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Gas-Phase Ozonolysis of Alkenes: Formation of OH from Anti Carbonyl Oxides

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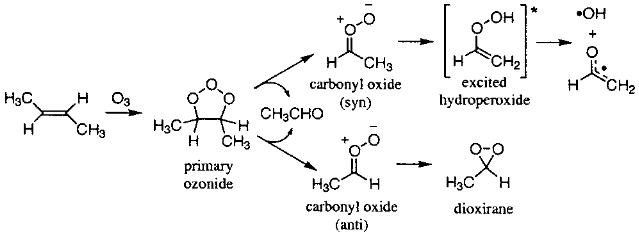
In recent years the gas-phase ozonolysis of alkenes has received renewed attention as a source of radicals in the earth's atmosphere. Numerous scavenger[1,2] and tracer[2,3] studies indicate that ozone−alkene reactions produce hydroxyl radicals (OH) in high yields. These conclusions have been confirmed by direct OH measurements using laser-induced fluorescence (LIF), carried out in our laboratory[4] and elsewhere.[5] Hydroxyl is a central species in the chemistry of the atmosphere, dominating the oxidation of most volatile organic compounds (VOCs), and playing a major role in processes such as urban smog formation and biomass burning. Formation of OH has long been understood to occur via photolytic channels, which are active only during the daytime. However, OH yields from ozonolysis are high enough to be a major contributor to total OH production during both the day and night.[6] Indeed, ozone−alkene reactions may be responsible for the high levels of nighttime OH observed very recently.[7]

The primary features of the gas-phase mechanism are generally accepted. As shown in Scheme 1, the first two steps follow the Criegee mechanism,[8] forming a carbonyl and a chemically activated carbonyl oxide. While the fraction of carbonyl oxide stabilized by the bath gas is a matter of some debate,[3d,4] the majority undergoes unimolecular reaction, either via chemically activated or thermal channels. The available pathways depend on the stereochemistry of the carbonyl oxide. Syn carbonyl oxides lead to OH formation, by α-hydrogen transfer forming a highly activated hydroperoxide, which quickly decomposes to OH. This channel is not available to anti carbonyl oxides, which undergo ring-closure to form dioxirane. There is little evidence of interconversion between the syn and anti species.

Scheme 1. Gas-Phase Ozone−Alkene Reaction Mechanism



The number of allylic hydrogens is a major determinant of OH yield from ozonolysis of a particular alkene. While this might suggest zero OH formation from ethene, yields are consistently found to be 12−18%,[1a,3ab,4c] indicating an additional pathway to OH formation involving vinylic hydrogens. The identity of this pathway is uncertain for ethene, and it is completely unknown whether this channel also contributes to OH formation for substituted alkenes with vinylic hydrogens. This is due in part to the difficulty in distinguishing OH formed from syn carbonyl oxides from any OH formed by a different pathway.

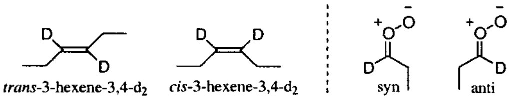


Figure 1. Deuterated alkenes studied in this work and the carbonyl oxides formed by their reactions with ozone.

Here we present measurements of radical yields from the ozonolysis of two alkenes labeled at their vinylic sites, *cis*- and *trans*-3-hexene-3,4-d_2 (Figure 1). Because of differences in reduced mass, OH and OD may be distinguished by the use of LIF, allowing for the direct investigation into any secondary hydroxyl-forming channel involving vinylic hydrogens.

Yield measurements are carried out using the techniques described in previous work from our laboratory.[4] Experiments are carried out in a 12.4-cm diameter flow tube. Ozone, generated by high-voltage corona discharge through oxygen, is introduced with the nitrogen carrier gas and is measured downstream in a UV absorption cell. The reaction is initiated when alkene is injected into the flow through a loop injector. Reaction times are long (100−500 ms), ensuring that thermalized carbonyl oxides undergo unimolecular reaction; at these time scales OH yields are known to be pressure-independent.[3d,4b] OH (OD) is measured using LIF, by exciting the $A^2\Sigma^+(v' = 1) \leftarrow X^2\Pi_{3/2}(v'' = 0)$ transition at 282.1 (287.9) nm and detecting the fluorescence at 309 nm. Absolute OH calibration is described in ref 4c. We periodically check our calibration by measuring the OH yield of ozone plus 2,3-dimethyl-2-butene (TME), which is well established to be 100% under these conditions.[3,4b,5] TME-d_{12} is used for OD calibration.

Hydroxyl radicals are measured at steady state, formed in yield Y_{OH} by the O_3−alkene reaction (rate = $Y_{OH}\, k_{O3}\, [O_3]$ [alkene]) and lost by the OH−alkene reaction (rate = k_{OH} [OH] [alkene]). OH yields follow from the steady-state relation:

$$Y_{OH} = k_{OH}/k_{O3}\ d[OH]_{ss}/d[O_3]$$

For *cis*- and *trans*-3-hexene, k_{OH} equals 6.7 and 6.8 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively (following ref 2), and k_{O_3} equals 1.44 and 1.57 × 10^{-16} cm^3 $molecule^{-1}$ s^{-1} (ref 9). Reaction rates of the deuterated alkenes in this study with OH, OD, and O_3 have not been measured, but the secondary kinetic isotope effects (SKIEs) are likely to be small (∼10%)[10] so that we assume the rates are those of the unlabeled alkenes.

