OH Yields in the Gas-Phase Reactions of Ozone with Alkenes

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Hydroxyl radical yields are reported for the gas-phase ozonolyses of a range of alkenes. 1,3,5-Trimethylbenzene was employed as an OH tracer, and the diminution in its concentration was used to calculate OH yields by both a simple analytical kinetic expression and a numerically integrated model. The following OH yields were obtained, relative to alkene consumed: ethene (0.14), propene (0.32), 2-methylpropene (0.60), 2,3-dimethyl-2-butene (0.89), isoprene (0.44), β-pinene (0.24), and α-pinene (0.83). A structure activity relationship (SAR) is presented for the estimation of OH yields based on structural moieties and reaction branching ratios. Reaction stoichiometries (Δ[alkene]/Δ[ozone]) are also reported, along with primary carbonyl yields measured in the presence and absence of excess SO_2, both under "OH-free" conditions. Reaction stoichiometries are shown to be correlated with alkene OH yields, and the mechanistic implications of this observation are discussed. The fractional increase in primary carbonyl yield in the presence of excess SO_2 is shown to be inversely related to the OH yield and is interpreted as a measure of the fraction of the vibrationally excited Criegee intermediate that is stabilized in air at a pressure of 1 atm.

Introduction

The gas-phase reactions of ozone with alkenes are important in the chemistry of the Earth's troposphere for a number of reasons.[1] First, they provide a direct means for the oxidation of unsaturated nonmethane hydrocarbons that competes with OH radical and NO_3 radical initiated processes, and second, they give rise to reactive intermediates that are themselves of atmospheric significance. Since the reactions can occur throughout the night as well as during the day, their importance is further enhanced.[2] Intermediates arising from ozone−alkene chemistry in the gas phase are believed to include a carbonyl oxide species, the Criegee intermediate (CI), which can further react with tropospheric trace constituents to form aerosols (e.g., $CI + SO_2 \rightarrow SO_3 \longrightarrow$ sulfate aerosols)[3,4] or phytotoxic species (e.g., $CI + H_2O \rightarrow$ hydroxymethylhydroperoxide).[5,6]

For some time, it was generally accepted that ozone−alkene reactions in the gas phase also give rise to the production of OH radicals.[6−11] Although this proposition has been questioned,[12] experiments in this laboratory,[13] and elsewhere,[14−16] have confirmed beyond reasonable doubt that OH radicals are indeed formed in the reactions. Calculations indicate that the reactions are not only the major tropospheric source of OH at night but may be the dominant source during the daytime where the incidence of anthropogenic alkenes is high, such as in an urban industrial setting, and may also significantly affect the atmospheric chemistry of rural air.[2]

A number of measurements of OH yields in the reactions of ozone with alkenes have been made. Early experiments relied heavily upon computer simulations of infrared spectroscopic and mass spectrometric data using adopted reaction schemes.[7−9] Later investigations employed OH radical scavengers giving rise to stable products, the concentrations of which allowed OH radical production yields to be determined after suitable calibration. Atkinson and co-workers employed cyclohexane as a scavenger,[10,16,17] deriving OH yields from the amounts of cyclohexanol and cyclohexanone formed; later, 2-butanol was employed as the scavenger, OH yields in this case being obtained from the amounts of 2-butanone formed.[11] Similar OH yields were determined using the two scavengers. Gutbrod et al.[18] employed CO as an OH radical scavenger and deduced production yields for OH by measuring the amounts of CO_2 formed from the reaction of OH + CO. These workers obtained OH yields between a factor of 2 and 3 smaller than those of Atkinson and co-workers.

More recent studies have adopted alternative experimental methodologies, and investigations both in this laboratory[19] and by Paulson and co-workers[20,21] have employed OH radical tracers, relatively large fractions of which are consumed by reaction with OH radicals. Analysis of the diminution in concentration of these tracers by various means allows the estimation of OH radical production yields. Paulson and co-workers have used 1,3,5-trimethylbenzene (TMB), xylene, and di-*n*-butyl ether as OH tracers,[20,21] while work from this laboratory has exclusively employed TMB.[19] McGill et al. analyzed their measured TMB concentration losses by a simple kinetic analysis and through the use of a numerically integrated kinetic model.[19] Paulson and co-workers[20,21] analyzed their results by solving a relative rate expression for alkene and tracer consumption numerically and through the use of a simpler approximation. McGill et al. obtained OH yields for the ozonolysis of 2-methyl-2-butene and *E*- and *Z*-2-butene that are consistent with those reported by Atkinson and co-workers. Paulson et al.[20] obtained yields for the ozonolysis of ethene and propene that agree within error with those of Atkinson and co-workers, although Paulson's ethene value is 50% higher than Atkinson's.[16] Paulson et al. also obtained OH radical formation yields in the same way for isoprene, α-pinene, and methyl vinyl ketone.[21] The values obtained were 0.25, 0.70, and 0.16, respectively, and are in good agreement with the results of Atkinson and co-workers.

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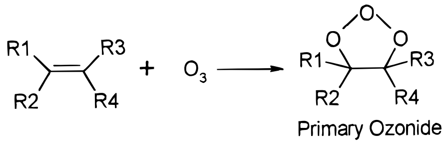
Neeb and Moortgat[23] have determined OH radical production yields from the change in the observed kinetics for the destruction of an alkene through ozonolysis when an OH scavenger (cyclohexane) is present and absent. Alkene concentrations were determined using long-path FTIR spectrophotometry, and the OH yields obtained were consistent with those of Atkinson and co-workers.

The OH radical is believed to be formed as a direct decomposition product of the vibrationally excited Criegee intermediate (see reaction 3b, mechanism section), and the portion of this intermediate that is collisionally quenched is also of chemical interest. An early study by Cox and Penkett[3] reported the formation of sulfuric acid aerosol when SO_2 is in the presence of ozone and an olefinic species. It was proposed that an intermediate formed in the ozone−olefin reaction was oxidizing SO_2 to SO_3 with subsequent H_2SO_4 aerosol formation. In certain cases they also measured a concomitant increase in the yield of primary carbonyl products. Later, Hatakeyama et al.[4] reported yields of stabilized Criegee intermediate from a range of different ozone−alkene systems. These workers determined the yield of H_2SO_4 production in the presence of excess SO_2 and equated this yield with the total yield of stabilized CIs. One difficulty with these experiments was that they took no account of the interference caused by OH radical formation. Very few other studies have been carried out and the yields of stabilized CIs are very uncertain.

Given the inconsistencies in the literature, in the present study we have measured OH yields for the reactions of O_3 with a range of alkenes using the tracer method. In addition, reaction stoichiometries and carbonyl yields were also determined. This latter in the presence and absence of excess SO_2 and in all cases under "OH-free" conditions.

