Product distributions from the OH radical-induced oxidation of but-1-ene, methyl-substituted but-1-enes and isoprene in NO_x -free air[†]

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Received 14th March 2000, Accepted 20th July 2000 Published on the Web 31st August 2000

Product distributions resulting from the OH-induced oxidation of but-1-ene, 2-methylbut-1-ene, 3-methylbut-1-ene and isoprene in air were measured in the absence of nitrogen oxides and compared with predictions based on currently accepted oxidation mechanisms. In the case of butenes, the observed distributions of carbonyl compounds, hydroxyketones, hydroxyalkanals and diols were evaluated to obtain probabilities for the initial attack of OH radical on the outer position of the double bond ($\gamma = 0.90 \pm 0.03$ for 2-Me-but-1-ene and $\gamma = 0.76 \pm 0.05$ for both but-1-ene and 3-Me-but-1-ene), for the probability of formation of stable products in the self-reaction of secondary β -hydroxyperoxyl radicals ($k_{ssb}/k_{ss} = 0.29 \pm 0.07$ for but-1-ene and $k_{\rm ssb}/k_{\rm ss} = 0.19 \pm 0.06$ for 3-Me-but-1-ene), and for the ratio of the reaction with oxygen vs. decomposition of β -hydroxyalkoxyl radicals, $k_3[O_2]/(k_4 + k_3[O_2]) = 0.25 \pm 0.04$ for but-1-ene and $= 0.38 \pm 0.04$ for 3-Me-but-1-ene. The last two values disagree with other published data, which suggest a smaller effect of oxygen. The oxidation of isoprene produced methacrolein and methyl vinyl ketone with a ratio 0.93 + 0.10, the ratio of methyl vinyl ketone and 3-methylfuran was 7.3 ± 1.0 . Other products were 1-hydroxy-3-methylbut-3-en-2-one (identified by mass spectrometry) and 3-methyl-3-oxo-butane (tentatively identified). The overall product distribution was complex and could not be fully elucidated. Computer simulations based on several mechanisms applied the relative probabilities for OH addition found for the but-1-enes. Comparison with the experimental data suggests probabilities for OH addition to the methylated double bond of 0.504 ± 0.027 (outer position) and 0.056 \pm 0.003 (inner position), and to the non-methylated double bond of 0.335 \pm 0.023 (outer position) and 0.105 ± 0.008 (inner position).

Introduction

The degradation of hydrocarbons in the atmosphere is largely initiated by reactions with the hydroxyl radical, OH, which has multiple sources such as ultraviolet photolysis of ozone in the presence of water vapor, the reaction of hydroperoxyl radicals with NO, and photolysis of nitrous acid.^{1.2} Whereas OH reacts with alkanes by hydrogen abstraction, the reactions with alkenes and alkadienes proceed primarily by the addition of OH to a double bond. In both cases, the reactions are followed by further addition of molecular oxygen to the newly created reactive site. This leads to the formation of alkylperoxyl radicals in the first case, and hydroxy-alkylperoxyl radicals in the second case. It is generally assumed that in the atmosphere both types of alkylperoxyl radicals, RO_2 , react with NO

$$RO_2 + NO \rightarrow RO + NO_2$$
 (major) (I)

$$\rightarrow \text{RONO}_2 \text{ (minor)}$$
 (II)

because such reactions have been found to be rapid for a number of alkylperoxyl radicals,^{3–5} and NO is present in daylight due to the photodissociation of NO₂ in addition to direct emissions. The alkoxyl radicals, RO, derived from alkanes undergo further reactions such as

$$RO + O_2 \rightarrow HO_2 + aldehyde/ketone$$
 (III)

 $RO \rightarrow R' + aldehyde$ (IV)

where R' is a carbon-centered radical of lower carbon number than R and the aldehyde formed in reaction (IV) contains one less carbon than that formed in reaction (III). Hydroxyalkoxyl radicals undergo reactions similar to those of alkoxyl radicals, but the fragmentation pathway (IV) has been found to dominate in most cases studied.⁵ Only for the HOCH₂CH₂O radical derived from ethene has hydrogen abstraction by oxygen been found to be important.^{6,7} Larger hydroxyalkoxyl radicals may also isomerise *via* internal hydrogen abstraction,^{5,8} and this reaction path can lead to additional complications. In atmospheric regions where the abundance of NO is low or in laboratory studies of the oxidation of hydrocarbons in the absence of NO_x(=NO + NO₂), peroxyl radicals react with themselves or with other peroxyl radicals present in the reaction system,⁹ for example

 $R_1O_2 + R_2O_2 \rightarrow alcohol + aldehyde/ketone + O_2$ (V)

$$\rightarrow R_1 O + R_2 O + O_2 \tag{VI}$$

$$R_1O_2/R_2O_2 + HO_2 \rightarrow R_1OOH/R_2OOH + O_2$$
 (VII)

where, in reaction (VI), RO radicals appear again as products. The partitioning between reactions (III) and (IV) and reactions (V) and (VI) can be determined, in principle, from the distribution of alcohols, aldehydes and ketones occurring as end products in appropriate laboratory studies.

The present paper deals with the oxidation of methylsubstituted but-1-enes induced by OH radicals, which we have studied in the absence of nitrogen oxides in order to determine

[†] Electronic Supplementary Information available. See http:// www.rsc.org/suppdata/cp/b0/b002053m/

the relative significance of pathways (III) and (IV) on the one hand, and (V) and (VI) on the other, in the hope that the information thus obtained might improve our understanding of the oxidation mechanism of important alkadienes such as isoprene. Fig. 1 shows the main reaction scheme for the oxidation of but-1-ene. Similar schemes apply to the methylsubstituted but-1-enes. The OH-induced oxidation of but-1ene in the presence of NO_x has previously been studied by Atkinson *et al.*¹⁰ and Aschmann *et al.*,¹¹ that of 3-methylbut-1-ene was studied by Atkinson *et al.*¹² In the present work we attempted an unambiguous analytical characterization of the diols and mixed hydroxyaldehydes or hydroxyketones expected to arise from reaction (III)–(V). Model calculations were performed to assist in the data evaluation and to compare calculated with observed product distributions.

The oxidation of isoprene induced by OH radicals has been repeatedly studied in the presence of NO_x .^{13–16} Although the yields of the products methacrolein, methyl vinyl ketone, 3methylfuran and formaldehyde are well characterized, most studies showed a deficit in the product balance indicating the occurrence of additional products. Mechanistic considerations suggest these products to be mainly hydroxycarbonyl compounds. Yu et al.¹⁷ and Kwok et al.¹⁸ have identified several of these compounds by mass spectrometry employing soft ionization techniques. We have oxidized isoprene under NO₂-free conditions similar to those in the oxidation of the but-1-enes in an attempt to detect some of these products and to determine the relative yields of the three main products under conditions different from those used previously. Here again, model calculations were performed to compare observed with expected product distributions. Ruppert and Becker¹⁹ have also studied the oxidation of isoprene in the absence of NO, and found unsaturated diols as evidence for the occurrence of the interaction of peroxyl radicals in this system.

Experimental

Apparatus and experimental procedures were similar to those described previously.²⁰ Reactions were carried out in glass bulbs of 2 L capacity. The interior walls were treated with dimethyl-dichlorosilane to minimize losses of hydroxy-carbonyl compounds and diols. Each bulb was provided with Teflon-stoppered shut-off valves, a silicone rubber septum, and a quartz finger reaching into the center of the bulb, into which a penray mercury lamp was inserted. Specialty quartz was used to block ozone-forming radiation ($\lambda < 235$ nm wavelength). The bulbs were filled with a gas mixture containing approximately 150 ppm H₂O₂ and 0.01–0.1% hydrocar-

bon (mole fraction) in synthetic air. The pressure was slightly above atmospheric. The reaction was started by placing the lit mercury lamp in the quartz finger to generate OH radicals by photolysis of H_2O_2 . Under these conditions, taking into account the known rate coefficients for reactions of OH radicals with H_2O_2 , the but-1-enes, and isoprene,^{3,5} more than 95% of the OH radicals were calculated to have reacted with the hydrocarbon. Following irradiation, the bulb was connected to the sample loop of a gas chromatography *via* a thin Teflon tube pushed through a hole pierced in the septum. Samples were transferred by means of a suction pump.

