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Products from the gas-phase reaction of some unsaturated alcohols with nitrate radicals

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Five structurally similar unsaturated alcohols, 2-propene-1-ol (allyl alcohol), 3-butene-2-ol, 2-methyl-3-butene-2-ol (MBO232), 2-butene-1-ol (crotyl alcohol) and 3-methyl-2-butene-1-ol (MBO321), were examined to clarify their atmospheric degradation pathways *via* oxidation initiated by NO_3 radicals. The reactions were investigated using a 0.153 m^3 static glass reactor equipped with long-path FTIR spectroscopy. The experiments were performed at a pressure of 1020 ± 5 mbar and at a temperature of 297 ± 2 K in air or nitrogen as the bath gas. The identified and quantified gas phase products were small carbonyl compounds such as acetone, formaldehyde, acetaldehyde, glycolaldehyde and 2-nitrooxy acetaldehyde. The specific products and their yields varied for the five studied alcohols as follows: formaldehyde 37(±1)% and 2-nitrooxy acetaldehyde 41(±7)% from allyl alcohol; acetaldehyde 28(±6)%, formaldehyde 2(±1)% and 2-nitrooxy acetaldehyde 33(±4)% from 3-butene-2-ol; acetone 63(±6)% and 2-nitrooxy acetaldehyde 67(±8)% from MBO232; acetaldehyde 12(±2)%, formaldehyde 10(±3)% and glycolaldehyde 7(±2)% from 2-butene-1-ol; acetone 21(±6)%, formaldehyde 11(±3)% and glycolaldehyde 29(±10)% from MBO321. In addition, yields were estimated for total organic nitrates using an average integrated absorption cross section of unspecified organic nitrates. Tentative reaction schemes were proposed from the yielded products. The distribution between bond breakage and other processes such as abstraction of a hydrogen atom from the alkoxy radical, formed in the degradation process, was estimated. The small carbonyl compounds were produced by the bond breakage mechanisms. Large multi-functional organic compounds *e.g.* 1-hydroxy-3-nitrooxy-3-methyl-2-butanone from MBO321 were proposed to be formed by hydrogen abstraction. From the product distribution, the contribution of the number of methyl group substituents at the α and γ carbon atoms, influencing the bond breakage pattern, is discussed. The observed bond cleavage trends are correlated to a substitution pattern where electron donating methyl substituents increase the stability of the leaving radical groups.

Introduction

In recent years, the scientific community has paid increasing attention to biogenic volatile organic compounds (BVOC) because such substances are thought to be important elements of atmospheric chemistry. The emission of BVOC, including compounds such as monoterpenes, isoprene and many other reactive hydrocarbons, is estimated at greater than 1000 Tg $year^{-1}$ of C.[1] BVOC often react with atmospheric oxidants as fast, or faster than anthropogenically emitted organic substances.[2] Thus, BVOC have a potential to contribute to the adverse effects that are caused by anthropogenic organic air pollutants, *e.g.* photochemical oxidant formation and haze. Some unsaturated C_5 alcohols have been identified as components of the complex BVOC mixture under certain conditions and have been quantified by several groups. In an early study by Goldan *et al.*,[3] 2-methyl-3-butene-2-ol (MBO232) was reported in mixing ratios of up to several ppb (nmol mol^{-1}) at a remote mountain site in Colorado, USA. This study showed that the concentration of MBO232 could exceed that of isoprene by a factor of between five and eight. Recently, Harley *et al.*[4] demonstrated significant emission of MBO232 from *P. contorta* Dougl. var. *latifolia* Engelm. (lodgepole pine) and *P. ponderosa* Laws. (ponderosa pine), that were in agreement with the concentrations of MBO232 measured by Goldan *et al.* Guenther *et al.* observed the direct emission of MBO232 from *P. teada* (loblolly pine) trees.[5] In addition, emission of two structurally similar compounds, 3-methyl-2-butene-1-ol (MBO321), and 3-methyl-3-butene-1-ol (MBO331) has been observed from different types of vegetation.[6] Degradation processes and products from this group of BVOC are of interest, considering the potentially high emission rates of these unsaturated alcohols to the atmosphere.

Degradation of unsaturated compounds in the atmosphere is often initiated by addition of OH, NO_3, O_3 or Cl atoms to the double bond. The substituent pattern of the carbon atoms in the double bond affects the electron distribution of the bond with consequences for addition rate and possibly also for product distribution. As an example, an alkyl group exerts a positive inductive effect and it makes the double bond more susceptible to electrophilic attack.[7] The strong connection between the number of alkyl groups attached to the carbon atoms and reaction rates is seen *e.g.* in the series ethene, propene, 2-butene, 2-methyl-1-propene and 2,3-dimethyl butene, with rate coefficients for nitrate radical reaction of 0.02, 0.94, 33, 940 and 5700 ($\times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}), respectively.[8]

A number of mechanistic studies regarding C_5 unsaturated alcohols have been reported for the OH- and O_3-initiated degradation,[9–14] while fewer investigations have been conducted

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for degradation by NO_3.[9,11] In a recent mechanistic study of the MBO232 reaction with NO_3 radicals by Fantechi *et al.*,[11] the authors reported a 68.7 and 13% yield of acetone and organic nitrates, respectively. Work on products and mechanisms by Alvarado *et al.*[13] for MBO232 reacting with OH radicals has also shown the formation of acetone, aldehydes and organic nitrates in the presence of NO. Formation of carbonyls and organic nitrates plays an important role in the atmosphere since they may be photolysed and thereby be a source of free radicals. Organic nitrates may act as a reservoir for NO_x and could be subject to long range transport.[15,16] A strong source of acetone is considered as being of importance for global atmospheric chemistry.[17–20]

In this work, five structurally similar unsaturated alcohols, including some of the MBOs, were examined to clarify their degradation pathways *via* oxidation initiated by NO_3 radicals. 2-propene-1-ol (allyl alcohol), 3-butene-2-ol, 2-methyl-3-butene-2-ol (MBO232), 2-butene-1-ol and 3-methyl-2-buten-1-ol (MBO321) were investigated. The last four compounds may be regarded as methyl substituted varieties of the basic compound 2-propene-1-ol. Fig. 1 illustrates the common structure within the dotted-line box and the five examined compounds.

