete *ab-initio* potential energy surface for the O₃-ethene reaction, extending from the reactants to available products.

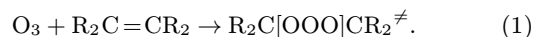
Introduction

The ozonolysis of olefins may produce hydroxyl radicals (OH) under atmospheric conditions (e.g. [Niki et al., 1987; Chew and Atkinson, 1996]). Recent calculations [Paulson and Orlando, 1996] show that, given typical urban olefin concentrations and accepted OH production efficiencies, ozonolysis could be a major urban radical source. In addition, recent theoretical work [Gutbrod et al., 1996], [Gutbrod et al., 1997] has identified accessible transition states to OH formation in probable reaction fragments. However, the experimental evidence for OH production is indirect, being based on the removal of alkanes during ozonolysis. Some evidence reported recently [Schafer et al., 1997] suggests that this extra oxidant may be an organic radical produced in the reaction and not OH, while other evidence [Paulson et al., 1997] appears to contradict this claim.

We can remove the ambiguity by studying ozone-olefin reactions with both direct observation of OH radicals and *ab initio* calculations. The calculations show how much internal energy is available to the reaction products and the likelihood that they will promptly decompose into OH and other radical fragments. Direct OH measurements in a flow tube shortly after reaction initiation with low reactant concentrations will minimize possible secondary radical sources.

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Ozonolysis of olefins initiates a complex series of reactions by producing unstable products with a large excess of internal energy. These transient species are extremely short lived but can undergo a series of isomerizations and decompositions before losing energy to the bath gas. The accepted mechanism proceeds as follows. Ozone reacts with an olefin to produce a vibrationally excited primary ozonide:



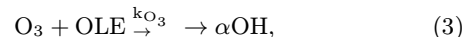
The ozonide then rapidly decomposes into an aldehyde and a carbonyl oxide (the Criegee intermediate):



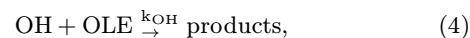
The aldehyde will not have sufficient internal energy to decompose. However, a large fraction of the carbonyl oxide will have ample energy to either immediately decompose or isomerize. Because it is the least stable isomer of R₂CO₂, the isomerization products will have increasingly more internal energy, and there will be many easily accessible dissociation pathways, most of which lead to radical products, including H, OH, and HO₂.

Experimental

We observe OH in steady state by adding an olefin to a flowing dilute mixture of O₃ in N₂ and measuring OH ~ 50 ms downstream. If OH production is limited by the O₃ - olefin reaction, with efficiency, α :



and OH removal is dominated by the olefin



α can be found from the steady-state expression:

$$\alpha = \partial(k_{\text{OH}}[\text{OH}]) / \partial(k_{\text{O}_3}[\text{O}_3]). \quad (5)$$

We find the slope either with a single measurement and an assumed zero intercept or by multiple measurements at different O₃ concentrations. The second approach is a stricter test of the expected relationship. In either case, the OH will be independent of the olefin concentration if the olefin is the only OH sink. Therefore, to determine the OH yield, we require accurate measurement of OH and O₃, and accurate knowledge of the two rate constants (table 1, [Atkinson, 1997]). Uncertainties from the kinetics alone are (~30%), probably more for the pressure dependent ethene rate.

Table 1. Rate constants for ozone and OH reactions.

cc/(molec sec)	ethene	isoprene	t,2-butene	TME
$k_{O_3}/(10^{-17})$	0.16	1.3	19	110
$k_{OH}/(10^{-12})$	3	100	65	110

Secondary chemistry is a concern. Some intermediate reactions are required to produce any OH; the prompt pathway is the unimolecular decomposition of vibrationally excited carbonyl oxide before it is collisionally quenched. In order to unambiguously attribute any observed OH to this prompt pathway, we must observe OH behavior consistent with equation 5 (independent of olefin and linear in O_3) under conditions excluding other possible channels. In particular, concentrations must be kept as low as possible to keep production time scales longer than the 50 ms available.