The sample loop of the gas chromatography was heated to 160 °C. A flame ionization detector was used in conjunction with a 50 m long CP-WAX 52-CB capillary column, 0.32 mm id, 1.2 μ m film thickness. The nitrogen carrier gas flow was 6.9 cm³ min⁻¹. The following column temperature program was mostly used: 40 °C constant for 2 min, followed by a rise of 20 °C min⁻¹ up to 160 °C, which was held for 10 min, followed by a further rise of 30 °C min⁻¹ up to 210 °C.

The alkenes but-1-ene, 2-methylbut-1-ene and 3-methylbut-1-ene, isoprene and the oxidized compounds propanal, 2methylpropanal, butanone, 1-buten-3-one (methyl vinyl ketone), 2-methylpropenal (methacrolein), 3-methylfuran, 1,2dihydroxybutane and 1-hydroxybutan-2-one were available commercially. The diols 1,2-dihydroxy-2-methylbutane and 1,2-dihydroxy-3-methylbutane were prepared by hydroxylation of the corresponding alkenes with performic acid as described by Criegee *et al.*,²¹ 1-hydroxy-3-methylbutan-2-one was prepared by reacting glycolnitrile with isopropylmagnesium bromide as described by Pfeil and Barth.²²

Product identification was made by comparison of peak retention times with those of authentic samples, as far as possible. In a number of cases a combination of gas chromatography and mass spectrometry (GC-MS) with conventional electron impact ionization was used for peak identification. In this case, the sample was injected by the freeze trap-flash heating procedure. Although the instrument was fitted with a similar separating column as that used for quantitative analysis as described above, a different carrier gas flow was required, which gave rise to changes in retention times and resulted in some uncertainty. Peak calibration was performed with gaseous samples as far as possible. Samples were prepared in the reaction bulb by successive dilution of a mixture of the pure substance and air to cover the concentration range encountered. Mixing ratios were determined by means of pressure measurements using capacitance manometers and applying the ideal gas law. Diols and the mixed hydroxycarbonyl compounds, which were not sufficiently volatile for the deter-



Fig. 1 Oxidation mechanism for but-1-ene.

mination of vapor pressures, were injected directly into the reaction bulb in known amounts by means of a calibrated syringe, followed by the admixture of air and further dilution. In cases where authentic samples were unavailable, the calibration factors were estimated by comparison with the signal response for similar compounds. The detector sensitivity varied insignificantly during the time of the experiments so that consistency checks were required only occasionally.

Results

Oxidation of but-1-enes

Product distribution. Fig. 2 shows a set of chromatograms that are typical for the product mixtures arising from the oxidation of but-1-ene and the two methyl-substituted but-1-enes. The patterns are similar. We have concentrated on the four major peaks and ignored other peaks that were marginal. Carbonyl compounds elute after about 3 min, diols after about 12 min. With but-1-ene and 3-methylbut-1-ene one finds hydroxyketones eluting after about 8 min, in the case of 2methylbut-1-ene the hydroxyketone is missing. This is expected from the tertiary hydroxyperoxyl radical involved. Whereas these products were unambiguously identified, an additional peak with lesser intensity occurred in each chromatogram slightly prior to the hydroxyketones. We have assigned these peaks to β -hydroxyalkanals for the following reasons: these compounds are among the expected products in each case (see Fig. 1); they occur with abundances comparable to the products already identified; and the retention times are close to those of the structurally similar hydroxyketones. The β -hydroxyalkanals could not be synthesized, however, so that positive confirmation by means of authentic samples was not possible. Breakdown patterns of the mass spectra supported our assignment, but the parent peaks were missing so that some ambiguity remained. In addition to the products mentioned the interaction between hydroxyalkylperoxyl and hydroperoxyl radicals lead to the formation of hydroxyhydroperoxides. Little is known about the stability of these compounds. Our experience with alkylhydroperoxides



Fig. 2 Chromatograms of gas mixtures resulting from the OH radical-induced oxidation of but-1-ene, 2-methylbut-1-ene and 3-methylbut-1-ene in air.

suggests that primary and secondary species do not survive passage through the GC column at elevated temperatures. Tertiary hydroperoxides are more stable. A tertiary hydroxyhydroperoxide is expected to be formed in the oxidation of 2-methylbut-1-ene. It is possible in this case that the peak identified as the diol, which is considerably larger than that of the corresponding β -hydroxyalkanal, contains a contribution from 1-hydroxy-2-hydroperoxy-2-methylbutane. Finally, one must consider the possibility of products formed by hydrogen abstraction from the side chain of the but-1-enes. The most facile abstraction process involves the tertiary hydrogen atom in 3-methylbut-1-ene. The tertiary peroxyl radical thus formed is expected to produce methyl vinyl ketone. Acetone and a vinyl radical are conceivable alternative products. Methyl vinyl ketone was not detected, and acetone, which on our column was masked by 2-methylpropanal, may arise by a different route (see below). Atkinson et al.,12 who looked for products resulting from H-abstraction from 3-methylbut-1-ene, did not observe methyl vinyl ketone, but found small amounts of methacrolein, which they interpreted to arise from Habstraction following a complex isomerization pathway. They concluded that H-abstraction occurs to about 5% of the overall reaction. We did not detect significant amounts of methacrolein and have ignored the abstraction pathway.

Atkinson *et al.*¹² have also found that the 1-hydroxy-3methyl-2-butoxyl radical resulting from 3-methylbut-1-ene can decompose in two ways, forming either 2-methylpropanal and HCHO or glycolaldehyde and acetone.

HOCH₂CH(O')CH(CH₃)₂ → HOCH₂ + (CH₃)₂CHCHO
→ HOCH₂CHO +
$$\cdot$$
 CH(CH₃)₂

Their data suggest that 20-25% of the decomposition follows the second pathway. On the column used in this study acetone and 2-methylpropanal eluted with almost identical retention times so that they could not be separated. Glycolaldehyde had a retention time of 8.0 min, and should have appeared shortly before 2-hydroxy-3-methylbutanal. Glycolaldehyde may have been present as a minor product, but we estimate that its yield after 30 min irradiation time was < 0.2 ppm.

Table 1 summarizes product distributions derived from quantitative analysis of the chromatograms. The response factor for β -hydroxyalkanals was estimated from that of the 1,2-diols. The response of the hydroxyketones was about 12% lower. Table 1 shows product concentrations obtained 15 and 30 min after starting the reaction. The evolution of products was linear with time for about 20 min. The yield after 30 min was slightly lower, but the relative distribution did not change and an average was taken. The product distributions were used to determine the branching ratios of reactions appearing in Fig. 1.

Model calculations. Fig. 1 shows that OH radicals may attach to the but-1-ene double bond either at the outer or at the inner position. The subsequent addition of oxygen leads to the formation of primary and secondary β-hydroxyperoxyl radicals in the cases of but-1-ene and 3-methylbut-1-ene, whereas the oxidation of 2-methylbut-1-ene involves primary and tertiary β -hydroxyperoxyl radicals. Products evolve from the mutual interactions of these radicals. Table 2 lists reactions that need to be considered. Model calculations were based on the FACSIMILE computer code,²³ and involved an iteration scheme to derive consistent values for the probability γ of OH attack at the outer position of the double bond, and the branching ratios $k_{\rm ssb}/k_{\rm ss}$, $k_3[{\rm O}_2]/(k_3[{\rm O}_2]+k_4)$ and the overall product distribution. A major problem in this approach was a proper choice of rate coefficients for reactions of hydroxyperoxyl radicals. It has been shown by numerous studies summarized in recent reviews9,24 that the rate coefficients for self-reactions of primary, secondary and tertiary alkylperoxyl radicals are of the order of $k_{pp} \approx 10^{-13}$, $k_{ss} \approx$

 Table 1
 Relative product distributions from the oxidation of methyl-substituted but-1-enes