Identification and yield of some products, leading to mass balance is presented. Tentative reaction schemes are proposed from the yield of products and the influence of the methyl group substitution is discussed.

Experimental set-up and procedures

The experiments were carried out in a 0.153 m^3 borosilicate glass reactor at 297(±2) K and 1020(±5) mbar pressure. Reactants and products were measured by long optical path Fourier transform infrared (FTIR) spectroscopy using a Nicolet Magna 560-spectrometer equipped with an MCT detector. Spectra were collected at 1.0 cm^{-1} resolution using a 40 m optical path length. Spectra of the reaction mixture were based on various numbers of scans (64, 84 or 180 at 1 scan s^{-1}) to obtain a balance between good spectral quality and time resolution at different stages of the reaction. A dilution system using pressure–volume measurements was employed to introduce known amounts of the various substances into the reactor. Synthetic air or nitrogen was used as bath gas. A detailed description of the set-up can be found elsewhere.[21]

The concentration of reactants and products in the experiments were determined by scaled subtraction using spectra of reference compounds at known concentrations. The scale factors were linear to concentration, *i.e.* Beer's law obeyed, over the concentration intervals employed. However, for 2-nitrooxy acetaldehyde (2-NAA) there was no possibility to achieve a good calibration owing to the instability of this compound. Its concentration in the reference spectrum was therefore estimated as described below for the unidentified organic nitrates. The NO_3 radicals were generated by thermal decomposition of N_2O_5. The N_2O_5 was synthesised in a separate set-up by the reaction of excess O_3 with NO_2 according to reaction (1) followed by reaction (2). The N_2O_5 was then trapped and stored at 195 K.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (1)$$

$$NO_2 + NO_3 \leftrightarrow N_2O_5 \qquad (2)$$

The experiments were conducted by first introducing the unsaturated alcohol to the reactor, confirming its concentration by FTIR spectroscopy and then adding N_2O_5 by a stream of bath gas. As an exception, for a few experiments with MBO232 and MBO321, N_2O_5 was prepared *in situ* by mixing O_3 with excess NO_2. A relatively high concentration of NO_2 (2.0 × 10^{14} molecule cm^{-3}) was present when MBO232 or MBO321 was added, to ensure that no O_3 was left. Further, some other experiments with even higher initial NO_2 concentration (4.9 × 10^{14} molecule cm^{-3}) were con-

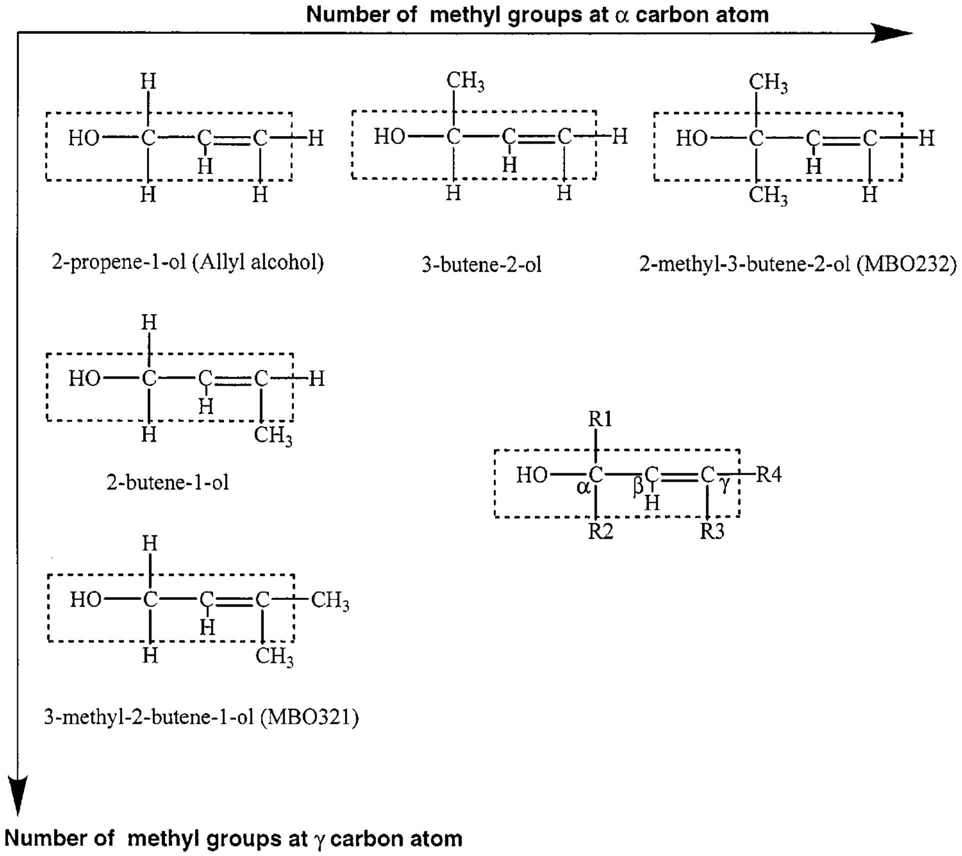


Fig. 1 Structure of the investigated compounds. The common structure possesses allyl alcohol-like carbon skeleton with a hydroxy group in the α position and double bond between the β and γ carbon atoms.

ducted to assess the role of NO_2 in the reaction mechanisms. Initial concentrations of the unsaturated alcohols and N_2O_5 are listed in Table 1. In all experiments, the reactions were monitored by FTIR spectroscopy, until concentration changes ceased. Yields were obtained from graphs of product formed *vs.* alcohol lost. For curved plots, *e.g.* for organic nitrates (R–ONO_2), the first few points after the concentration of the transient peroxy nitrate had decreased to less than 3% of reacted alcohol, were used to obtain an estimate of lower limit yields. The end $RONO_2$ measured at the termination of an experiment represents a situation where less volatile products have equilibrated between the gas phase and reactor walls and/or aerosol particles. The error for the average values is given as one standard deviation. Further discussion of the influence of peroxynitrate formation on product yield will follow later in this paper.