The high pressure flow system we used has been extensively described (e.g. [Donahue et al., 1996]). We generate O_3 far upstream (7 m) in one of two high voltage ozonizers and introduced into the center of a 10 m/s flow of N_2 carrier gas. Olefins are injected roughly 50 cm upstream of an LIF detection axis where radicals are normally injected during a kinetics experiment. In this way, the olefin forms a plume that diffuses into a well mixed O_3 profile. Measurements are made well before the plume encounters the tube wall.

We measure O_3 with FTIR, and OH with LIF. The FTIR and LIF axes are separated by 9cm. OH measurement is nearly identical to that described by [Wennberg et al., 1994], including the calibration technique, accounting for quenching by both N_2 and O_2 . OH calibration is, however, the leading source of error ($\sim 50\%$).

Results

We conducted two sets of experiments, all in nitrogen between 4 and 6 torr. Oxygen mixing ratios from the ozonizer were typically 1%. The first set was carried out with high O_3 ($\sim 10^{14} \text{ cm}^{-3}$) and olefin concentrations between 10^{13} cm^{-3} and 10^{14} cm^{-3} . Olefins used were ethene, trans-2-butene, isoprene, and 2,3 dimethyl 2-butene (TME). OH yields were based on single O_3 concentrations. In the sec-

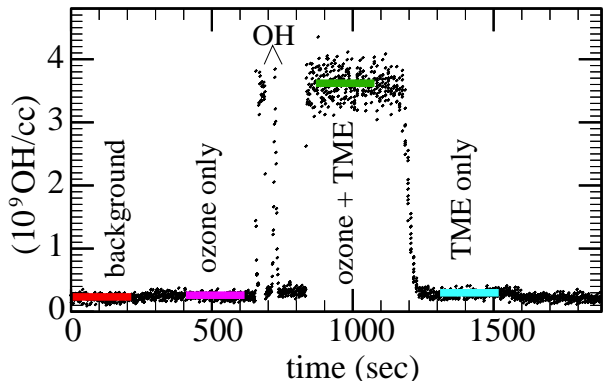


Figure 1. OH radicals 50 ms after initiation of the reaction of O_3 and 2,3-dimethyl 2-butene (TME). Four averages are: no reagents, O_3 only, O_3 + TME, and TME only. Structure after OH signal jump shows the OH line as the LIF laser is scanned over the resonance frequency.

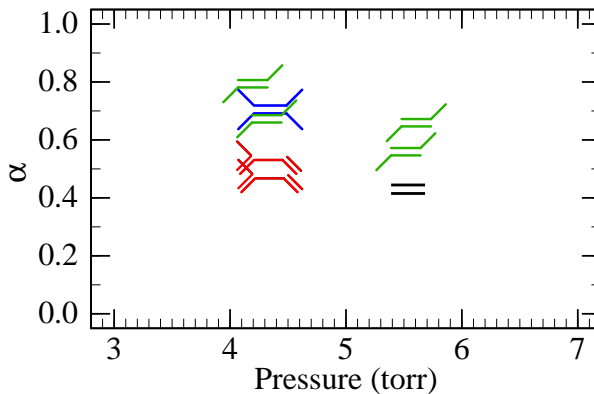


Figure 2. OH production efficiency vs pressure for ethene, trans 2-butene, isoprene, and TME.

ond experiment, using only TME, the O_3 concentration was varied between 10^{12} cm^{-3} and $2.5 \times 10^{13} \text{ cm}^{-3}$.

A representative run is shown in figure 1. The figure shows OH LIF data during four stages of a single measurement with TME: background, O_3 only, both reagents, and TME only. The non-zero background is due to laser scatter. Just after the TME was added, the LIF laser was tuned off resonance, scanned over the OH transition, then returned to the peak; the peak seen in the figure is certainly OH.