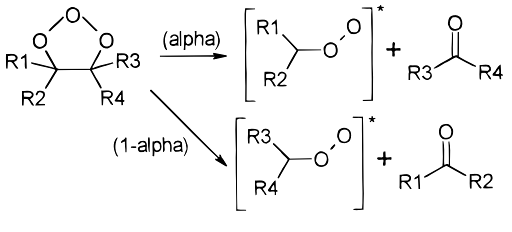
Mechanism

The gas-phase reactions of ozone with alkenes are generally accepted to be electrocyclic processes (see, e.g., ref 9), specifically [3 + 2] cycloadditions, proceeding via the production of a cyclic primary ozonide (POZ).



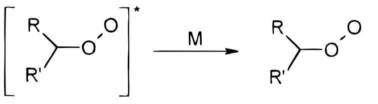
(1)

The POZ then rapidly decomposes to give a pair of Criegee intermediates (CI) and carbonyl compounds (in the case of symmetric alkenes, only one CI and one carbonyl compound are formed).

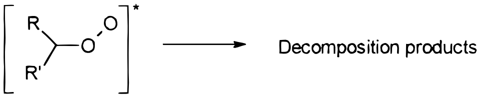


(2)

The CI may then be collisionally stabilized or decompose. It is the decomposition of the excited CI that is believed to give rise to OH radicals, in addition to other closed-shell and radical products.

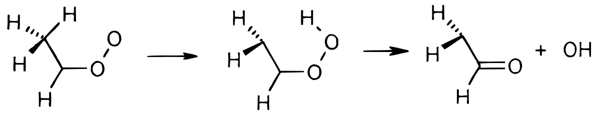


(3a)



(3b)

OH radical production can result from a 1,4-sigmatropic shift within the CI followed by bond fission to form OH, as has been suggested by, for example, Niki et al. and Martinez and Herron.[25]



(4)

Experimental Section

The experimental apparatus employed for this study comprised a static reaction chamber with attached gas chromatograph (GC) with flame ionization detection (FID).[13,19] A mixture of the alkene under study and the relevant intermediate scavenger or tracer (cyclohexane and/or SO_2 for carbonyl yield experiments, and 1,3,5-trimethylbenzene (TMB) for OH yield experiments) was prepared in a 50 L collapsible Teflon chamber using dry synthetic air (BOC) as the diluent gas. Typical initial hydrocarbon concentrations employed were 10 ppmv of the alkene, 2000 ppmv of cyclohexane, and 10−50 ppmv of TMB. Typical initial ozone mixing ratios ranged from ca. 0.5 to 8 ppmv. Experiments were carried out by admitting a known concentration of ozone, to a pressure of ca. 8 Torr, into a 0.5 L borosilicate glass reaction chamber, and adding a sample of the hydrocarbon mixture such that a total pressure of 1 atm (760 ± 10 Torr) was effected. Mixing of reactants is sufficiently fast on the time scale of the reactions studied as previous investigations of the ozonolysis of 2-methyl-2-butene were carried out in the glass reaction chamber and also in the Teflon bag.[13] The results in each case were found to be the same, and this indicated that wall losses were not a problem. This particular alkene is also one of the fastest reacting with ozone of those studied, and as such, mixing is not a problem for the other alkenes looked at. Experiments were carried out at 296 ± 3 K. Ozone was generated as a mixture in O_2 by passing oxygen through a Fischer ozone generator, its purity being determined spectrophotometrically by absorption at $\lambda = 254$ nm. After the mixture was left for sufficient time for the ozone to react (as estimated by a simple kinetic model), the contents of the glass bulb were separated and detected by GC-FID (Perkin-Elmer, model 8420). This procedure was typically repeated for six different initial ozone concentrations during each study. Chromatographic peak heights were related to concentrations after calibration with pure standards. A 30 m, 0.25 mm diameter DB5 capillary column was used for the separation of the terpenes α- and β-pinene; a 25 m, 0.53 mm diameter Poraplot Q capillary column was used for all other alkenes. A typical temperature program employed held the column isothermally at 200 °C for 10 min. All gaseous reagents employed were of ≥95% purity and were used without further processing; all other reagents employed were of analytical grade and underwent a freeze−pump−thaw cycle before being used.

Results and Discussion

OH Yields. Experiments to determine the OH yields for the reactions of ozone with alkenes were carried out in the presence

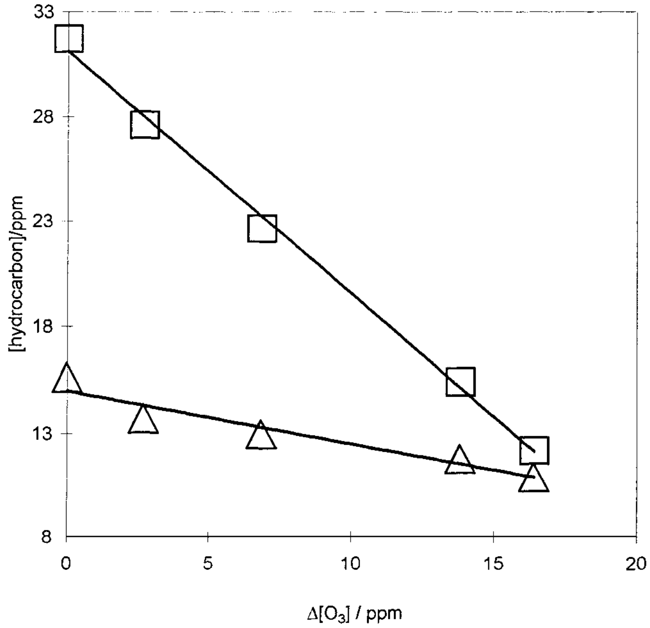
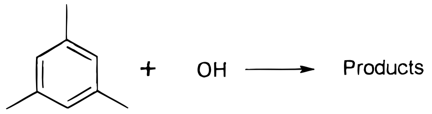


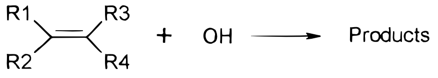
Figure 1. Experimental data for the ozonolysis of 2-methylpropene (open square) in the presence of TMB (open triangle).

of TMB. The rate constant for the reaction of OH with TMB is sufficiently large ($k_5 = 5.75 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1})[22] that it can destroy a significant fraction of the OH formed in the ozonolysis reaction without being present in huge excess over the alkene.



(5)

The other major loss process for OH in these systems is reaction with the alkene.