In order to estimate the yield of total organic nitrates in the experiments, a C_{1-10} nitrates' average integrated band area (IBA) absorption cross section for the ONO_2 nitrooxy group band located between 800 and 900 cm^{-1},[22] was used in analogy to previous studies to estimate the concentration of one or more organic nitrates formed.[21,23–26] With this method, the total organic nitrates measured contain all the products that have absorption between 800 and 900 cm^{-1}. Table 2 shows the list of organic nitrates and their cross sections from previous studies.[21,24–26] The values indicate that the cross sections do not change drastically despite the difference in molecular structure of the organic nitrates. Therefore, it is concluded that using the average cross section value is an acceptable way of estimating the total yield of organic nitrates.

The stability and wall adsorption characteristics of the individual alcohols were investigated by introducing them into the reactor and monitoring the concentration over time. Typically, less than 1% h^{-1} was lost and with 3% for MBO321 being the extreme case. This loss rate was insignificant compared to the rate of reaction, thus it was not taken into account for the yield calculation.

Chemicals used were: 2-propene-1-ol (>95%, Merck), 3-butene-2-ol (>97%, Merck), MBO232 (>98%, Aldrich), 2-butene-1-ol (>97%, mixture of *cis* and *trans*, Aldrich), MBO321 (>99%, Aldrich), and glycolaldehyde dimer (>98%, Fluka). For all the investigated compounds, freeze–pump–thaw cycles were repeated several times to eliminate dissolved

Table 1 Experimental conditions. All experiments were made at 297(±2) K and 1020(±10) mbar

Investigated compound	Initial concentration/molecule cm^{-3}		
	[N_2O_5]	[Unsaturated alcohol]	[NO_2]
Allyl alcohol	1.9×10^{14}	8.7×10^{14}	—
Allyl alcohol	2.0×10^{14}	8.7×10^{14}	—
3-Butene-2-ol	1.9×10^{14}	8.9×10^{14}	—
3-Butene-2-ol	2.0×10^{14}	8.4×10^{14}	—
3-Butene-2-ol	2.0×10^{14}	8.5×10^{14}	4.9×10^{14}
3-Butene-2-ol	2.0×10^{14}	1.0×10^{15}	4.9×10^{14}
3-Butene-2-ol	1.9×10^{14}	1.7×10^{15}	4.9×10^{14}
MBO232	1.5×10^{14}	1.3×10^{15}	$\sim 2.0 \times 10^{14}$
MBO232	1.5×10^{14}	2.0×10^{14}	$\sim 2.0 \times 10^{14}$
MBO232	2.2×10^{14}	2.4×10^{14}	—
MBO232	2.2×10^{14}	2.4×10^{14}	—
MBO232	1.8×10^{14}	1.5×10^{15}	—
MBO232	1.7×10^{14}	1.5×10^{15}	4.9×10^{14}
MBO232	1.8×10^{14}	1.6×10^{15}	4.9×10^{14}
MBO232	1.9×10^{14}	1.8×10^{15}	4.9×10^{14}
2-Butene-1-ol	2.4×10^{14}	9.3×10^{14}	—
2-Butene-1-ol	1.4×10^{14}	9.2×10^{14}	—
MBO321	1.2×10^{14}	2.8×10^{14}	$\sim 2.0 \times 10^{14}$
MBO321	9.1×10^{13}	2.0×10^{14}	$\sim 2.0 \times 10^{14}$
MBO321	1.5×10^{14}	2.5×10^{14}	—
MBO321	1.5×10^{14}	2.4×10^{14}	—
MBO321	1.6×10^{14}	2.7×10^{14}	—
MBO321	1.8×10^{14}	3.0×10^{14}	—
MBO321	3.2×10^{13}	3.7×10^{13}	—
MBO321	2.7×10^{14}	3.8×10^{14}	—

Table 2 Absorption cross sections used to obtain an average value for this study[21,24–26a]

Compound	IBA absorption cross section /cm $molecule^{-1}$ (base 10)	Ref.
Methyl nitrate	0.854(±0.02)	25
Ethyl nitrate	1.09(±0.02)	25
Isopropyl nitrate	1.09(±0.05)	25
3-Nitroxy-2-butanone	1.31(±0.04)	21
2,3-Butyl di-nitrate	1.37(±0.05)[b]	21
3-Nitroxy-2-butanol (*RR*; *SS*)	1.23(±0.02)	21
3-Nitroxy-2-butanol (*RS*; *SR*)	1.18(±0.02)	21
2-Nitro-3-butyl nitrate	1.46(±0.07)	21
C10-alkyl nitrates	1.46(±0.09)	24, 26
Average	1.25(±0.20)	

[a] The average nitrate absorption cross section (1.25×10^{-17} cm $molecule^{-1}$) was used to calculate the yield of total organic nitrate. The stated errors are at the 95% confidence level. [b] The value indicated is one half of the original cross section.

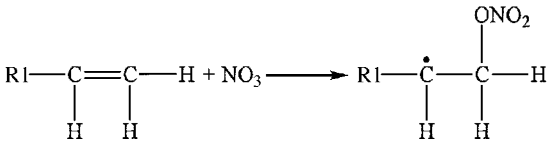
gases before use in the dilution system. Synthetic air (20% O_2 in N_2 99.996%, AGA Gas AB) was employed as bath gas for the experiments. Reference spectra used for the authentication and quantification of the products were taken in nitrogen (99.996%, AGA Gas AB).