The results of the first set of experiments are shown in figure 2. Though $[OH]$ varies by 2 orders of magnitude, the OH production efficiencies are all within a factor of 2. At low pressures and room temperature, we found significant OH yields (0.4 to 0.8) from all four olefins. Our accuracy is $\sim 50\%$, though the ratios of yields are better known (conservatively 30%) because the OH calibration accuracy is removed. While there is no statistically significant difference in the yields, the internal olefins do have higher yields than the terminal olefins. This is loosely consistent with reported efficiencies under atmospheric conditions, though we see higher yields for the terminal olefins.

A second experiment with TME is shown in figure 3, which shows the steady state OH as O_3 is varied. The slope of this line (0.7) is the OH yield. The yield is identical to that shown for TME in figure 2, though the maximum O_3 is a factor of 4 lower than in that experiment. The data in figure 3 are linear to the lowest O_3 used (10^{12} cm^{-3}) with a statistically insignificant intercept. In each run, the TME was briefly increased from 10^{13} to 10^{14} cm^{-3} with both reactants present. The OH signal did not change.

During some measurements we added an atomic resonance lamp. While the lamps have not been calibrated, we did observe strong H-atom resonance fluorescence during the O_3 + trans-2-butene reaction. In no case did we see signal with an O-atom lamp. This is consistent with H-atom production and no O-atom production.

Theoretical

In figure 4 we show a theoretical potential energy surface for the O_3 + ethene reaction. We have qualitatively similar results using Moller-Plesset (UMP2/6-31+G**) and Density Functional theory (B3LYP/6-31+G**//B3LYP/6-31+G(3df,2p)). To our knowledge, this is the first published complete *ab initio* reaction coordinate for this reaction at

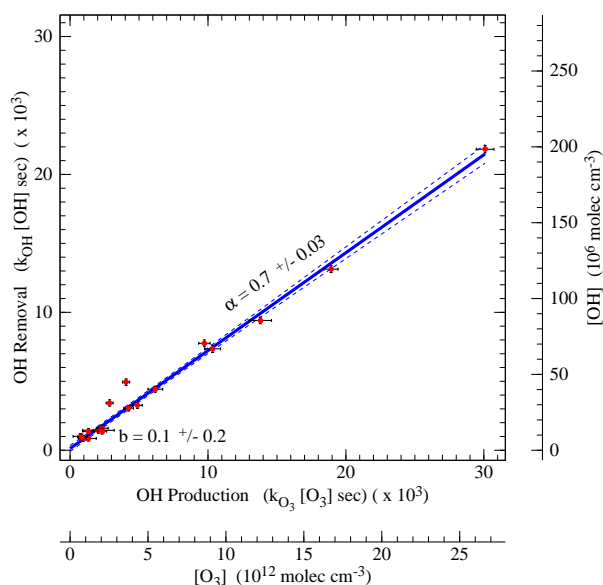


Figure 3. OH production from TME as a function of $[O_3]$. The OH concentration depends linearly on the O_3 concentration. Primary axes are scaled by rate constants to give production and loss rates; secondary axes are unscaled concentrations. The slope (α) is thus the yield.

a consistent level of theory. The figure is drawn to scale, but the scale is intentionally left off, reflecting the inherent uncertainty of the calculation. Detailed results will be published later. The enthalpy of the initial reaction ($O_3 + C_2H_4 \rightarrow$ ozonide) is ~ -60 kcal/mole. Figure 4a shows the reaction coordinate for the initial reaction, while figure 4b follows the carbonyl oxide singlet surface after decomposition of the ozonide. The horizontal bar in both figures shows the energy atop the barrier for the initial reaction; in 4b it therefore is the maximum possible internal energy of the carbonyl oxide. Our primary objective is to emphasize the enormous internal energy involved in this reaction – energy which can only be removed by multiple collisions – and thus the likelihood of rapid unimolecular decomposition.