	Retention t	ime	Yield (ppm)	B elative yield (9/)	
Product	Exp. Auth.		15 min	30 min	Average
But-1-ene:					
Propanal	2.44	2.44	5.94 ± 0.14	10.25 ± 0.25	50.6
2-Hydroxybutanal	8.04	_	0.83 ± 0.06	1.52 ± 0.05	7.0
1-Hydroxybutan-2-one	8.59	8.56	2.85 ± 0.15	4.92 ± 0.15	24.2
1,2-Dihydroxybutane	12.49	12.49	2.04 ± 0.07	3.87 ± 0.08	18.2
Total			11.66 ± 0.42	20.49 ± 0.53	
2-Me-but-1-ene:					
Butanone	3.64	3.64	11.09 ± 0.14	18.31 ± 0.33	80.8
2-Hydroxy-2-Me-butanal	7.47	_	0.65 ± 0.03	1.09 ± 0.02	4.6
1,2-Dihydroxy-2-Me-butane	11.74	11.76	1.93 ± 0.03	3.31 ± 0.06	14.3
Total			13.67 ± 0.2	22.71 ± 0.41	
3-Me-1-butene:					
2-Me-propanal ^a	2.65	2.65	6.13 ± 0.30	10.8 ± 0.25	48.1
2-Hydroxy-3-Me-butanal	8.19	_	0.85 ± 0.04	1.61 ± 0.08	6.9
1-Hydroxy-3-Me-butan-2-one	8.40	8.40	3.68 ± 0.07	6.76 ± 0.14	29.5
1,2-Dihydroxy-3-Me-butane	13.69	13.66	1.80 ± 0.08	3.82 ± 0.07	15.5
Total			12.46 ± 0.22	22.99 ± 0.54	
⁴ The signal may include a contribution	of acetone.				

 10^{-15} and $k_{\rm tt} \approx 2.5 \times 10^{-17}$ (unit: cm³ molecule⁻¹ s⁻¹). The rate coefficients for a cross-combination reaction may be estimated by taking the root over the product of the rate coefficients for the two self-reactions.²⁵ Experimental data for the rate coefficients of β-hydroxyperoxyl radicals have also been obtained: rate coefficients for the self-reactions of hydroxyethylperoxyl, 2-hydroxy-3-butylperoxyl and 2-hydroxy-2,3dimethyl-3-butylperoxyl were 2.1×10^{-12} , 6.9×10^{-13} and 4.9×10^{-15} cm³ molecule⁻¹ s⁻¹, respectively.^{26,27} The β hydroxy functionality evidently accelerates the rates of the self-reactions compared to the simple alkylperoxyl radicals. On the basis of these data, we have adopted for the selfreactions of the primary, secondary and tertiary hydroxyradicals involved in the oxidation peroxvl of methyl-substituted but-1-enes the rate constant values listed in Table 2. Values for the rate constants of cross-combination reactions were estimated by the method outlined above for alkylperoxyl radicals.²⁵ For comparison, we also performed calculations using rate coefficients applicable to simple alkylperoxyl radicals. The differences in the results were minor. Reactions with HO₂ radicals, which are formed in the reaction sequences following formation of β -hydroxyalkoxyl radicals, generally are rapid. We have used rate coefficients similar to those reported by Jenkin and Hayman.²⁶

All the reactions involving two organic peroxyl radicals admit two (in the case of cross-reactions three) channels leading either to hydroxyalkoxyl radicals or to diols and mixed hydroxy-carbonyl compounds. The first channel is designated a, the other(s) b or b and c, respectively. As the observed product distribution with four identified products allows only three independent parameters to be determined, further assumptions are necessary for the branching ratios of the self- and cross-reactions of primary peroxyl radicals. The branching ratio for the self-reaction of hydroxyethylperoxyl radicals according to Barnes *et al.*⁶ is $k_{ppb}/k_{pp} = 0.50 \pm 0.06$ at 298 K. Thus, we have assumed standard conditions $k_{\rm ppa}/k_{\rm pp} = 0.5, \ k_{\rm psa}/k_{\rm ps} = 0.5, \ k_{\rm psb} = k_{\rm psc}$ as shown in Table 2, but in order to determine their influence on the calculations we have also varied k_{ppa}/k_{pp} and k_{psa}/k_{ps} within the range 0.3–0.7. For the interaction of primary with tertiary peroxyl radicals, we have assumed $k_{pta}/k_{pt} = 0.67$, $k_{ptc}/k_{pt} = 0.33$. In this case $k_{ptb}/k_{pt} = 0$, because the reaction site lacks an abstractable hydrogen atom. Table 3 shows values for γ and two other branching ratios calculated from the measured product distributions. The range attached to each individual result is that derived by varying the branching ratios of reactions involving primary peroxy radicals within the indicated range. Experimental uncertainties are not included here. Table 3 includes the calculated fractional yields of hydroperoxides. These products contribute appreciably to the total product yield. The effect is greatest in the oxidation of 2-methylbut-1ene because of the comparatively low rate of the self-reaction

Table 2 Rate coefficients used for reactions of hydroxyperoxyl radicals^a

$\begin{array}{l} OH + Bu + O_2 \rightarrow R_pO_2\\ OH + Bu + O_2 \rightarrow R_sO_2\\ OH + Bu + O_2 \rightarrow R_sO_2\\ OH + Bu + O_2 \rightarrow R_tO_2\\ R_pO_2 + R_pO_2 \rightarrow 2 R_pO + O_2\\ R_sO_2 + R_sO_2 \rightarrow 2 R_sO + O_2\\ R_sO_2 + R_sO_2 \rightarrow R_sO + R_s=CO + O_2\\ R_sO_2 + R_sO_2 \rightarrow R_sO + R_s=CO + O_2\\ R_pO_2 + R_sO_2 \rightarrow R_pO + R_sO + O_2\\ R_pO_2 + R_sO_2 \rightarrow R_pO + R_sO + O_2\\ R_pO_2 + R_sO_2 \rightarrow R_pO + R_s=CO + O_2\\ R_pO_2 + R_sO_2 \rightarrow R_sO + R_sO + O_2\\ R_pO_2 + R_sO_2 \rightarrow R_sO + R_sO + O_2\\ R_sO_2 + R_sO_2 \rightarrow R_sO $	1-γ γ γ α b α b b	$R_{OH} \approx 9 \times 10^{11b}$ $k_{pp} = 2.0 \times 10^{-12}$ $k_{ss} = 4.0 \times 10^{-13}$ $k_{psa} = 4.5 \times 10^{-13}$ $k_{psb} = 2.25 \times 10^{-13}$ $k_{psc} = 2.25 \times 10^{-13}$
$R_sO_2 + R_sO_2 \rightarrow 2 R_sO + O_2$ $R_sO_2 + R_sO_2 \rightarrow R_sOH + R_s=CO + O_2$ $R_sO_2 + R_sO_2 \rightarrow R_sOH + R_sO + O_2$	a b	$k_{\rm ss} = 4.0 \times 10^{-13}$ $k_{\rm ssa} = 4.5 \times 10^{-13}$
$R_{p}^{P}O_{2}^{2} + R_{s}^{2}O_{2}^{2} \rightarrow R_{p}^{P}OH + R_{s}^{2}=CO^{2} + O_{2}$ $R_{p}O_{2} + R_{s}O_{2} \rightarrow RCHO + R_{s}OH + O_{2}$ $R_{p}O_{2} + R_{s}O_{2} \rightarrow 2RO + O_{2}$		$k_{\rm psb}^{\rm psa} = 2.25 \times 10^{-13} k_{\rm psc} = 2.25 \times 10^{-13} k_{\rm psc} = 5.0 \times 10^{-15} $
$R_1O_2 + R_1O_2 \rightarrow 2R_1O + O_2$ $R_1O_2 + R_pO_2 \rightarrow R_1O + R_pO + O_2$ $R_1O_2 + R_pO_2 \rightarrow R_1OH + RCHO + O_2$		$k_{\text{pta}} = 5.0 \times 10^{-14}$ $k_{\text{pta}} = 6.7 \times 10^{-14}$ $k_{\text{ptc}} = 3.3 \times 10^{-14}$
$R_pO_2 + HO_2 \rightarrow R_pOOH + O_2$ $R_sO_2 + HO_2 \rightarrow R_sOOH + O_2$ $R_tO_2 + HO_2 \rightarrow R_tOOH + O_2$		$k_{\rm pHO_2} = 1.5 \times 10^{-11}$ $k_{\rm sHO_2} = 1.5 \times 10^{-11}$ $k_{\rm tHO_2} = 1.5 \times 10^{-11}$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$		$k_{\rm HO_2} = 2.5 \times 10^{-12}$

^{*a*} Rate coefficients in cm³ molecule⁻¹ s⁻¹. ^{*b*} Rate of radical formation in molecule cm⁻³ s⁻¹.