One of the products, 2-nitrooxy acetaldehyde (2-NAA), from NO_3 oxidation of allyl alcohol, 3-butene-2-ol and MBO232 was synthesised for qualitative analysis. This compound was prepared by nitration of glycolaldehyde with N_2O_5 in much the same way as described by Kames *et al.* for preparation of various organic nitrates from alcohols.[27] First, 0.5 g (0.0042 mol) of glycolaldehyde dimer $(C_2H_4O)_2$ was suspended and partly dissolved in CCl_4 (8 g) at room temperature. The suspension was then solidified by cooling to 197 K, a vacuum applied, and 0.7 g (0.0065 mol) of N_2O_5 was sublimated onto the frozen solid mixture. The temperature of the mixture was then raised to 273 K, again taking the liquid suspension form, stirred for 20 min and further gradually raised to 293 K with continuous stirring for another 20 min. A greenish coloured liquid, containing impure 2-NAA, was separated on top of the CCl_4 phase. Attempts to remove HNO_3 that was also formed during the reaction were only partially successful. Repeated extraction with cold, NaCl-saturated water finally gave an aqueous phase with pH 5–6 indicating that the HNO_3 was essentially removed and that the ester was not hydrolysed rapidly. However, on standing at room temperature for 20 min, the product again became acidic and gave off NO_2. Thus, the compound is thermally unstable and difficult to prepare in a pure state for quantitative work. Organic nitrates are potentially dangerous because of explosion hazard; therefore, anyone contemplating their synthesis and use should employ accepted safety procedures.

The product was analysed with GC/MS and FTIR. The mass spectrum showed the molecular ion peak at m/z 105 and the NO_2 typical for organic nitrates at m/z 46. The gas phase FTIR spectrum showed strong characteristic organic nitrate absorbance at 1678, 1285, and 842 cm^{-1}.

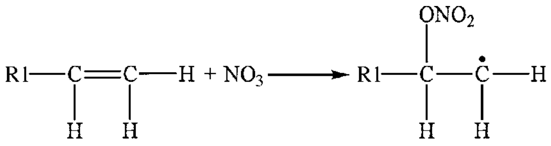
Results and discussion

Table 3 shows the observed products and the fractional molar yield of identified compounds. In addition, estimated yields of unidentified compounds, that are useful for assessing reaction paths, are given. The degradation of unsaturated organic compounds by NO_3 radicals is initiated by addition to one of the carbon atoms in the double bond.[2] The tendency of NO_3 addition to the less substituted carbon atom and to produce the more stable radical product is in accordance with the "anti-Markovnikov's" rule in reaction (3a). However, it has often been observed that the less stable radical is also formed in a significant yield and it is therefore necessary to consider both possibilities.[28]



$$\mathrm{R1{-}\underset{H}{C}{=}\underset{H}{C}{-}H + NO_3 \longrightarrow R1{-}\underset{H}{\overset{\bullet}{C}}{-}\underset{H}{\overset{ONO_2}{C}}{-}H}$$

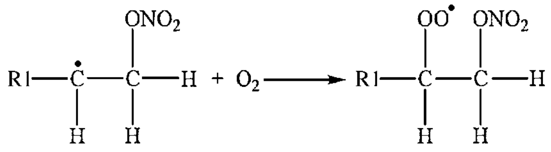
(3a)



$$\mathrm{R1{-}\underset{H}{C}{=}\underset{H}{C}{-}H + NO_3 \longrightarrow R1{-}\underset{H}{\overset{ONO_2}{C}}{-}\underset{H}{\overset{\bullet}{C}}{-}H}$$

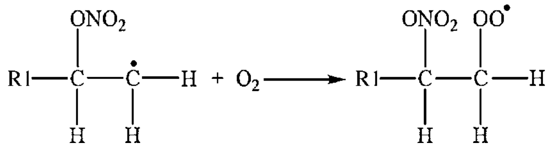
(3b)

Under atmospheric conditions and in the present experiments, *i.e.* in the presence of oxygen, the initially formed alkyl radical in reaction (3a) or (3b), will add O_2 to form a nitrooxy-substituted alkylperoxy radical in reaction (4a) or (4b).



$$\mathrm{R1{-}\underset{H}{\overset{\bullet}{C}}{-}\underset{H}{\overset{ONO_2}{C}}{-}H + O_2 \longrightarrow R1{-}\underset{H}{\overset{OO^\bullet}{C}}{-}\underset{H}{\overset{ONO_2}{C}}{-}H}$$

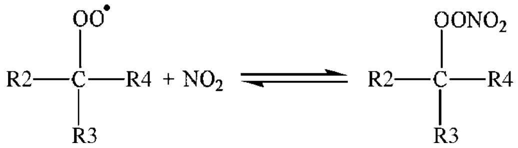
(4a)



$$\mathrm{R1{-}\underset{H}{\overset{ONO_2}{C}}{-}\underset{H}{\overset{\bullet}{C}}{-}H + O_2 \longrightarrow R1{-}\underset{H}{\overset{ONO_2}{C}}{-}\underset{H}{\overset{OO^\bullet}{C}}{-}H}$$

(4b)

The peroxy radicals thus formed may react with NO, NO_2, NO_3, HO_2 or other peroxy radicals in the atmosphere.[2,29] However, in the present experiments NO is excluded as reactant. In the presence of NO_2, an alkyl peroxynitrate may be formed in equilibrium with the alkylperoxy radical and NO_2 according to reaction (5).



$$\mathrm{R2{-}\underset{R3}{\overset{OO^\bullet}{C}}{-}R4 + NO_2 \rightleftharpoons R2{-}\underset{R3}{\overset{OONO_2}{C}}{-}R4}$$

(5)

For all the experiments, formation of an alkyl peroxynitrate was shown by the presence of IR bands at ~1730 and ~790

Table 3 Summary of the molar based product yields[a]