It is likely that the carbonyl oxide will either decompose to form CHO and OH (via TS1) or isomerize to form vibrationally excited dioxirane (via TS2). Except for carbonyl oxide generated with insufficient energy to decompose, decomposition is likely because of the enormous exothermicity of the isomerizations. Several pathways produce OH, and more produce HO_x radicals. Production of $O(^3P)$ requires triplet CH_2O and is inaccessible. These results are consistent with the findings of [Gutbrod et al., 1996], though we calculate a higher OH yield for the initial step (decomposition of the carbonyl oxide) because we account for the density of states of the transition states. If all of the available energy is deposited in the carbonyl oxide, approximately 15% of the reaction will immediately produce OH (via TS1).

The branching ratios of the subsequent decompositions are difficult to calculate. However, only dioxymethylene among the carbonyl oxides has low barrier molecular pathways (giving $H_2 + CO_2$ and $H_2O + CO$). The unimolecular decomposition pathways of formic acid are all competitive because the lower energy molecular transition states are much tighter than the higher energy radical forming

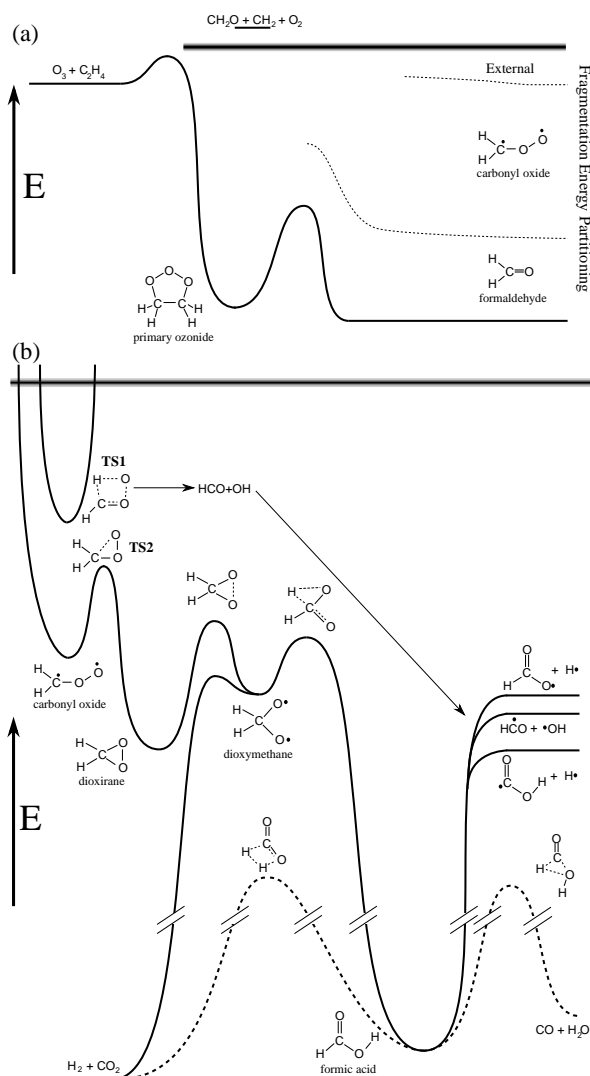


Figure 4. Theoretical O_3 -ethene reaction coordinate. (a) Formation and decomposition of primary ozonide. (b) Isomerization and decomposition of carbonyl oxide. The arrow is ~ 50 kcal/mole.

transition states. Substitution changes hydrogen transfers to methyl transfers, effectively eliminating these pathways. This may explain the general tendency for terminal olefins to show lower OH yields. In addition, other calculations [Gutbrod et al., 1996] have shown that the initial decomposition of the carbonyl oxide into OH radicals is lower in energy than the isomerization pathway for substituted carbonyl oxides; because the resulting transition state is both lower in energy and looser than the three-center isomerization, it will dominate. Our calculations on the substituted system (not shown here) confirm this result.