Table 3 Oxidation of but-1-enes induced by reaction with OH radicals: probability γ for OH attack at the outer position of the double bond; probability for the formation of stable products in the self-reactions of secondary hydoxyperoxyl radicals; ratio of reaction pathways of secondary hydroxyalkoxyl radicals, and fraction of products, f(ROOH), appearing as hydroperoxides^{*a*,*b*}

Alkene	γ	$k_{\rm ssb}/k_{\rm ss}$	$k_3[O_2]/(k_4 + k_3[O_2])$	k_4/s^{-1c}	f(ROOH)
But-1-ene 3-Me-but-1-ene ^d	0.76 ± 0.05 0.76 ± 0.04 0.78 ± 0.05	$\begin{array}{c} 0.29 \pm 0.07 \\ 0.19 \pm 0.06 \\ 0.16 \pm 0.05 \end{array}$	0.25 ± 0.04 0.38 ± 0.04 0.32 ± 0.04	1.3×10^{5} 6.9×10^{4} 9.0×10^{4}	0.36 0.38 0.38
2-Me-but-1-ene	0.90 ± 0.03			_	0.45

^{*a*} For definition of rate coefficients see Fig. 1. ^{*b*} Assumed range for $k_{ppa}/k_{pp} = 0.5 \pm 0.2$, $k_{psa}/k_{ps} = 0.5 \pm 0.2$, $k_{psb} = k_{psc}$. ^{*c*} Rate constant, if $k_3 = 8 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. ^{*d*} First line: according to the mechanism of Fig. 1; second line: assuming two pathways for the decomposition of the 1-hydroxy-3-methylbutan-2-oxy radical with yields of 78% 2-methylpropane and 22% glycolaldehyde.

of tertiary hydroxy-2-methyl-2-butylperoxyl radicals. In view finding of Atkinson et al.¹² of the that the HOCH₂CH(O')CH(CH₃)₂ radical appearing as intermediate in the oxidation of 3-methylbut-1-ene may enter into two decomposition pathways, additional calculations were performed assuming a 22:78 partitioning between the products glycolaldehyde and 2-methylpropanal. The rate constant and the branching ratio for the self-reaction of the 2-propylperoxyl radicals formed concurrently with glycolaldehyde was taken from Heimann and Warneck,²⁰ the corresponding values for the cross-reactions with other peroxyl radicals were estimated as described above. The results are included in Table 3. The calculations were mainly done to obtain yields of products predicted to occur in addition to those detected and listed in Table 1, namely, acetone, propan-2-ol and glycolaldehyde. Their calculated yields after 30 min of irradiation are (in ppm) 0.086 ± 0.02 , 0.028 ± 0.006 and 2.3 ± 0.4 , respectively. The yields of acetone and propan-2-ol are low, because most of the 2-propylperoxyl radicals react with HO₂ to form 2-propyl hydroperoxide. The yield of glycolaldehyde is substantial, so that this substance should have been observed as a signal in our chromatograms.

Oxidation of isoprene

Product distribution. Isoprene was reacted under experimental conditions similar to those described above for the but-1enes. Relatively high mole fractions of isoprene, namely 100-1000 ppm, were used in order to suppress losses of the major products methacrolein and methyl vinyl ketone by secondary reactions with OH radicals. The use of much smaller concentrations in the range 5-50 ppm produced an undesirably large scatter of the results, which we were unable to remove. Fig. 3 shows a chromatogram of the product series. The temperature programme was slightly modified compared to that described earlier, resulting in a slower elution of products at later times. The leading peaks are due to methacrolein and methyl vinyl ketone with retention times 5.4 and 6.7 min, respectively; 3methylfuran eluted after 5.7 min. Most of the peaks appearing later are small and difficult to identify. In contrast to the study of the but-1-enes we had no authentic samples for hydroxycarbonyl compounds, so that GC-MS was the only method available for product identification. Mass spectra obtained for the largest peaks, numbered 6, 10, 14, are shown in Fig. 4. Included for comparison are mass spectra for methacrolein, 1-hydroxybutan-2-one and 1-hydroxy-3-methylbutan-2-one.

Peak #4 was identified as 3-methylbut-3-enal. As the intensity of the product was low, it was included only in the total count but not in the mechanism to be discussed later. Peak #6 can be assigned to 3-methylbut-3-en-2-one.²⁸ This product may arise from a rearrangement of the radical resulting from the addition of OH to the third carbon atom of isoprene as shown in Fig. 5. The assignment of the next peak is more problematic. The mass spectrum for peak #10 lacks the fragmentation pattern in the range 37–42 u that is characteristic of the CH₃C=CH₂ group (compare with methacrolein), and it features a strong signal at 43 u, which indicates either CH₃CO⁺ or C₃H₇⁺ as fragments, or both. The signal with the highest mass number that is clearly above the background appears at 86 u. If this were the parent peak, the most reasonable assignment of the mass spectrum would be to 2methylbutan-3-one. This ketone, however, should elute at a much earlier time, that is, with a retention time closer to that of methyl vinyl ketone, whereas the observed retention time is more characteristic of that of a difunctional compound. We have considered butan-2,3-dione, but found that the spectral intensity distribution is not fully consistent with the published mass spectrum.²⁷ In addition, it is difficult to identify a route to its formation. Yu et al.¹⁷ have shown that 1-hydroxy-3buten-2-one (hydroxymethyl vinyl ketone) occurs as a product in the oxidation of isoprene in the presence of NO_x. This compound also features a parent peak at 86 u. The fragmentation pattern is expected to include a peak at 55 u from the elimination of CH₂OH. Although this is observed, the companion peak expected to occur at 31 u is weak. In contrast, the mass spectrum of 1-hydroxybutan-2-one shows strong signals at 31 and 29 u in addition to the peak at 57 u resulting from the loss of CH₂OH. Also inconsistent with 1hydroxybut-3-en-2-one are the peak at 71 u, which signals the loss of methyl, and the strong peak at 43 u. We have looked for alternatives and note that 3-oxo-butanal would feature a strong mass 43 fragment peak and a parent peak at 86 u. However, elimination of the CHO group would require a fragment peak at 57 u, which is missing from the mass spectrum. We conclude that an assignment based on a parent peak at 86 u is difficult to justify on the basis of the observations. The two compounds identified in the oxidation of 3-methylbut-1ene: 1-hydroxy-3-methylbutan-2-one (shown in Fig. 4) and 2hydroxy-3-methylbutanal, feature mass spectra in which the parent peaks at 102 u are practically absent and either the CH₂OH or the CHO group is split off to produce peaks at 71 and 73 u, respectively. For comparison and future reference, we present here the spectral intensity distributions (mass 102



Fig. 3 Chromatogram of products resulting from the oxidation of isoprene in NO_x -free air: Peak identification (1) methacrolein, (2) 3-methylfuran, (3) methyl vinyl ketone, (6) 2-methylbut-1-en-3-one; (10) 2-methyl-3-oxo-butanal (tentative, see text), (14) 1-hydroxy-3-methylbut-3-en-2-one.