Compound	Acetone (%)	Acetaldehyde (%)	HCHO (%)	Glycolaldehyde (%)	Nitrooxy acetaldehyde (%)	Initial R–ONO_2 (estimate) (%)	End R–ONO_2 (estimate) (%)
Allyl alcohol $n = 2$	ND	ND	37(±1)	<2	41(±7)	53(±10)	30(±1)
3-Butene-2-ol $n = 2$	ND	27(±7)	2(±2)	ND	32(±6)	41(±6)	32(±5)
3-Butene-2-ol[b] $n = 3$	ND	28(±6)	2(±1)	ND	33(±4)	54(±10)	45(±5)
MBO232 $n = 5$	63(±6)	ND	4(±1)	ND	67(±8)	71(±12)	63(±6)
MBO232[b] $n = 3$	59(±1)	ND	1(±0)	ND	63(±5)	71(±10)	64(±14)
2-Butene-1-ol $n = 2$	ND	12(±2)	10(±3)	7(±2)	ND	38(±6)	27(±1)
MBO321 $n = 8$	21(±6)	ND	11(±3)	29(±10)	ND	60(±39)	29(±6)

[a] n = number of experiments carried out. ND = not detected. [b] High initial NO_2 (4.9×10^{14} molecule cm^{-3}) concentration.

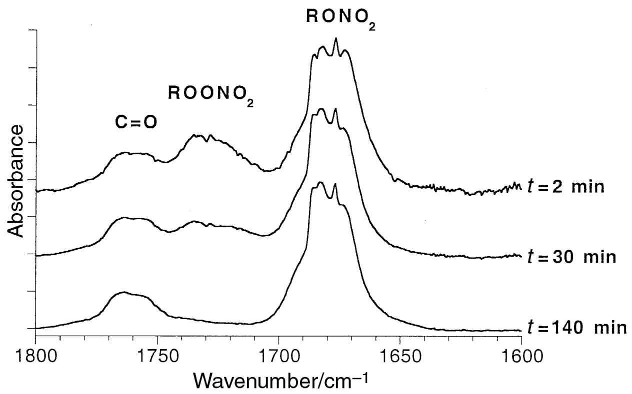


Fig. 2 An example of peroxy nitrate and total organic nitrates formation in a MBO232 experiment. Spectra are scaled, offset and subtracted with MBO232, HCHO, acetone, HNO_3, N_2O_5, NO_2, H_2O and HO_2NO_2. The absorbance is given in arbitrary units.

cm^{-1}. Fig. 2 illustrates the formation and disappearance of the peroxynitrate as time advances. The peroxynitrate serves as a temporary storage for the peroxy radical. To obtain more accurate values, when estimating the total alkyl nitrate concentration, IR absorption due to the presence of the nitrooxy peroxynitrate was subtracted.

Products from the reaction of a peroxy radical with another peroxy radical may be the corresponding oxy radicals.[2,29] Another possible outcome from the reaction between two peroxy radical entities is the formation of an alcohol and a ketone by elimination of molecular oxygen. For the investigated compounds, this may produce tri-functional species (hydroxycarbonyl nitrate, dihydroxynitrate). This process is not accessible for the tertiary alkylperoxy radicals.[2] Also, the HO_2 and NO_3 reactions with peroxy radicals could give alkoxy radicals in high yield. The reaction with HO_2 can produce an organic hydroperoxide in a second channel as is shown in reaction (6).

$$ROO + HO_2 \rightarrow ROOH + O_2 \qquad (6)$$

This channel is very important in certain cases, *e.g.* the reaction between the methylperoxy radical and HO_2 produces methyl hydrogenperoxide in a yield close to 100%.[30]

The further reaction of the oxy radicals is the crucial step to determine the product distribution.[31,32] The possible reaction channels for the oxy radicals produced from the investigated compounds are shown in Figs. 3–7.

As can be seen in Table 3, a closed mass balance has not been achieved from the detected products for any of the investigated compounds. These poor mass balances need to be considered, since no significant remaining unidentified absorption feature could be observed in the residual infrared spectra from any experiment.

One possible cause is production of compounds with functional groups that do not absorb infrared radiation strongly, and therefore, can not be detected. As an example, the epoxide functional group does not absorb strongly in the IR. Epoxides have been observed as major products from NO_3 initiated degradation of unsaturated compounds under conditions of low pressure and low oxygen concentration.[33] Thus, taking the conditions of the present investigation into account, significant epoxide formation appears unlikely. However, no reference IR spectra were available for identification or to set any upper limits for epoxide yield. Another type of compound for which no reference spectra were available is hydroperoxide. Hydroperoxide may be formed from nitrated peroxy radicals reacting with HO_2 according to reaction (6).

Another cause may be loss of substances from the gas phase. The loss may take place in two ways. A substance may either be adsorbed to the walls of the reactor or it may form an aerosol. The first event was indicated by the formation and decay of the total organic nitrates (alkyl nitrates) with time. In all experiments, the decay continues after all N_2O_5 has disappeared. No other conceivable reactant is present at a concentration high enough to cause such loss. Unimolecular decomposition is a possibility, but the decomposition should