(6)

OH yields were determined by monitoring [TMB] as a function of the change in ozone concentration, $\Delta[\text{O}_3]$. The alkene was always in excess over the ozone, and the reactants were left long enough that the initial concentration of ozone was equal to $\Delta[\text{O}_3]$. If the OH yield (relative to ozone consumption) for a given ozonolysis reaction is β, the total concentration of OH formed in an experiment is given by $\beta\Delta[\text{O}_3]$. The magnitude of the change in [TMB] is given by $f\beta\Delta[\text{O}_3]$, where f is the fraction of the OH formed that reacts with TMB, and for a small change in ozone concentration, we can write

$$[\text{TMB}] = [\text{TMB}]_0 - \frac{k_5[\text{TMB}]}{k_5[\text{TMB}] + k_6[\text{alkene}] + k_{\text{loss}}}\beta\Delta[\text{O}_3] \qquad \text{(I)}$$

where $[\text{TMB}]_0$ is the initial concentration of TMB and k_{loss} is a rate constant representing other loss processes for OH, such as reaction with products. For small $\Delta[\text{O}_3]$, a plot of [TMB] vs $\Delta[\text{O}_3]$ is expected to give a straight line with a slope of $-k_5[\text{TMB}]_i\beta/\{k_5[\text{TMB}]_i + k_6[\text{alkene}]_i + k_{\text{loss}}\}$. In fact, such plots were found to be linear over the full range of conditions we studied, as is shown in Figure 1 for the ozonolysis of methylpropene, along with a plot of [methylpropene] vs $\Delta[\text{O}_3]$.

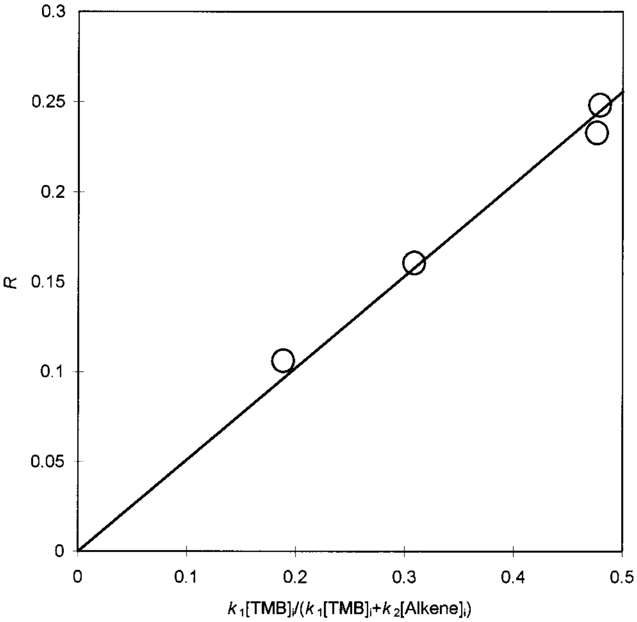


Figure 2. Plot for analytical treatment of experimental results for isoprene, where $R = \Delta[\text{TMB}]/\Delta[\text{O}_3]$.

The figure is typical in that the scatter in the TMB plot is greater than in the alkene plot. For very small values of $\Delta[\text{O}_3]$, $k_{\text{loss}} \approx 0$ because product concentrations are very small and wall losses for OH are expected to be small compared to reaction with the alkene and TMB. For larger values of $\Delta[\text{O}_3]$, the TMB and alkene terms in the denominator of eq I decrease but are at least partially compensated for by increases in k_{loss} due to the reaction of OH with products. The fact that no curvature is observed in plots of [TMB] vs $\Delta[\text{O}_3]$ indicates that the slope, R, of such plots is given by $-\beta k_5[\text{TMB}]_i/\{[k_5[\text{TMB}]_i + k_6[\text{alkene}]_i\}$. Hence OH yields relative to ozone consumed are readily obtained. Plots of $-R$ vs $k_5[\text{TMB}]_i/\{[k_5[\text{TMB}]_i + k_6[\text{alkene}]_i\}$ have been shown to be linear,[19] and a plot for isoprene is shown in Figure 2. The parameter β is the OH yield relative to ozone consumption, whereas most previous reports quote the yield relative to alkene consumption, α. To convert β to α, one simply divides by the reaction stoichiometry, Δ[alkene]/Δ[ozone]. The stoichiometries were measured in separate experiments under “OH-free” conditions (in excess cyclohexane); as discussed later, in many cases they were greater than unity.

In addition, each alkene ozonolysis system was analyzed through the use of a numerically integrated model implemented using FACSIMILE.[24] Each model comprised the rate coefficient and branching ratios for the reaction of ozone with the alkene, as well as the rate coefficients for the reactions of OH with the alkene, TMB, and the carbonyl products. Rate constants and product branching ratios were taken from the literature,[1] and β was varied to give the best fit between model and experimental data. Both TMB and alkene concentrations were used in this procedure, the best fit being determined by a least-squares method. The model does not attempt to fully describe the complex chemistry that goes on in each system but concentrates on the reactions that are likely to be the dominant loss processes for the hydroxyl radical. A typical model employed, in this case for isoprene, is listed in Table 1. Although not included here, early models developed in this laboratory for the analysis of the ozonolysis of 2-methyl-2-butene in the presence of a scavenger, also included the production of HO_2 via several decomposition channels. Reaction of HO_2 with O_3 can, in principle, lead to additional OH radical production. However,

TABLE 1: Reactions Comprising Model for Ozonolysis of Isoprene

reaction	rate constant[a]
O_3 + isoprene → (0.17)MVK + Criegee1	$0.17 \times 12.8 \times 10^{-18}$
O_3 + isoprene → (0.44) MA + Criegee1	$0.44 \times 12.8 \times 10^{-18}$
O_3 + isoprene → (0.39) HCHO + Criegee1	$0.39 \times 12.8 \times 10^{-18}$
Criegee1 → β x OH	1×10^{6} [b]
Criegee1 → (1-β) x other products	1×10^{6} [b]
OH + TMB → products	57.5×10^{-12}
OH + isoprene → products	101×10^{-12}
OH + MVK → products	18.8×10^{-12}
OH + MA → products	27.6×10^{-12}
OH + HCHO → products	9.37×10^{-12}
O_3 + MVK → product + Criegee2	4.76×10^{-18}
O_3 + MA → product + Criegee3	1.08×10^{-18}
Criegee2 → (0.16) OH	1×10^{6} [b]
Criegee2 → (0.84) other products	1×10^{6} [b]
Criegee3 → (0.20) OH	1×10^{6} [b]
Criegee3 → (0.80) other products	1×10^{6} [b]

[a] Reference 24, units in molecule/cm^3/s system. [b] Estimated rate constants chosen to be fast on time scale of other reactions.

TABLE 2: Initial Hydrocarbon Concentrations, Measured Reaction Stoichiometries, and OH Yields (Relative to Alkene) from This Study

alkene	$[\text{alkene}]_i$[a] (ppm)	$[\text{TMB}]_i$[a] (ppm)	analytical OH yield	modeled OH yield	Δ[alkene]/$\Delta[O_3]$
ethene	16	12			
	26	31	(0.23)	(0.25)	0.97 ± 0.07
	25	19		0.14	
propene	16	17	0.33	0.31	1.02 ± 0.07
2-methyl-	15	20			
propene	15	14	0.58	0.65	1.18 ± 0.11
	32	15			
2,3-dimethyl-2-butene	13	32	0.88	0.90	1.23 ± 0.10
Isoprene	10	17			
	13	10	0.45	0.43	1.15 ± 0.10
	21	9			
β-pinene	7	35	0.24	0.24	1.20 ± 0.41
α-pinene	8	17	0.83		0.99 ± 0.10

[a] Conditions for OH-yield experiments.

this modeling study indicated that HO_2-mediated OH formation is not significant in the reactions of ozone with alkenes and is therefore not included in the current simulations.