Fig. 4 Mass spectra of peaks number 6, 10, 14 and methacrolein observed as products of the oxidation of isoprene, and of 1-hydroxy-butan-2-one and 1-hydroxy-3-methylbutan-2-one observed in the oxidation of but-1-ene and 3-methylbut-1-ene, respectively.

plus the six most prominent peaks); 1-hydroxy-3methylbutan-2-one: 1, 22, 43, 17, 4, 9, 4% for mass numbers 102, 71, 43, 41, 39, 31, 29, respectively; 2-hydroxy-3-methylbutanal: nil, 21, 15, 21, 16, 12, 15% for mass numbers 102, 73, 60, 55, 43, 41, 29, respectively. The mass spectra of the corresponding hydroxy-carbonyl compounds formed in the oxidation of isoprene would have parent peaks at 100 u, but according to our experience with products from 3-methylbut-1-ene the parent peaks are expected to be extremely weak. We now consider this possibility. The fragment peak at 71 u may then be assigned to the elimination of CHO and the peaks at 86 and 85 u to the elimination of CH₂ and CH₃, respectively. There is no elimination of CH₂OH, because the corresponding signals at 69 and 31 u are absent. Accordingly, the mass spectrum suggests an assignment to either one of the two compounds 2-hydroxy-3-methylbut-3-enal or 2-hydroxy-2methylbut-3-enal. The first would be inconsistent with the high intensity of the signal at 43 u and the absence of the CH₂C=CH₂ group fragmentation pattern. 2-hydroxy-2methylbut-3-enal would be more consistent with these features, but it is not expected to be formed in high yield, because addition of OH to the inner carbon atom of the methylated double bond of isoprene has a low probability. We have, therefore, considered yet another possible candidate compound, namely 2-methyl-3-oxo-butanal, which also features a parent peak at 100 u. The mass spectrum of this compound is expected to contain fragment peaks at 85, 71 and 43 u resulting from elimination of CH₃, CHO and CH₃CO. It appears that this compound is most consistent with the observed mass spectrum. We conclude that peak #10 may be assigned to 2-hydroxy-2-methylbut-3-enal as well as to 2methyl-3-oxo-butanal. Whereas the former is an expected product, the latter is unexpected. Fig. 5 shows a possible route to its formation.

Peak #14, as the gas chromatogram in Fig. 3 shows, consists of a not fully resolved doublet (14 and 14a). The resolution achieved by GC-MS was similar to that evident in Fig. 3, so that the mass spectrum of peak #14 may contain contributions from two compounds. The mass of peak #14a was complex and could not be evaluated. In contrast to peak #10, the spectrum associated with peak #14 features a distinct parent peak at 100 u, and the fragment peak at 69 u suggests elimination of CH₂OH. In this case the elimination of CH₂OH is confirmed by the appearance of a signal at 31 u. The mass spectrum also shows the characteristic fragmentation pattern of the CH₃C=CH₂ group in the range 37 to 42 u, with signals at 39 and 41 u being dominant. In many respects the spectrum is similar to that of 1-hvdroxy-3-methylbutan-2one, so that it can be confidently assigned to 1-hydroxy-3methylbut-3-en-2-one. The presence of a peak at 71 u suggests loss of CHO. Although this may be a fragment from the identified compound, we cannot preclude that it is due to contamination.

Table 4 summarizes product yields observed in the oxidation of isoprene. Because of the deliberately chosen high concentrations of isoprene it was not possible to derive absolute product yields based on the consumption of isoprene. The yields for methyl vinyl ketone (MVK), methacrolein (MAC) and 3-methylfuran were calculated from experimental calibration factors. For the products that were characterized only by mass spectrometry, the calibration factors were estimated by means of compounds with similar structures. The relative yields thus obtained were found to vary little between each run. Averaged values are shown in the last column of Table 4. The molar ratio of methacrolein to methyl vinyl ketone is 0.93 ± 0.10 , markedly larger than that found in the presence of NO_x, which is about 0.71, but it decreased slightly with



Fig. 5 Suggested reaction schemes for the formation of the products 3-methylbut-3-en-2-one and 2-methyl-3-oxo-butanal.

Table 4 Relative product distributions obtained from the oxidation of isoprene

		$Yield/\mu mol\ mol^{-1}$	Deletine sield		
Product	Retention time/min	15 min ^{<i>a</i>}	30 min ^{<i>a</i>}	Average	
Methacrolein	5.43	3.96 ± 0.11	7.28 ± 0.15	0.350 ± 0.010	
3-Methylfuran	5.74	0.52 ± 0.08	1.21 ± 0.12	0.052 ± 0.005	
Methyl vinyl ketone	6.67	4.05 ± 0.10	8.21 ± 0.20	0.376 ± 0.015	
Peak $#4^{b}$	7.33		0.14 ± 0.03		
Peak $\#6^{c}$	8.63	0.22 ± 0.02	0.45 ± 0.02	0.021 ± 0.001	
Peak #10	14.24	1.50 ± 0.08	2.70 ± 0.14	0.131 ± 0.007	
Peak $\# 14^d$	17.40	0.80 ± 0.12	1.30 ± 0.20	0.067 ± 0.010	
Total		11.05 ± 0.51	21.31 ± 0.85		

time when the reaction bulb was left standing after irradiation and before analysis. 1-hydroxy-2-methylbut-3-en-2-hydroperoxide is expected to be a major product under NO_x -free conditions (see calculations). This compound is expected to decompose by forming methyl vinyl ketone, which would explain the decrease in the MAC/MVK ratio.

Calculated product distribution. The FACSIMILE computer program²³ was used to calculate product distributions. The overall reaction mechanism was similar to the scheme described by Jenkin et al.29 with certain modifications outlined below. A list of reactions is given in the Electronic Supplementary Information.[†] The oxidation mechanism for isoprene involves six isomeric radicals resulting from the addition of OH as shown in Fig. 6. Further addition of oxygen leads to the corresponding peroxyl radicals. These include the tertiary species A, a secondary radical D and the primary radicals B, C, E and F. In order to account for the results of our product studies we have tentatively added another peroxyl radical G originating from the rearrangement of the precursor radical of F (see Fig. 5). Self- and cross-reactions of the primary species **B** and **E** resulting from a shift of the double bond are expected to yield 4-hydroxymethylbutenaldehydes and 1,4-diols in addition to 3-methylfuran. Gu et al.13 and Paulson and Seinfeld³⁰ assigned 3-methylfuran to arise from isomerization of the hydroxyalkoxyl radicals derived from species B and E, and we followed their suggestion. Jenkin et al.²⁹ adopted an alternative route first suggested by Atkinson et al.,³¹ assuming 3-methylfuran to be formed from the hydroxyalkoxyl radicals derived from species C and F. It is currently not possible to decide which one of the two pathways is more realistic. The secondary species D is expected to produce 1.2-hydroxyketone and 1.2-diol in addition to methacrolein. Primary peroxyl radicals were assumed to yield 50% aldehydes and alcohols and 50% alkoxyl radicals in most cases. For the secondary species \mathbf{D} we applied the partitioning between ketone/alcohol and alkoxyl radical that was derived for 3-methylbut-1-ene: 0.175: 0.825. The tertiary radical A

was assumed to form 20% of 1,2-dihydroxy-2-methylbut-3-ene in cross-reactions with other peroxyl radicals. Alkoxyl radicals resulting from species **C** and **F** were assumed to undergo fragmentation leading to methyl vinyl ketone and methacrolein, respectively. The alkoxyl radicals derived from **A**, **B**, **E** and **D** may follow alternative routes of decomposition and reaction with oxygen. The associated product distributions were described by the parameters α , κ and j, which are defined as follows:

A: 1-hydroxy-2-methylbut-3-en-2-oxy

$$\xrightarrow{\alpha} \text{ methyl vinyl ketone}$$

$$\xrightarrow{1-\alpha} 1-hydroxybut-3-en-2-one$$

B: 1-hydroxy-2-methylbut-2-en-4-oxy

 $\xrightarrow{\kappa} 3\text{-methylfuran}$ $\xrightarrow{1-\kappa} 4\text{-hydroxy-3-methylbut-2-enal}$

E: 1-hydroxy-3-methylbut-2-en-4-oxy

$$\xrightarrow{\kappa}$$
 3-methylfuran
$$\xrightarrow{1-\kappa}$$
 4-hydroxy-2-methylbut-2-enal

D: 1-hydroxy-3-methylbut-3-en-2-oxy

$$\xrightarrow{1-j} \text{methacrolein}$$

$$\xrightarrow{1-j} 1-\text{hydroxy-3-methylbut-3-en-2-one}$$

Calculations were carried out for two initial conditions: one case assumed the presence of NO_x under conditions similar to those reported by Tuazon and Atkinson,¹⁴ who used ethyl nitrite as an indirect source of OH; in the second case NO_x -



Fig. 6 Isomeric peroxyl radicals produced by the addition of the OH radical to isoprene: A-F are commonly assumed, G is tentative.

free conditions were assumed similar to those used for the but-1-enes. The Electronic Supplementary Information† lists the participating reactions in a simple code based on the assignment of peroxyl radicals in Fig. 6. The associated rate coefficients were initially assumed to be the same as in Table 2, except for the self-reactions of the radicals **B** and **E**, for which a value of 6.8×10^{-13} was used, similar to that given by Jenkin et al.³² for the self-reaction of the allyl-peroxyl radical. Subsequently, the rate coefficients reported more recently by Jenkin et al.29 were used. The results differed little, however.