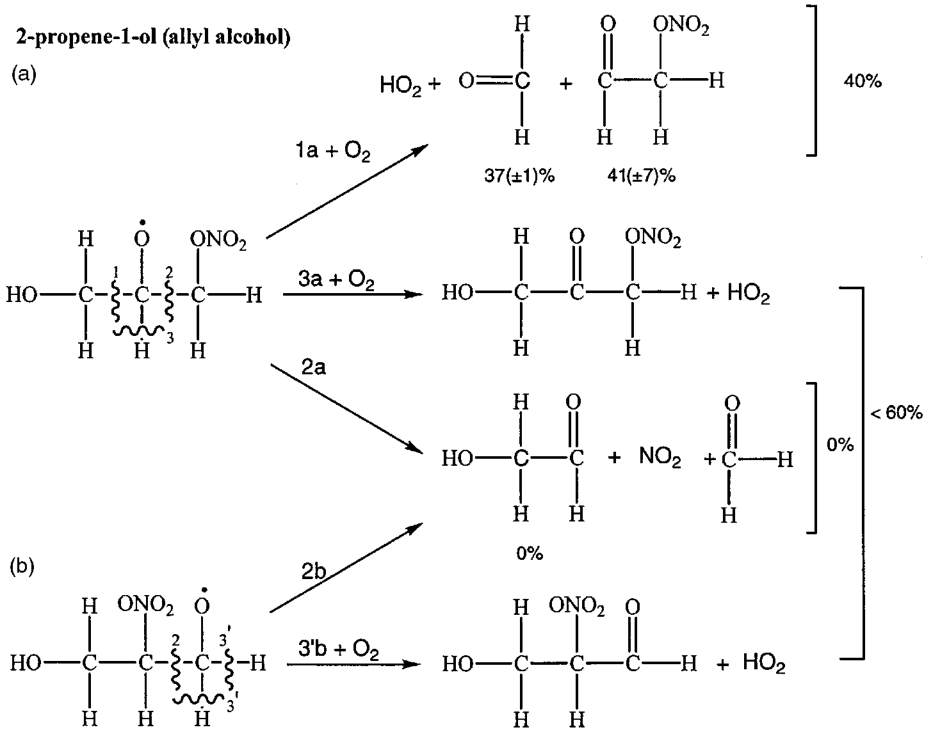


Fig. 3 Possible degradation paths of alkoxy radicals originating from the NO_3 initiated oxidation of allyl alcohol. Cases a and b refer to attack at the least and most substituted carbon atom respectively. Yields of the quantified products are given as molar percentages. The <60% value is an estimated upper limit yield.

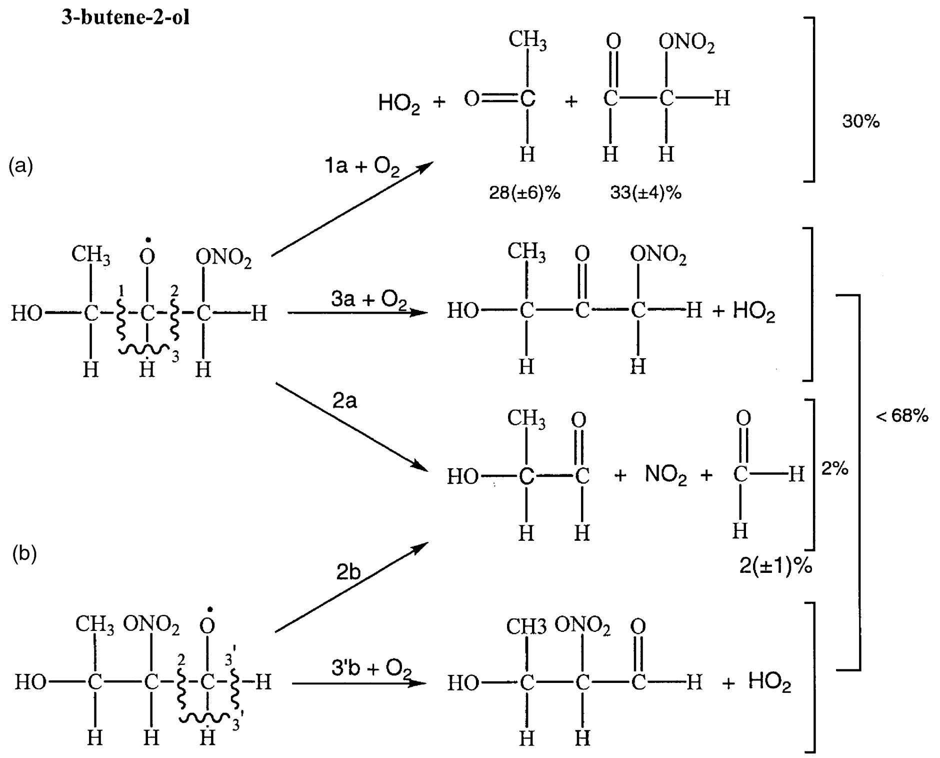


Fig. 4 Possible degradation paths of alkoxy radicals originating from the NO_3 initiated oxidation of 3-butene-2-ol. Cases a and b refer to attack at the least and most substituted carbon atom respectively. Yields of the quantified products are given as molar percentages. The <68% value is an estimated upper limit yield.

give detectable products and no such products were seen. The total organic nitrate eventually approaches an equilibrium between gas phase and wall surface (Table 3). Until the equilibrium is reached, the composition of the gas phase organic nitrates changes with time. This is due to the fact that different nitrates have different affinities for the wall surface. This is illustrated by the peak shape of the nitrate band between 1600 and 1700 cm^{-1} as is shown in Fig. 2 for an MBO232 experiment. As time progressed, the shape of the peak and its integrated band area changed because of selective adsorption of nitrates to the reactor wall.

The second type of event, aerosol formation, is sometimes but not always manifested by a wavelength-dependent displacement of the baseline in FTIR spectra. This is caused by a