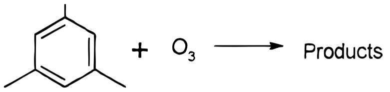
Table 2 lists OH yields (relative to alkene consumption) derived using the two analysis methods; (the agreement between the two methods of analysis is very good and adds confidence to the experimental methodology employed). Also included in the table are TMB and alkene concentrations for the experiments and reaction stoichiometries (Δ[alkene]/Δ[ozone]), measured under "OH-free" conditions. Most of the yields were derived exactly as has been described above, but further discussion of the α-pinene and ethene experiments is required.

The α-pinene POZ is expected to fall apart to give CIs with carbonyl termini. The fate of these CIs is not known, but decomposition is likely to be an important process. Given the difficulty of modeling the chemistry of these species and the equivalence of modeled and analytical results for the other alkenes, the analytical method alone was used to obtain the OH yield for the reaction of ozone with α-pinene.

As shown in Table 2, the OH yields obtained by the analytical method and from our first simple model for the reaction of O_3 with ethene were significantly larger than those reported by other workers. Because the reaction of ozone with ethene,

$$= + O_3 \rightarrow \text{products} \qquad (7)$$

is slow ($k_7 = 1.6 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}), the destruction of TMB by ozone,



(8)

could, in principle, interfere with the determination of the OH yield. There is some uncertainty in the literature as to the rate constant for reaction 8; a recent measurement by Paulson and co-workers[26] ($k_8 = 2.9 \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1}) suggested that the reaction was too slow to be important here, but earlier determinations indicated larger rate constants. Experiments were therefore carried out to determine the rate of disappearance of TMB in the presence of ozone in our reaction vessel. The concentration of TMB was monitored in excess O_3, and the pseudo-first-order rate constant obtained was plotted as a function of $[O_3]$ to obtain a bimolecular rate constant, as illustrated in Figure 3a. Although the bimolecular rate constant obtained ($k_8 = 2.9 \times 10^{-20}$ cm^3 $molecule^{-1}$ s^{-1}) is an order of magnitude faster than that reported by Paulson and co-workers[26] it is still too slow to affect our OH yields. However, the intercept in Figure 3a indicates a significant first-order component to the TMB destruction.

This loss of TMB is probably due to a heterogeneous reaction with ozone; such losses were not observed in the absence of ozone. Given an initial TMB concentration of ca.10 ppmv, the intercept corresponds to a bimolecular rate constant of 5.3×10^{-19} cm^3 $molecule^{-1}$ s^{-1}. That the effective bimolecular rate constant was of this magnitude was confirmed in a relative rate experiment. The procedure for the OH yield experiment for ethene was repeated, but in the presence of 2000 ppmv cyclohexane to remove OH radicals. The data obtained were plotted as for a relative rate experiment,[27] as illustrated in Figure 3b. From this plot and the known rate constant[1] for reaction 7 of 1.6×10^{-18} cm^3 $molecule^{-1}$ s^{-1}, $k_8 = 3.5 \times 10^{-19}$ cm^3 $molecule^{-1}$ s^{-1} was obtained. Clearly, this is not a true bimolecular rate constant but shows that the destruction of TMB can be approximated by assuming it is destroyed in a gas-phase bimolecular reaction with a rate constant of ca. 5×10^{-19} cm^3 $molecule^{-1}$ s^{-1}. The model used to describe the ozone−ethene system was modified to include reaction 8 with $k_8 = 5 \times 10^{-19}$ cm^3 $molecule^{-1}$ s^{-1}, and an OH yield of 0.14 was obtained. This yield is not very sensitive to the value used for k_8; changing the rate constant by 50% in either direction causes a change in the quoted yield of less than 10%. A greater error limit in this OH yield is however quoted in Table 3 of ±50% of the reported value and reflects this additional source of uncertainty.

Taking the mean value of modeled and analytical OH yields with respect to alkene consumed, the results of this study are summarized in Table 3 along with the results of other groups. For almost all compounds, the results of this study are in good agreement with the results of Atkinson and co-workers[10,11,16,17] and with the recent work of Paulson and co-workers[20,21] and Neeb and Moortgat.[23] The OH yields reported by Gutbrod et al.[18] are significantly lower than the others. Why this discrepancy arises is not entirely clear, but CO and CO_2 are known products of the reactions between ozone and alkenes. Furthermore, Horie and Moortgat[28] have observed increased CO_2 concentrations on addition of CO to the ozone−ethene system, and they attributed this observation to increased ozone conversions; that is, changes in CO_2 concentrations can arise even without the involvement of OH.

For all the compounds studied over a range of alkene/tracer concentration regimes in this and our previous investigation,[19]