The relative probability of OH addition at the inner and outer position of the isoprene double bonds was assumed to be the same as for the but-1-enes: 90:10 for the methylated double bond and 76: 24 for the non-methylated one. In order to estimate the probability for the addition of OH radicals to either of the two double bonds, we made use of the experimentally observed ratios of methyl vinyl ketone to methacrolein and to 3-methylfuran in the presence of NO_x . Under these conditions one expects the seven peroxyl radicals shown in Fig. 6 to be largely converted to the corresponding alkoxyl radicals. The formation of nitrates in the reactions of peroxyl radicals with NO, for which a uniform yield of 12% was assumed, would not greatly alter the peroxyl radical distribution. If, as shown in Fig. 6, the probability for OH addition to the left-hand side is designated y, the probability for 1,4-isomeric shift of the double bond is designated z and x, respectively, and the fraction of peroxyl radical F derived from its precursor is p, the ratio of the yield of the major products is

$$\frac{[MVK]}{[MAC]} = \frac{y(0.9z\alpha + 0.1)}{(1 - y)(0.76jx + 0.24p)}$$
(1)

$$\frac{[MVK]}{[MFU]} = \frac{(y/\kappa)(0.9z\alpha + 0.1)}{0.9y(1-z) + 0.76(1-y)(1-x)}$$
(2)

We have provisionally set $\kappa = 0.5$ and z = x. The ratios of yields [MVK]/[MAC] reported in the literature as 1.35 (Gu et al.¹³), 1.38 (Tuazon and Atkinson¹⁴), 1.44 (Paulson et al.¹⁵), 1.4 (Grosjean et al.³³) and 1.45 (Miyoshi et al.¹⁶). The average value is 1.4. The ratios of yields that have been reported for

Table 5 Calculated values for v. the site of OH addition to isoprene. and x = z, the degree of 1,4-isomeric shift to form radicals **B** and **E**, for several parameters^a

k	j	а	р	У	x = z
0.5	0.62	1.0	1.0	0.508	0.858
0.5	1.0	1.0	1.0	0.590	0.840
0.5	0.62	0.75	1.0	0.569	0.875
0.5	1.0	0.75	1.0	0.648	0.862
0.5	1.0	1.0	0.2	0.529	0.853
0.5	1.0	1.0	0.0	0.511	0.857

text for definitions of parameters

methyl vinyl ketone and 3-methylfuran are: 6.44 (Tuazon and Atkinson¹⁴), 7.19 (Gu et $al.^{13}$) and 8.88 (Paulson et $al.^{15}$). The average is about 7.5. These data were then used in combination with eqn. (1) and (2) to evaluate y and x = z for several values of the parameters α , *j* and *p*. Table 5, which summarizes the results, shows that little variation occurs for $x = z \approx 0.85$, whereas y covers a wider range of values between 0.51 and 0.65.

Table 6 summarizes the calculated product distributions. One important result is that, in the absence of NO_x , methyl vinyl ketone and methacrolein are predicted to occur in nearly equal yields, which agrees with the experimental observations. In fact, the calculated yields of methyl vinyl ketone, methacrolein and 3-methylfuran differ little, regardless of assumptions made in the individual runs, so that it is not possible to distinguish between the different cases that were considered by comparing the results with experimental data.

Hydroperoxides are predicted to be formed in high yields, in agreement with the results of Jenkin et al.29 Most of the many other products are formed in small yields making it difficult to quantify them under any experimental conditions. 1-Hydroxybut-3-en-2-one and 1-hydroxy-3-methylbut-3-en-2one are the only compounds that would occur in fairly high yield under favorable conditions. The former compound was not observed, although we should have been able to detect it experimentally, indicating that the parameter α must be close

Table 6 Calculated percentage product distributions resulting from the OH-induced oxidation of isoprene in the presence and absence of NO_x (source of OH is either ethyl nitrite^{*a*} or hydrogen peroxide^{*b*}), depending on the branching factory y

C	C ₂ H ₅ ONO ^{<i>a</i>}						H ₂ O ₂ ^b						
<u>y</u>		0.508	0.590	0.569	0.648	0.529	exp. ^c	0.508	0.590	0.569	0.648	0.529	exp. ^d
Methacrolein M	AC	23.88	27.21	21.09	23.61	24.70	22 ± 5	18.62	21.89	16.74	18.69	19.72	19.1 ± 1.0
Methyl vinyl ketone M	VK	33.69	38.37	29.75	33.40	34.87	32 ± 7	18.14	21.87	18.90	22.22	18.60	20.5 ± 1.2
3-Methylfuran M	FU	4.24	4.85	3.75	4.20	4.42	4.8 ± 0.6	2.54	3.04	2.38	2.77	2.66	2.8 ± 0.3
Formaldehyde He	СНО	58.19	66.17	59.93	67.19	60.18	63 ± 10	36.81	43.02	38.20	44.15	38.37	
1,2 Dihydroxy-2-methylbut-3-en AG	OH + COH		_			_		2.29	2.67	2.72	3.10	2.78	
1,2 Dihydroxy-3-methylbut-3-en D	OH + FOH	_	_	_	_	_		5.37	3.44	4.83	3.90	3.49	
1,4-Dihydroxy-2-methylbut-2-en BO	OH + EOH	_	_	_	_	_		1.91	2.16	1.69	1.86	1.98	
2-Hydroxy-2-methylbut-3-enal Co	СНО	_	_	_	_	_		1.05	1.23	1.20	1.38	1.10	
2-Hydroxy-3-methylbut-3-enal FG	СНО	_	_	_	_	_		2.47	2.08	2.19	1.80	0.46	
4-Hydroxy-2-methylbut-2-enal EG	СНО	2.05	1.92	1.57	1.41	2.02		2.14	2.09	1.77	1.60	2.14	
4-Hydroxy-3-methylbut-2-enal BC	СНО	2.50	3.28	2.46	3.08	2.69		2.63	3.58	2.78	3.51	2.06	
1-Hydroxy-3-methylbut-3-en-2-one D	СО	9.40	_	8.36		_		10.76	3.37	10.00	3.18	3.74	3.7 ± 0.6
1-Hydroxybut-3-en-2-one H	MVK	_	_	8.60	9.63	_		_	_	3.18	3.99	_	
Methanol Cl	H ₃ OH	_	_	_	_	_		_	_	0.66	0.80	_	
3-Methylbut-3-en-2-one	-		_			0.79			_	_	_	0.90	1.1 ± 0.1
2-Methyl-3-oxo-butanal ^e G	СНО		_			6.26			_	_	_	6.40	7.1 ± 0.4
1-Hydroxy-2-methylbutan-3-one G	ОН	_	_	_	_	_		_	_	_	_	1.72	
Organic nitrates		10.51	10.49	10.47	10.45	10.40	~11	_	_	_	_	_	
OH + MAC secondary products		0.55	0.61	0.48	0.65	0.53		0.06	0.07	0.05	0.06	0.06	
OH + MVK secondary products		0.46	0.51	0.41	0.55	0.45		0.03	0.04	0.03	0.04	0.03	
1-Hydroxy-2-hydroperoxy-2-methylbut-3-ene AG	ООН		_			_		22.09	23.83	23.64	25.14	22.59	
1-Hydroxy-2-hydroperoxy-3-methylbut-3-ene D	ООН	_	_	_	_	_		5.33	4.09	4.20	3.13	5.02	
Hydroxyhydroperoxides total		_	_	_	_	_		31.72	31.87	31.40	31.41	31.00	

^{*a*} Initial concentrations (unit: molecule cm⁻³): $[C_2H_5ONO] = 2.4 \times 10^{14}$, $[NO] = 1.9 \times 10^{14}$, $[NO_2] = 2.3 \times 10^{13}$, $[C_5H_8] = 2.4 \times 10^{14}$, after 4 min reaction time. ^{*b*} Initial concentrations (unit: molecule cm⁻³): $[H_2O_2] = 3 \times 10^{14}$, $[C_5H_8] = 2.5 \times 10^{16}$, after 15 min reaction time. ^{*c*} From Tuazon and Atkinson¹⁴ as corrected by Atkinson. ^{5 *d*} Prorated observed product distribution. ^{*e*} Tentative assignment.