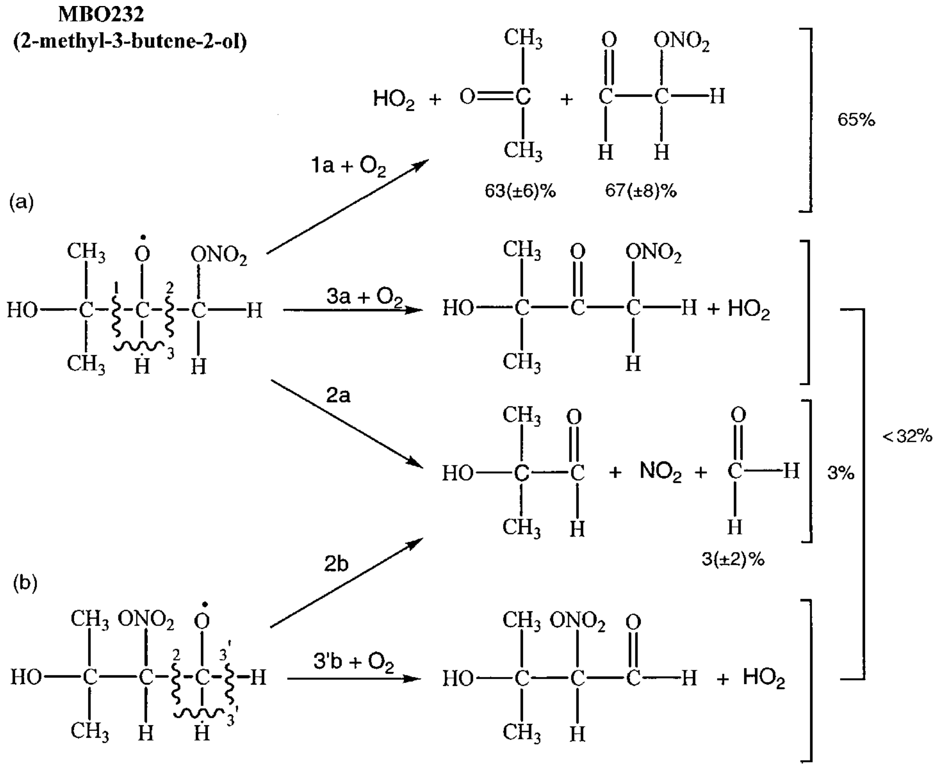


Fig. 5 Possible degradation paths of alkoxy radicals originating from the NO_3 initiated oxidation of MBO232. Cases a and b refer to attack at the least and most substituted carbon atom respectively. Yields of the quantified products are given as molar percentages. The <32% value is an estimated upper limit yield.

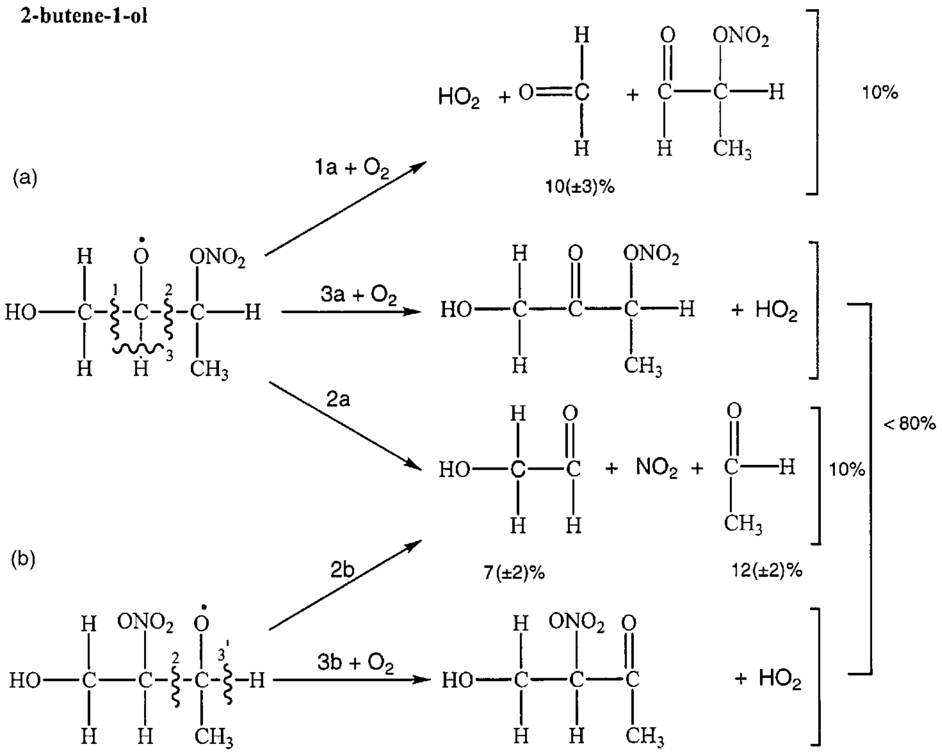


Fig. 6 Possible degradation paths of alkoxy radicals originating from the NO_3 initiated oxidation of 2-butene-1-ol. Cases a and b refer to addition at the β and γ carbon atom respectively. Yields of the quantified products are given as molar percentages. The <80% value is an estimated upper limit yield.

particle size-dependent scattering of IR radiation. In order to have this scattering effect, the particle concentration must be high enough and the particles should have physical dimensions similar to the wavelength of the radiation. Energy will then be lost by scattering radiation from the optical path. The spectrometer will interpret this as a broad absorption, as is illustrated in Fig. 8 (a) and (b). Such a baseline shift is a strong indication of the presence of aerosols. On the contrary, the absence of a baseline shift can not rule out the existence of particles, since a low concentration of large particles could pass unnoticed while the same condensed mass distributed in smaller particles may cause noticeable scattering.

As indicated above, both wall adsorption and aerosol formation occurred in the present investigation and provide an explanation to the notably poor mass balances. The main property causing molecules to adsorb or condense is low vapour pressure, which is expected from high molecular weight compounds and from polar substances. High molecular weight