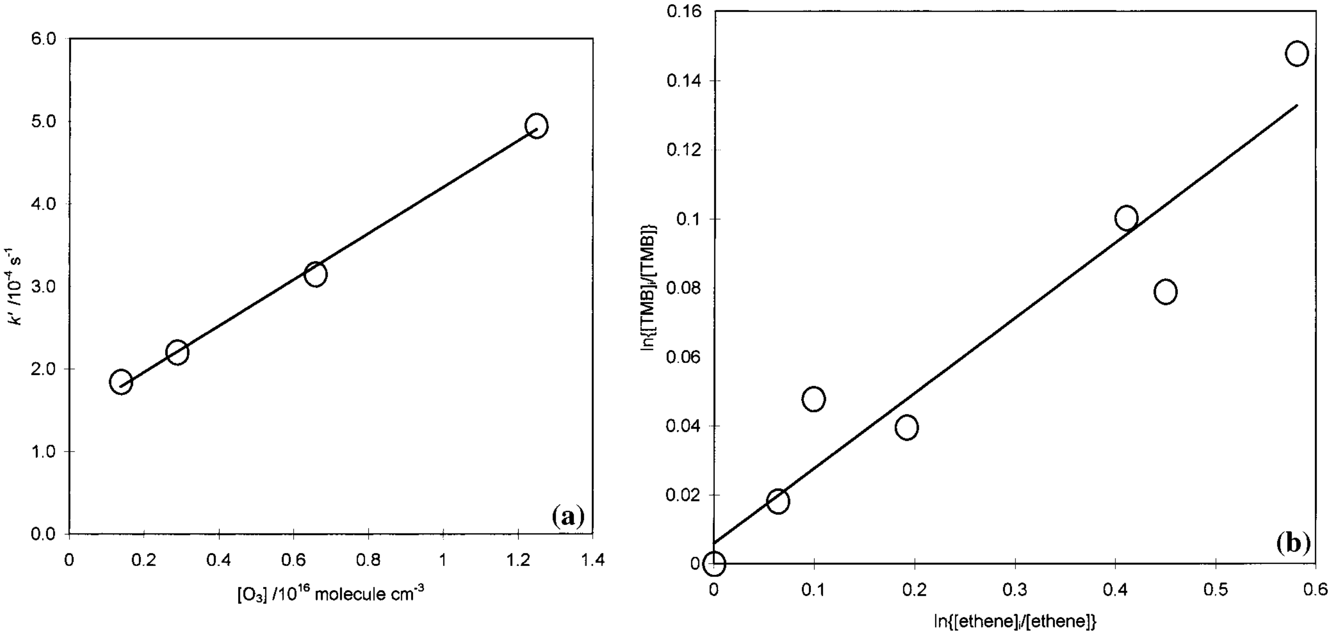


Figure 3. (a) Second-order rate plot for ozone + TMB. (b) Relative rate plot for the reaction of ozone with ethene and TMB.

TABLE 3: Summary of OH Yields from This Laboratory and Other Groups of Workers

alkene	this lab	Atkinson	Paulson	Moortgat	Gutbrod	**average**
ethene	0.14[a]	0.12[d]	0.18[f]		0.08[h]	**0.13**
propene	0.32[b]	0.33[d]	0.35[f]	0.34[g]	0.18[h]	**0.34**
2-methylpropene	0.60[b]	0.84[d]		0.60[g]		**0.69**
Z−2-butene	0.33[c]	0.41[d]			0.17[h]	**0.37**
E−2-butene	0.54[c]	0.64[d]			0.24[h]	**0.59**
2-methyl-2-butene	0.82[c]	0.89[d], 0.93[e]				**0.87**
2,3-dimethyl-2-butene	0.89[b]	1.00[d], 0.80[e]			0.36[h]	**0.90**
isoprene	0.44[b]	0.27[d]	0.25[f]	0.26[g]	0.19[h]	**0.26**
β-pinene	0.24[b]	0.35[d]				**0.30**
α-pinene	0.83[b]	0.85[d], 0.76[e]	0.70[f]			**0.79**

[a] Error estimated at ca. ±50%. [b] This study, statistical errors at ca. ±25%. [c] Reference 19. [d] References 10, 16, and 17. [e] Reference 11. [f] References 20 and 21. [g] Reference 22. [h] Reference 18.

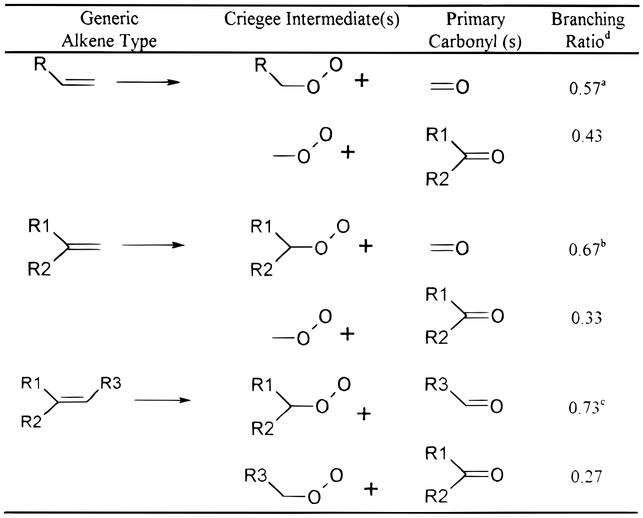
the values for the OH yields from the analytical and modeled evaluation all lie within ±25% of the average value. We therefore take this value as a reasonable estimate of errors due to statistical fluctuations in the data. Systematic errors are more difficult to assess, but the good agreement with the results from a number of groups using a variety of methods indicates that they should be relatively small. However, our value for the OH yield from the reaction of O_3 with isoprene is higher by about 70% compared to the other groups, and it is not clear where the discrepancy arises. There were no unusual experimental difficulties associated with these measurements and, as illustrated in Figure 2, the data were of good quality. It is worth noting that there have been two other high OH yields reported for the ozonolysis of isoprene; Donahue et al.[15] reported a value obtained at a few Torr total pressure of 0.7 ± 0.03 for 2,3-dimethyl-2-butene and around 0.50 for isoprene, while earlier work reported by Paulson gave a value of 0.68 for isoprene.[29] This latter value comes from a study where methycyclohexane was used as an OH tracer. Methylcyclohexane reacts relatively slowly with OH, and as such only ca. 4% of the tracer initially present was actually destroyed in the study. This will result to a larger uncertainty in the reported result.

The final column in Table 2 lists OH yields derived from the average of those reported here and in refs 10, 11, 16, 17, 19, 20, 21, and 22. The only data omitted are our OH yield for the ozonolysis of isoprene and the yield reported by Paulson et al. for the ozonolysis of ethene; some of their experiments were carried out using TMB as a tracer, which, at least in our system, can lead to high OH yields if heterogeneous destruction of TMB by O_3 is not considered.

The OH yields vary in a systematic way with the structure of the alkene, and Atkinson has identified a correlation with the number of β-hydrogens present in the Criegee intermediates that are formed. A very simple, empirical SAR has been applied to the determination of OH yields in the ozonolysis of monoterpenes by Sidebottom and co-workers.[30] OH yields are estimated by structural analogy with one or more alkene species. Some degree of success is attained, but in a number of cases, OH yields are overestimated. To improve on this work, we have developed a SAR that retains the simple empirical nature of OH yield estimation but takes account of the intermediates involved, as well as the geometrical and spatial requirements of the hydroperoxide mechanism of OH production (reaction 4).[31−33] If this mechanism generates OH with 100% efficiency, the $(CH_3)_2COO$ CI and the *syn*-CH_3CHOO CIs should always give OH radicals, while the *anti*-CH_3CHOO CI should not.