Published on 31 August 2000. Downloaded by Universidad de Oviedo on 31/10/2014 15:21:18.

to unity. The yield of 1-hydroxy-3-methylbut-3-en-2-one was less than that predicted by setting the parameter j = 0.62, so that competition between reaction with oxygen and decomposition of the alkoxyl precursor radical is less favorable than wefound for the oxidation of 3-methylbutene. Evidently, decomposition toward methacrolein is preferred, and 1hydroxy-3-methylbut-3-en-2-one is formed primarily by crosscombination reactions of peroxyl radicals involving species **D** as one of the reactants. Our assignment of peak #10 as 2methyl-3-oxo-butanal must be considered tentative. Nevertheless, when allowance is made for the formation of this product along the suggested pathway, it is possible to bring calculated and experimentally estimated yields of the two products 3-methylbut-3-en-2-one and 2-methyl-3-oxo-butanal into approximate agreement.

Discussion

Methyl-substituted but-1-enes

It has been possible to observe and quantify the mixed hydroxy-carbonyl compounds and diols expected as products from the oxidation of but-1-enes. The observed fraction of 2hydroxyalkanals provided an indication for the relative probability of OH addition at the two sites of the double bond (Table 3). The behavior of but-1-ene and 3-methylbut-1-ene is similar: OH attack occurs to $76 \pm 5\%$ at the outer position, to $24 \pm 5\%$ at the inner position. With 2-methylbut-1-ene the probability in favor of the terminal position is higher, about 90%. The probability in the case of the first two but-1-enes is similar to that found by Tuazon and Atkinson³⁴ for the reaction of OH with methyl vinyl ketone, where OH addition to the terminal carbon atom occurs with $72 \pm 21\%$ probability. The result that addition at the terminal position atom is favored is in agreement with previous estimates based on structural considerations.³ It is also known that the rate coefficient for OH addition to methyl-substituted double bonds is about twice that for unsubstituted double bonds.35 For example, for but-1-ene $k_{OH} = 3.1 \times 10^{-11}$, for 3-methylbut-1-ene $k_{OH} = 3.2 \times 10^{-11}$, whereas for 2-methylbut-1-ene $k_{OH} = 6.5 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (ref. 3, 34). Peeters *et al.*,³⁶ following earlier work of Atkinson³⁷ aimed at establishing group additivity rules, have argued that the differences in the rate coefficients should depend mainly on the type of radical generated, i.e. whether it is a primary, secondary or tertiary radical, and they assigned site-specific rate coefficients of 0.45×10^{-11} , 3.0×10^{-11} and 5.5×10^{-11} cm³ molecule⁻¹ s^{-1} , respectively, which they derived from the known rate coefficients for the reactions with ethene, but-2-ene, and 2,3dimethylbut-2-ene.^{3,35} The total rate coefficient for each compound is then obtained from the sum of the site-specific rate coefficients. Accepting the scheme of Peeters et al.³⁶ leads to the following predicted percentages for OH addition at the outer and inner positions of the double bonds: 87:13 for but-1-ene and 3-methylbut-1-ene, and 92:8 for 2-methylbut-1-ene. The observed values 76: 24 and 90: 10 agree approximately with prediction, the former less well than the latter. Our values for γ depend critically on the observed relative yields for the 2-hydroxyalkanals. If we had overestimated their yields from but-1-ene and 3-methylbut-1-ene by a factor of two, the values for OH addition to the outer and inner positions of the double bond would be 0.87: 0.13, in much better agreement with prediction.

The product distributions observed for the oxidation of but-1-ene and 3-methylbut-1-ene provide branching ratios for the self-reaction of secondary hydroxy-alkylperoxyl radicals and relative probabilities $k_4/(k_4 + k_3[O_2])$ for the break-up of hydroxyalkoxyl radicals vs. their reaction with oxygen. The data in Table 3 suggest values for $k_{\rm ssb}/k_{\rm ss}$ of 0.29 \pm 0.07 and 0.19 \pm 0.06, respectively. These values are lower than those

known for alkylperoxyl radicals,⁹ but the radical-terminating reaction pathway is still important. Similarly, $k_4/(k_4$ $+ k_{3}[O_{2}]$ is 0.75 + 0.04 and 0.62 + 0.04, respectively, indicating that the reaction with oxygen cannot be entirely neglected. Atkinson et al.,¹⁰ who studied the oxidation of but-1-ene in the presence of NO., found a propanal yield of 0.94 + 0.12 relative to hydrocarbon consumption. From the present data one calculates a propanal yield of 0.81 ± 0.04 under similar conditions, where the range reflects mainly the estimated analytical uncertainties. Both values are consistent within the margin of error. Aschmann et al.¹¹ recently reported 1-hydroxybutan-2-one to occur as a product from the OHinduced oxidation of but-1-ene in the presence of NO_x. Gas chromatographic analysis indicated a molar yield of 0.005 in air at atmospheric pressure, and of 0.024 in a gas mixture containing about 90% of oxygen, whereas our results would suggest a much higher yield of about 0.19. The difference is difficult to explain. In our system, the fraction of 1-hydroxy-2butoxyl radicals reacting with oxygen is assessed mainly from the difference between the yields of hydroxyketones and diols relative to that of the alkanal decomposition product. It does not depend much on the probability of OH addition to either side of the double bond. Varying the parameters in the calculations within a fairly wide range did not greatly change the results. In order to reduce the ratio $k_3[O_2]/(k_4 + k_3[O_2])$ derived for but-1-ene from 0.25 to 0.1, the yield of 1hydroxybutan-2-one would have to be about halved or that of butane-1,2-diol raised by about 50%. We consider this unlikely in view of the 5-7% precision observed in calibrating the signals. The calibration curves for 1-hydroxyketones and diols were linear and met the zero point with little deviation indicating that losses on the walls of the reactor were not overly significant. Aschmann et al.¹¹ worked with a 7900 L Teflon chamber, which also should have minimized wall losses, but the gas mixture was stirred by fan so that the products experienced wall contact more frequently.

For the oxidation of 3-methylbut-1-ene the results of Atkinson *et al.*¹² indicate that the yield of 2-methylpropanal and glycolaldehyde combined is 0.85 ± 0.12 relative to hydrocarbon consumption. From the present data we calculate a yield of 0.75 ± 0.05 under similar conditions assuming that the glycolaldehyde/2-methylpropane ratio is similar. We did not detect glycolaldehyde, although the calculations showed that it should have been observable. If the yield of glycolaldehyde were significantly lower than that reported by Atkinson *et al.*,¹² the yield of 2-methylpropanal in the presence of NO_x would be 0.71. While both results lie within common error limits, our ratio $k_4/(k_4 + k_3[O_2])$ is lower than that derived from the data of Atkinson *et al.*¹² by a margin similar to that observed for the oxidation of but-1-ene.