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Table 1. Yields of OH and OD from the Ozonolysis of 3-Hexenes

alkene	Y_{OH}[a]	Y_{OD}[b]	$Y_{OH} + Y_{OD}$
trans-3-hexene	0.53 ± 0.02	0	0.53 ± 0.02
trans-3-hexene-3,4-d_2	0.49 ± 0.02	0.07 ± 0.01	0.56 ± 0.03
cis-3-hexene	0.30 ± 0.02	0	0.30 ± 0.02
cis-3-hexene-3,4-d_2	0.23 ± 0.02	0.11 ± 0.01	0.34 ± 0.03

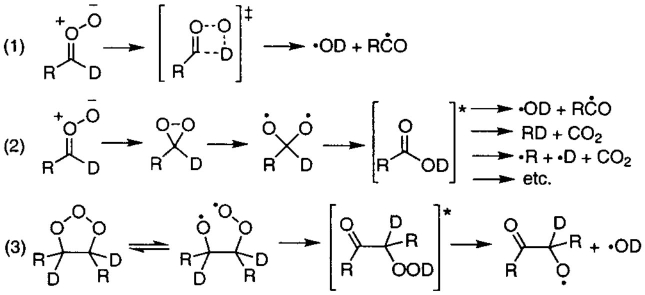
[a] Averages of 14+ measurements. [b] Averages of 6−7 measurements.

Experimental OH and OD yields measured at 6 Torr and 298 K are shown in Table 1. Uncertainties (1σ) reflect precision as well as potential errors from incomplete deuteration of the alkenes. Yields are independent of laser power, indicating no laser-generation of radicals. Measured OH yields from the unlabeled 3-hexenes agree with those from a recent tracer study,[2] which found yields of 0.36 ± 0.07 and 0.53 ± 0.08 for *cis*- and *trans*-3-hexene, respectively.

OD is formed in the ozonolysis of both deuterated alkenes, with the Y_{OD}:Y_{OH} ratio significantly greater for the *cis* alkene than for the *trans*. Within the error of the measurements, the sum of measured OH and OD yields from the deuterated species equals the OH yield from the unlabeled species. The fact that this sum is slightly high may arise from SKIEs of the rate constants or from the possibility that TME-d_{12} produces OD in yields slightly below unity. In either case the differences in Y_{OD}:Y_{OH} ratios from the two alkenes are not affected.

This work provides conclusive evidence that the ozonolysis of substituted alkenes produces hydroxyl radicals via a pathway involving vinylic hydrogens. As shown in Scheme 2, anti carbonyl oxides may lead to OH (OD) formation by (1) concerted dissociation via a four-membered TS[11] or (2) isomerization of dioxirane to an excited ("hot") carboxylic acid via a dioxyalkane intermediate, followed by fragmentation into many radical and molecular species.[12] It has also been suggested that (3) hydroxyl radicals may be formed not by the carbonyl oxide but rather the decomposing ozonide.[3d,13]

Scheme 2. Possible Mechanisms of OD Formation



In mechanisms (1) and (3), the rate-limiting step is a hydrogen transfer, so that the primary kinetic isotope effect introduced by deuterium substitution should lead to a large decrease in total OH yield. On the other hand, the rate-determining step in mechanism (2) is ring-closure to form the dioxirane, which should exhibit no primary kinetic isotope effect. Since no significant decrease in total OH yield is observed, the likely OH formation channel is pathway (2), decomposition of the "hot acid" arising from rearrangement of the anti carbonyl oxide. This is supported by methane yields from 2-butene ozonolysis, believed to occur by the same channel. Ozonolysis of *cis*- and *trans*-2-butene produces CH_4 in yields of ~0.17 and ~0.11, respectively;[14] the relative yield of 3:2 is in excellent agreement with relative OD yields from the deuterated hexenes in this study. While further work is necessary, it is reasonable to assume this is also the channel by which OH is formed in the ozone−ethene reaction.

The large differences in radical yields from *cis*- and *trans*-3-hexene likely arise from differences in carbonyl oxide syn:anti ratios. Assuming 100% OH yield from syn carbonyl oxides (the TME value) and 15% yield from anti carbonyl oxides (the ethene value), OH and OD yields from both alkenes give reasonably consistent syn:anti ratios, ~50:50 for *trans*-3-hexene and ~20:80 for *cis*-3-hexene. Recent calculations on 2-butene ozonolysis[3c,15] indicate that steric interactions within the ozonide decomposition TS lead to a preference for formation of anti carbonyl oxides from cis-alkenes, but little preference from trans alkenes, in excellent agreement with the present results.

Hydroxyl formation from anti carbonyl oxides is not a minor channel, accounting for roughly one-third of the total OH yield from *cis*-3-hexene. For larger cis alkenes, as well as terminal alkenes, the steric interactions affecting ozonide decomposition are expected to have a still greater effect on syn:anti ratios,[16] so that this channel may be a more important, even dominant, contributor to total OH formation from the ozonolysis of larger alkenes.

Anti carbonyl oxides thus play an important role in radical formation from gas-phase ozone−alkene reactions. This role has largely been ignored in mechanistic studies of OH formation, explaining why models of the ozonolysis of less-substituted alkenes tend to under-predict measured OH yields.[4b,17] These results also imply that anti and unsubstituted carbonyl oxides behave similarly, as do syn and disubstituted carbonyl oxides. Thus, in studies of gas-phase ozonolysis reactions, only two major classes of carbonyl oxide need to be considered.

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Supporting Information Available: Preparation and characterization of deuterated compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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