The ozonolysis of ethene gives rise to OH with yield 0.13, although the hydroperoxide mechanism cannot operate. In general, the following OH yields are expected for the generic CIs: R_1R_2COO, 1.0; RCHOO, 0.5 (assuming an equal mixture of *syn*- and *anti*-CI); H_2COO, 0.13. Given yields for the formation of primary carbonyl compounds (which are easier to measure than OH yields) OH yields can be estimated. For example, 2-methylbut-2-ene produces acetone with yield 0.31

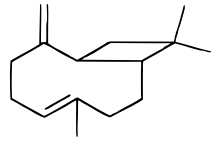
TABLE 4: Branching Ratios for Ozonolyses of Generic Alkenes



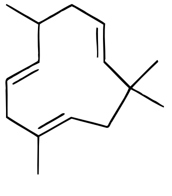
[a] Calculated as mean of values for propene, 1-butene, 1-pentene, 3-methyl-1-butene, and 1-hexene. [b] Calculated as mean of values for 2-methylpropene, 2-methyl-1-butene, 2-methyl-1-pentene, 2,3-dimethyl-1-butene, and 2,3,3-trimethyl-1-butene. [c] Calculated as mean of values for 2-methyl-2-butene, 3,4-diethyl-2-hexene, and 2,4,4-trimethyl-2-pentene. [d] All values taken from ref 24. Values for propene and 2-methyl-2-butene include results from this laboratory.

and acetaldehyde with yield 0.69. The primary yields of the Criegee intermediteas are therefore 0.69 for $(CH_3)_2COO$ and 0.31 for CH_3CHOO, and an OH yield of 0.84 is predicted, which can be compared with the average value in Table 2 of 0.87. It is assumed that, in the generic CIs listed above, the R groups contain H atoms in the β-position to the carbonyl oxide functionality. The more substiuted CI that arises from the ozonolysis of β-pinene has β-hydrogens on both sides of the carbonyl oxide functionality, but one of them is attached to a bridgehead carbon atom and is expected to be difficult to abstract. Therefore, the OH yield from this CI is 0.5 rather than 1.0. The predicted OH yield from the ozonolysis of β-pinene is therefore 0.41 rather than 0.80, which would be expected if the bridgehead hydrogen atom were treated as the other hydrogens. If the primary carbonyl yields have not been measured for an alkene, they can be estimated on the basis of determinations of yields for similar compounds, as displayed in Table 4.

Table 5 is a list of measured OH yields (from the average in Table 3 or from the work of Atkinson and co-workers) along with predicted OH yields, and the estimated yield is plotted as a function of the measured yield in Figure 4. On the whole, the agreement is good, although there are exceptions. For example, the very low measured yield of 0.06 must be compared with our estimated yield of 0.83 for β-caryophyllene, while for α-humulene, a predicted yield of 0.83 compares with a measured yield of 0.25.



Beta-caryophyllene



alpha-humulene

TABLE 5: Measured and Predicted OH Yields

alkene	OH yield (measured)[a]	R_1R_2CO yield[b]	R_3R_4CO yield	OH yield (predicted)
ethene	0.13	1.00		0.13
propene	0.34	0.35	0.65	0.37
Z−2-butene	0.37	1.00		0.50
E−2-butene	0.59	1.00		0.50
2-methyl-2-butene	0.87	0.31	0.69	0.84
2,3-dimethyl-2-butene	0.90	1.00		1.00
α-pinene	0.79	c	c	0.87
β-pinene	0.30	0.22	0.78	0.22
1-butene	0.41	0.35	0.65	0.37
2-methylpropene	0.60	0.32	0.68	0.72
1-pentene	0.37	0.52	0.48	0.30
2-methyl-1-butene	0.83	0.28	0.72	0.75
1-hexene	0.32	0.53	0.47	0.30
2,3-dimethyl-1-butene	0.50	0.38	0.62	0.67
1-heptene	0.27	0.55	0.45	0.29
1-octene	0.32	0.50	0.50	0.31
cyclopentene	0.61	c	c	0.50
cyclohexene	0.68	c	c	0.50
methylcyclohexene	0.90	c	c	0.87
1,2-dimethylcyclohexene	1.01	c	c	1.00
camphene	0.18	0.36	0.64	0.04
3-carene	1.06	c	c	0.87
limonene	0.86	c	c	0.87
myrcene	1.15	c	c	0.87
cis- and *trans*-ocimene	0.63	c	c	0.87
sabinene	0.26	0.50	0.50	0.31
terpinolene	1.03	0.40	0.60	1.00
α-cedrene	0.67	c	c	0.50
α-copaene	0.38	c	c	0.50
β-caryophyllene	0.06	c	c	0.87
α-humulene	0.22	c	c	0.87

[a] Recommended results from Table 2, and average results from ref 1. [b] Corresponds to most substituted primary carbonyl product. [c] Branching ratio taken from Table 3.

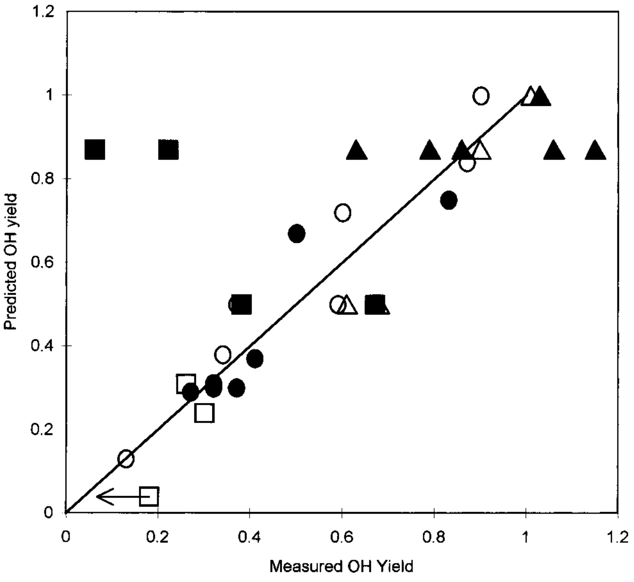


Figure 4. Predicted versus measured OH yields: simple alkenes (open circle); simple alkenes measured this work (closed circle); terpenes (closed triangle); sesquiterpenes (closed squares); strained terpenes with external double bonds (open square); cyclic alkenes with internal double bonds (open triangle).

These examples apart, the root-mean-square deviation between the predicted and measured OH yields is less than 20%, which is good considering the difficulty of measuring the OH yields.

The assumption that OH radicals are formed in the hydroperoxide mechanism is supported by the SAR in Figure 4. Furthermore, the SAR also suggests that OH radicals are formed with unit efficiency when this mechanism can operate. A recent theoretical paper[34] based on ab initio calculations and statistical rate theory indicated that for $(CH_3)_2COO$ the formation of OH should be ca. 60−80% efficient at 1 atm. This is consistent with OH yields measured for the ozonolysis of 2,3-dimethyl-2-butene, if perhaps a little low. Further experiments, particulary studies on the pressure dependence of OH formation, may shed light on this matter. One aspect of the reactions that has not been considered in the development of the SAR concerns the distinction of *syn*- and *anti*-CIs from POZs formed from alkenes with a single alkyl group at one (or both) end of the double bond. For *E*- and *Z*-2-butene, it is assumed that equal concentrations of the *syn*- and *anti*-CIs are formed. However, in all measurements, the OH yield from the ozonolysis of *E*-2-butene is always greater than that for *Z*-2-butene. Calculations indicate that this difference arises because the POZs from the two compounds give *syn*- and *anti*-CIs in different ratios.[35]

The presented SAR can operate successfully for simple alkenes and monoterpenes, but conjugated systems are more difficult to describe. Included in the OH yield predictions reported in Table 5 are values for myrcene and *cis*- and *trans*-ocimene. All three of these compounds contain three centers of unsaturation, but it is expected that the reactivity of the simplest double bonds will dominate over those that are conjugated. As such, SAR predictions are based on this assumption. One final point is that although the SAR seems to predict accurate OH yields for the ozonolysis of a wide range of compounds, very recent work from Paulson et al.[36] suggests that it has some limitation. For example, these workers report a significant fall in the OH yield of terminal alkenes as the chain length increases, and this area of research merits further work.