The assumption, based on data available for several alkoxyl radicals,3,5 that the rate coefficient for the reaction with oxygen is approximately 8×10^{-15} cm³ molecule⁻¹ s⁻¹ suggests values for k_4 of 1.3×10^5 s⁻¹ and 0.7×10^5 s⁻¹ for the decomposition of the 1-hydroxybutan-2-oxy radicals resulting from but-1-ene and 3-methylbut-1-ene, respectively. If glycolaldehyde were formed to the extent observed by Atkinson et al.,¹² the latter rate coefficient would be $\sim 1.0 \times 10^5$ s⁻¹. The rate constant for decomposition of the hydroxyethoxyl radical is similar, namely 1.5×10^5 s⁻¹ (ref. 3, 6, 7). Orlando et al.⁷ have shown that in this case about 25% of the HOCH₂CH₂O radicals decompose promptly while the others are thermalized and undergo competition between decomposition and reaction with oxygen. For 1-hydroxypropyl-2-oxy radicals derived from propene Vereecken et al.38 calculated that 80% decompose promptly, while the others are thermalized but also decompose at a high rate, $2.4 \times 10^7 \text{ s}^{-1}$ at 298 K and atmospheric pressure, whereas Atkinson³⁹ calculated a total decomposition rate of $\sim 1 \times 10^5$ s⁻¹, more in line with the above data.

Isoprene

Our search for products that are suggested to arise from the oxidation of isoprene in addition to methyl vinyl ketone, methacrolein and 3-methylfuran has been only partly successful, but we were able to identify the 1,2-hydroxy-carbonyl compound that according to our mechanism is expected to arise from species D (see Fig. 6). Comparison with the results of calculations indicates that decomposition of the 1-hydroxy-3-methylbut-3-en-2-oxy radical to form methacrolein is preferred over its reaction with oxygen. Ruppert and Becker¹⁹ reached the same conclusion because they found that varying the concentration of oxygen has little influence on the yield of methacrolein. Another identified product is 2-methylbut-1-en-3-one. The mass spectrum of peak #10indicates 2-methyl-3oxo-butanal to be a major product. We reiterate that identification of the latter product is tentative. Paulson and Seinfeld³⁰ have postulated a similar product, namely 1hydroxybut-1-en-3-one, to be formed from species E. This product would undergo enolisation and relax to 3-oxobutanal. The mass spectrum observed for peak #10 was not consistent with 3-oxo-butanal, however. Provided our interpretation of the mass spectrum of peak #10 is correct, the products assigned to peaks numbered 6 and 10 suggest a rearrangement of the radical preceding the formation of species F (see Fig. 5), so that another species G would be formed. The calculations show that by including this route into the mechanism it is possible to simulate the experimentally observed yields of peaks numbered 6 and 10 in Fig. 3, if a partitioning between F and G is chosen that favors G.

There was no evidence for the formation of 1-hydroxybut-3en-2-one, so that we cannot support the suggestion of Jenkin et al.²⁹ for a loss of methyl from the 1-hydroxy-2-methylbut-3en-2-oxyl radical at high yield. The generation of methyl radicals in the system is considered necessary for the formation of methanol, which Ruppert and Becker¹⁹ found to occur with a yield of $1.7 \pm 0.3\%$ in the absence of NO_x. Neither the calculations of Jenkin et al.²⁹ nor our own calculations, which are based on similar assumptions, led to methanol yields of the required magnitude. An alternative route to the formation of methyl radicals may be a decomposition of the 2-hydroxy-2methylbut-3-enyl radical resulting from OH addition to isoprene at the 2-position (the precursor to species C in Fig. 6).

 $\label{eq:CH2} \begin{array}{c} \mbox{-}\mathrm{CH}_2\mathrm{C(OH)(CH_3)CH=CH_2} & \xrightarrow{-\mathrm{CH}_3} \mathrm{CH}_2=\mathrm{C(OH)CH=CH}_2\\ \\ \mbox{-}\mathrm{CH}_2=\mathrm{C(OH)CH=CH}_2 \rightarrow \mathrm{CH}_3\mathrm{COCH=CH}_2 \end{array}$

where 2-hydroxybuta-1,3-diene formed as the second product would undergo enolisation to methyl vinyl ketone.

Ruppert and Becker¹⁹ also observed 1,2-hydroxy-2methylbut-3-ene and 1,2-hydroxy-3-methylbut-3-ene as products with yields of $4.7 \pm 1.4\%$ and $2.4 \pm 0.9\%$, respectively. Our calculations indicated yields of 2.3-3.1% for the former compound and of 3.4-5.4% for the latter. The first is smaller and the second greater than the observed values. Jenkin *et al.*²⁹ found yields of 3.9% and 1.7%, which agree better with the observations. The formation of 1,2-hydroxy-2-methylbut-3-ene occurs predominantly in cross-reactions of the tertiary peroxyl radical **A**, that of 1,2-hydroxy-3-methylbut-3-ene arises mainly from the self- and cross-reactions of the secondary peroxyl radical **D**, and the yields of both diols depend greatly on the chosen branching ratios.

The following % yields of methacrolein and methyl vinyl ketone were previously reported: Miyoshi,¹⁶ 22 and 17, Ruppert and Becker,¹⁹ 17.8 \pm 1.4 and 15.3 \pm 1.2. The corresponding ratios are 1.29 and 1.16 \pm 0.18, respectively. The ratio observed here is 0.93 \pm 0.10, which is smaller but still in agreement with the previous data within common error margins. The calculations show that while the yield of methacrolein (in the absence of NO₂) is fairly constant with time,

that of methyl vinyl ketone is much smaller initially and rises with time until it approaches that of methacrolein. Accordingly, the ratio of both yields changes with time. The experimental data confirmed this behavior by a slight decrease of the MAC/MVK ratio when the irradiation time was increased from 15 to 30 min. The reason is that tertiary peroxyl radicals of type A initially prefer to react with HO₂ to form hydroperoxide before their concentration builds up sufficiently to support the self-reaction and cross-reactions with other peroxyl radicals. The yield of tertiary hydroperoxide, in turn, is calculated to be high initially, before it decreases as methyl vinyl ketone builds up. Calculated relative yields of methacrolein, methyl vinyl ketone and 3-methylfuran in the absence of NO_x depend somewhat on the parameter y, which was derived from the observed relative yields in the presence of NO_x. Although the calculated relative yields agree well with the experimental data regardless of the assumptions made, the lowest MAC/MVK ratio, about 0.86, was found for $\alpha = 0.75$. The alternative route to the formation of methyl radicals discussed above would not affect the MAC/MVK ratio.

Peeters et al.²⁷ predicted for the addition of OH to isoprene a probability y = 0.65 at the methylated double bond and 1 - y = 0.35 at the non-methylated one. They assumed that the addition occurred mainly at the outer ends of the double bond and only to 5% each at the inner position. Jenkin et al.,29 who adopted these factors in their calculations, found it necessary to assume $\alpha = 0.75$ and a correspondingly high yield of 1-hydroxybut-3-en-2-one in order to account for [MVK]/ $[MAC] \approx 1$ in the absence of NO_x. We have applied our results obtained for the but-1-enes, that is, we have assumed a ratio of 90:10 for the addition of OH to the methylated double bond (outer and inner position) and a ratio of 76:24 to the non-methylated bond, taking y to be a parameter determined from the [MVK]/[MAC] ratio in the presence of NO_x. The highest value, v = 0.65, was obtained with $\alpha = 0.75$. However, the observed yield of 1-hydroxybut-3-en-2-one was too low as that the high value y = 0.65 can be supported. The lowest value, y = 0.51, can also be disregarded in view of the fairly low yield of 1-hydroxy-3-methylbut-3-en-2-one observed compared to that predicted by the calculations based on j = 0.62. It appears that 0.53 < y < 0.59, the precise value depending on the choice of mechanism. These results suggest the following probabilities for OH addition to the four unsaturated carbon atoms in isoprene (see Fig. 6): 0.504 ± 0.027 (first), 0.056 ± 0.003 (second), 0.105 ± 0.008 (third), 0.335 ± 0.023 (fourth). The value for y clearly is somewhat smaller than that predicted by Peeters et al.³⁶ but probably still within the common error margins. It remains to be verified whether conjugated alkadienes can be assumed to behave in a similar way as alkenes, so that the relative probabilities of OH addition to the individual carbon atoms in isoprene suggested here require further confirmation.

Acknowledgements

Financial support of this work by the German Federal Ministry for Research and Technology is gratefully acknowledged.

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