We have not calculated the energy distribution of the primary ozonide decomposition products. While the carbonyl oxide will not receive all of the available energy, it is likely that it will receive a large share and thus tend to be unstable. Some fraction will, however, be generated with too little energy to surmount either the decomposition or the isomerization barrier and will thermalize. Our theoretical findings therefore support the experimental finding of large

OH radical yields, but they by no means rule out the formation of significant amounts of thermalized carbonyl oxides as well.

In order to understand both any pressure dependence to observed radical yields and any production of thermalized carbonyl oxides, we must first understand the energy distribution of the reaction products. Only those products initially near a transition state energy will be likely to show sensitivity to pressure; those above barriers by more than 10 kcal/mole will never survive, while those below barriers will inevitably be thermalized.

Discussion

We observe large OH production in all reactions studied, and the OH steady state is controlled as expected by the O₃-olefin reaction and the subsequent OH-olefin reaction. Our theoretical calculations support the conclusion that this OH is produced by prompt decomposition of vibrationally excited carbonyl oxide produced in the initial reaction.

While any direct HO_x production has atmospheric significance, our aim is to isolate each HO_x species. Ozone can convert HO₂ and H to OH. The reaction O₃ + HO₂ is slow (2×10^{-15}), so in the 50 ms available at most 10^{-3} of any HO₂ could be converted to OH, even at our highest O₃ concentrations. The reaction O₃ + H is fast (3×10^{-11}) and could convert H to OH at the O₃ concentrations used in the first experiment; this has been observed previously [Finlayson et al., 1974]. Competition among O₃, O₂ and hydrocarbons for H must be considered in all experiments; however, the linearity of figure 3 to 10^{12} O₃ rules out a large H + O₃ source in the TME + O₃ reaction. Similar experiments for other olefins will require greater OH sensitivity.

Radical production from reactions between intermediate radicals (i.e. CR₂OO) and the reactants would not have atmospheric significance. Our lowest concentration experiment had 10^{12} O₃ and 10^{13} TME cm⁻³. Under these conditions a fast reaction between the carbonyl oxide and O₃ or TME could have gone to completion. The rate constant would have to be over 6×10^{-11} for O₃ and 6×10^{-12} for TME. If CR₂OO were to abstract a hydrogen atom from a hydrocarbon, it would produce CR₂OOH, which is known to rapidly decompose into CR₂O and OH. However, while carbonyl oxides react rapidly with olefins, two factors argue against OH production. First, it is unlikely that an abstraction channel is fast enough, and second, given the high observed OH yields, a secondary reaction would need equally high OH yields to be the cause. It is unlikely that the dominant, additive pathway produces OH.

To extend these results to atmospheric conditions, we must perform experiments at higher pressures with more oxygen. To more strictly exclude secondary reactions, we must perform experiments at lower radical concentrations (roughly 10 times lower than here). We must also improve the accuracy of both our OH measurements and the OH and O₃ kinetics. These experiments are under way; before then quantitative comparison with published yields is not prudent.

Conclusions

We observe high yields of OH in the ozonolysis of ethene, trans-2-butene, isoprene, and 2,3 dimethyl 2-butene. The OH observation is direct and unequivocal. Theoretical cal-

culations of the C₂H₄ + O₃ and CH₂OO surfaces strongly support our contention that this OH is a product of the prompt decomposition of vibrationally excited carbonyl oxides. The few other possible pathways involving secondary reactions of carbonyl oxides with the reagents are highly unlikely. While this direct measurement is relatively inaccurate, as it depends on absolute measurement of rate constants and OH concentrations, it strongly supports complementary indirect measurements based on alkane removal from O₃-olefin systems, and contradicts recent assertions [Schafer et al., 1997] that OH is not produced directly in these reactions.

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