Insufficient measurements have been made on the ozonolysis of congugated systems to allow a systematic analysis of how OH yields vary with hydrocarbon structure for such compounds. OH yields have been reported for 1,3-butadiene and isoprene, but the choice of site for ozone attack for asymmetric dienes and the effect of conjugation are, at present, uncertain. Trends in OH yields for oxygenated unsaturated species present similar problems.

Reaction Stoichiometries. Reaction stoichiometries (Δ[alkene]/Δ[ozone]) are listed in Table 2. The reason for the nonunity stoichiometries obtained under "OH-free" conditions is unclear. The deviations from unity are real, extreme care having been taken particularly with the stoichiometry measurements for the reaction of ozone with 2-methyl-2-butene. The stoichiometry plots from the reaction of ozone with this compound are shown in both the presence and absence of 2000 ppmv cyclohexane in Figure 5, along with a similar plot for ethene (cyclohexane present). The stoichiometries correlate with the OH yields for simple alkenes as illustrated in Figure 6. Although some OH will react with the alkene, even under "OH-free" conditions, this does not explain fully the observed deviation from unity. For 2,3-dimethyl-2-butene, typical concentrations of 10 ppmv alkene and 2000 ppmv cyclohexane result in a maximum alkene loss of 5% from reaction with OH. In the case of 2-methyl-2-butene, additional experiments were carried out with a concentration of the alkene of 1 ppmv and 2000 ppmv cyclohexane, and a stoichiometry of 1.2 was still obtained. The correlation observed in Figure 6 indicates that the excess consumption of alkene may be linked to the fragment formed as OH is released from the Criegee intermediate. As already discussed, formation of OH is thought to result from the decomposition of the Criegee intermediate, with the concomitant formation of a radical of the type $CH_2{=}CRO^{\bullet}$. Little is know of the kinetics of these radicals, although it is expected that under our conditions they will react with O_2 to generate a peroxy radical of the type $^{\bullet}O_2CH_2CR{=}O$. These radicals are expected to react with other peroxy radicals such as HO_2 and c-$C_6H_{11}O_2^{\bullet}$; some limited information is available about the kinetics of these radicals.[37−39] Neeb and Moortgat[22] have considered the reactions of this type of radical in a model used to describe the ozonolysis of methylpropene. In principle, the large stoichiometries observed in the present work could result from the reaction between the peroxy radical and the alkene. However, although such a process might be able to explain the results shown in Figure 6, peroxy radicals generally react slowly with alkenes, having large activation barriers. In the absence of additional information, we will not speculate further on the meaning of Figure 6.

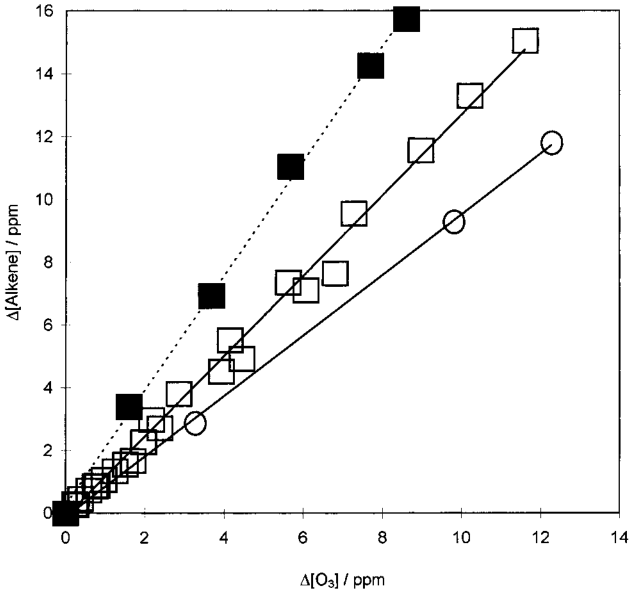


Figure 5. Stoichiometry plots for 2-methyl-2-butene in the presence (open square) and absence (closed square) of excess cyclohexane and ethene (open circle) in the presence of excess cyclohexane.

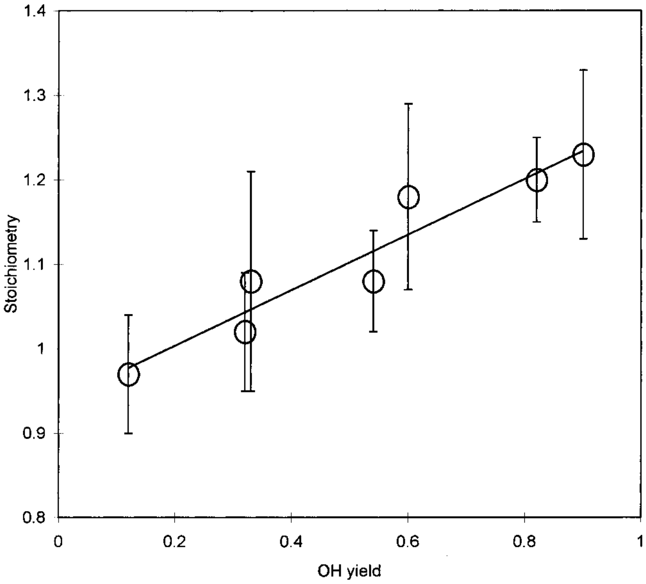


Figure 6. Correlation between stoichiometry and OH yield for ozone−alkene reactions.

Primary Carbonyl Yields. Table 6 lists primary carbonyl yields measured in this work for the ozonolysis of a variety of alkenes, along with yields measured in the presence of 2000

TABLE 6: Primary Carbonyl Yields from the Ozonolysis of Various Alkenes and Terpenes under Varying Conditions

alkene	SO_2[a]/ ppm	Δ[carbonyl]/Δ[alkene]	increase in carbonyl	total CI yield	Hatakeyama yield[h]
propene	0	0.34 ± 0.01[b]			
propene	2000	0.42 ± 0.05[b]	0.12	**0.22**	0.25 ± 0.02
Z-2-butene	0	0.83 ± 0.08[b]			
Z-2-butene	2000	1.02 ± 0.13[b]	0.19	**0.19**	
E-2-butene	0	0.98 ± 0.20[b]			
E-2-butene	2000	1.11 ± 0.17[b]	0.13	**0.13**	0.19 ± 0.03
2,3-dimethyl-2-butene	0	1.04 ± 0.10[f]			
2,3-dimethyl-2-butene	2000	1.15 ± 0.18[f]	0.11	**0.11**	
2-methyl-2-butene	0	0.35 ± 0.03[f]			
2-methyl-2-butene	2000	0.40 ± 0.20[f]	0.08		
2-methyl-2-butene	0	0.66 ± 0.02[b]		**0.10**	
2-methyl-2-butene	2000	0.71 ± 0.21[b]	0.15[g]		
β-pinene	0	0.23 ± 0.09[c]			
β-pinene	2000	0.28 ± 0.08[c]	0.06	**0.14**	0.25 ± 0.02
isoprene	0	0.32 ± 0.04 (ma)[d]			
isoprene	2000	0.38 ± 0.17 (ma)[d]	0.15		
isoprene	0	0.13 ± 0.02 (mvk)[e]		**0.28**	
isoprene	2000	0.17 ± 0.05 (mvk)[e]	0.25		

[a] 2000 ppmv cyclohexane present. [b] Ethanal. [c] Nopinone. [d] Methacrolein. [e] Methylvinyl ketone. [f] Propanone. [g] Ratio of attack at the more substituted double bond to the less substituted double bond is assumed equal to the ma/mvk ratio. [h] References 4 and 40.

ppmv of SO_2. What is clear is that, in all cases, the yield measured in the presence of SO_2 is always higher than the yield measured in its absence. Qualitatively, this effect can be understood in terms of reaction 9.

$$R_1R_2COO + SO_2 \rightarrow SO_3 + R_1R_2CO \qquad (9)$$

Quantitatively, the fractional increase in carbonyl yield can be equated to the fraction of that CI that is stabilized. Unfortunately, the errors associated with the carbonyl yields are relatively large and combine to give large errors in the stabilized CI yield. For symmetrical alkenes, the fractional increase in carbonyl yield can be equated to the fraction of that CI which is stabilized and is also equal to the total fraction of stabilized CI. For unsymmetrical alkenes, the fraction of the CI that is stabilized is given by the change in carbonyl yield divided by the yield of the CI that gives rise to it (which is equal to one minus the carbonyl yield). Thus, for propene, the stabilization yield for methyl carbonyl oxide is given by the change in ethanal yield (0.08) divided by one minus the carbonyl yield (0.66) to give a value of 0.12. Values for stabilization yields for the CIs corresponding to all the carbonyls measured in this study are listed in Table 6. Although the errors are expected to be large, conclusions can be drawn from the numbers. For the compounds that can give rise to methyl carbonyl oxide, four stabilization yields with values between 0.12 and 0.19 are obtained, while for dimethyl carbonyl oxide, two similar values of 0.08 and 0.11 are determined; i.e., the general trend that the CIs decompose more easily as they become more substituted is observed. For 2-methyl-2-butene and the symmetrical alkenes, the total CI stabilization yields can be calculated directly. For the other compounds, formaldehyde was not determined but an estimate of the total stabilization yield can be made if it is assumed that 40% of the H_2COO formed in the reactions is stabilized.[4,40] Although the stabilized yield of H_2COO may be dependent upon the nature of the parent alkene, this value is probably a reasonable approximation for the compounds studied. These yields are also given in Table 6, along with the stabilization yields given by Hatakeyama et al.,[40] with which they can be compared directly. The yields obtained here are within 50% of the yields of Hatakeyama et al.,[40] which, given the large errors in these experiments, must be taken as reasonable agreement. The total CI yields are plotted as a function of (1 − OH yield) in Figure 7. While the plot shows significant scatter, there is a correlation between the two quantities that is entirely consistent with the accepted mechanism for the reactions.

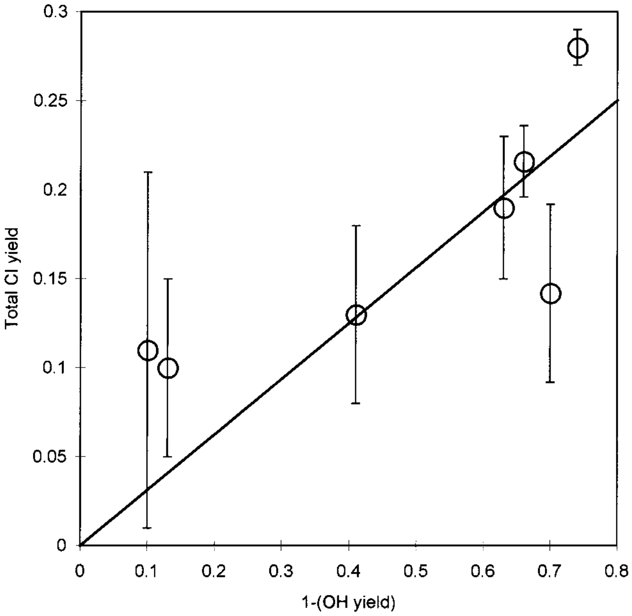


Figure 7. Correlation between total stabilized CI yield and 1-(OH yield). Data from Tables 6 and 3. Error bars reflect the range of values used to determine the average OH yields.

Conclusions

OH yields obtained in this study for the ozonolysis of a range of alkenes are in good agreement with earlier determinations by Atkinson and co-workers[10,11,16,17] and the more recent results of Paulson and co-workers[20,21] and Neeb and Moortgat.[22] Only the OH yield determined for the ozonolysis of isoprene shows a significant deviation from the results of the other workers. A set of OH yields that are internally consistent has now been determined by a number of groups using a number of methods: scavenger (cyclohexane, 2-butanol), tracer (TMB, DMB), and kinetic. Given the variety of the methods used, a reliable database now seems to exist. The work of Horie and Moortgat[28] indicates that the low yields reported by Gutbrod et al.[18] may have resulted from the complexities brought about by the addition of CO to their reaction systems.

The SAR that we have presented allows OH yields to be predicted for the ozonolysis of unsaturated compounds, providing reaction does not take place at a conjugated site. The rationale behind the development of the SAR is that OH is formed via the hydroperoxide mechanism, and the fact that it works provides evidence to support this mechanism. The measured OH yields correlate with the reaction stoichiometries (Δ[alkene]/Δ[ozone]) measured under "OH-free" conditions. This relationship would seem to indicate that the excess consumption of alkene is related to the radical that is generated when OH is formed, although the details of how this occurs are not clear. Primary carbonyl yields measured in the presence and absence of SO_2 appear to provide information about the fraction of stabilized CI formed in the reactions. These yields show a linear correlation with (1 − OH yield), as expected on the basis of the reaction mechanism, and are in general agreement with the yields reported by Hatakeyama et al.[4,40]

The high OH yields reported here support the conclusions of Paulson and Orlando[2] that the reactions of ozone with alkenes can be important sources of the hydroxyl radical in a variety of atmospheric environments. The evidence supporting the hydroperoxide mechanism for OH formation and the correlation of OH yields with reaction stoichiometries highlights the role that radicals such as $^{\bullet}CH_2CHO$ and $^{\bullet}O_2CH_2CHO$ may play in atmospheric chemistry.

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