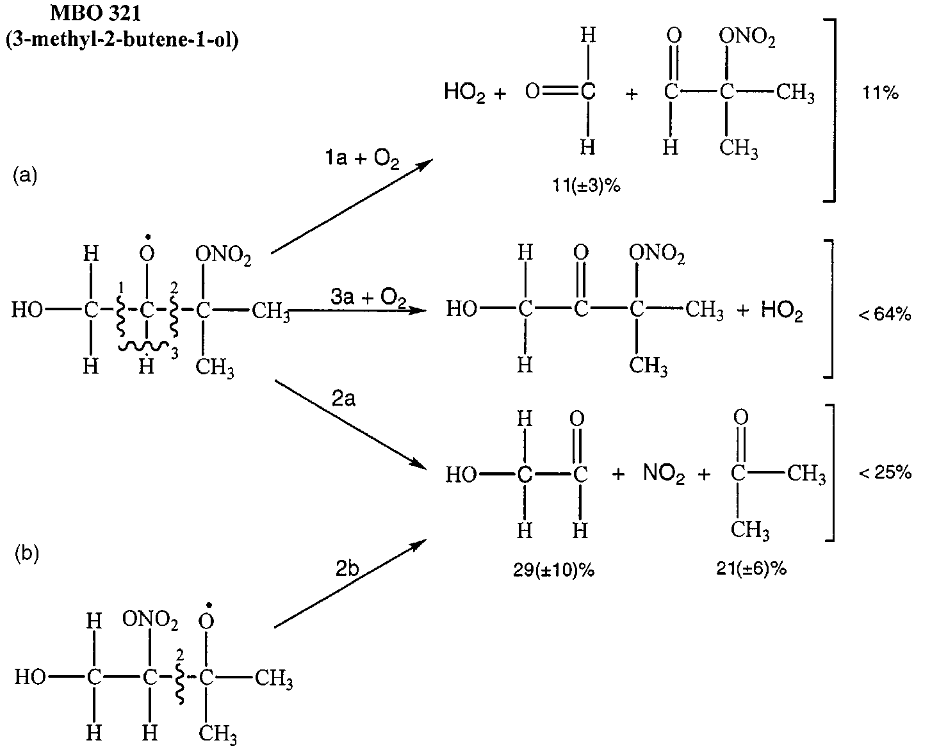


Fig. 7 Possible degradation paths of alkoxy radicals originating from the NO_3 initiated oxidation of MBO321. Cases a and b refer to attack at the least and most substituted carbon atom respectively. Yields of the quantified products are given as molar percentages. The <64% and <25% values are estimated upper limit yields.

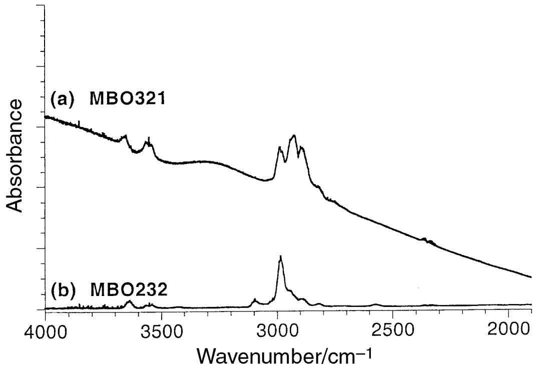


Fig. 8 IR spectra of reacted MBO321 (a) and MBO232 (b) with NO_3. Spectra were taken 1 min after mixing the alcohols with N_2O_5. An example of MBO321 FTIR spectrum (a) with base line shift due to the presence of aerosol.

products are not anticipated in the present investigation, since the starting material contains five or fewer carbon atoms. The other crucial factor, the polarity of a substance, is often dependent on the number and type of the substituent groups. No volatility information is, to the best of the authors' knowledge, available for the triply substituted products, which are illustrated in the reaction schemes or for the hydroperoxides that are products from reaction (6). To have some idea about the physical properties of these compounds, one can consider similar substances such as glyceraldehyde (2,3-dihydroxypropanal) and dihydroxyacetone (1,3-dihydroxypropanone). The melting point of dihydroxyacetone is 363 K and glyceraldehyde has a vapour pressure of 1 mbar at 418 K.[34,35] It is therefore reasonable to assume that the volatility of triply substituted products such as those indicated in Figs. 3–7 is low. Thus, the most likely explanation for the poor mass balances is that such compounds disappear from the gas phase.

The suggested triply substituted compounds formed in path 3 (Figs. 3–7) originate from H atom abstraction by O_2 giving an HO_2 radical. HO_2 is also formed from degradation *via* path 1. In the presence of NO_2, HO_2 may form peroxynitric acid (HO_2NO_2). In all experiments, HO_2NO_2 was observed although the concentration varied significantly both between different reacting compounds and between different experiments. The reason for the variability in HO_2NO_2 concentration is that it strongly depends on the rate of HO_2 production, total conversion of alcohol at the particular NO_2 concentration, and temperature of the experiments. The HO_2 eventually disappears *via* its self-reaction or slow loss on the reactor walls, in addition to the initial possible loss by a reaction (6) producing organic hydroperoxides.

Allyl alcohol

Allyl alcohol yielded 37(±1)% of HCHO, 41(±7)% of 2-NAA, and 53(±10)% of total initial nitrates including the 2-NAA and unidentified organic nitrates, most of which disappeared with time. Path 1a is the only route to HCHO since no glycolaldehyde was seen and all the 37% of HCHO has to be formed this way. This is supported by the estimated yield of 41% of 2-NAA. The amount of alcohol reacting according to path 1a is thus about 40%. It is suggested that the remaining 60% either produced hydroperoxide *e.g. via* reaction (6) or triply substituted compounds *via* paths 3a or 3b in Fig. 3.

3-Butene-2-ol

Two initial NO_2 concentrations were used for this compound (*cf.* Table 1). For "low" NO_2 concentration experiments, the NO_2 present originated only from the dissociation of N_2O_5. The average acetaldehyde yield from both the "high" and "low" NO_2 experiment was 28(±5)% with no distinctive difference between the two initial concentrations of NO_2. The only plausible way to form acetaldehyde is path 1a in Fig. 4, in agreement with the 33(±4)% yield of 2-NAA. It is concluded that path 1a accounts for about 30% of the reacted alcohol, with no influence of the initial NO_2 concentration. Cleavage of the original double bond is an insignificant route as shown by the 2% yield of formaldehyde.

A high NO_2 concentration will reduce the initial concentration of NO_3 by shifting the N_2O_5 equilibrium, however, no effect of this shift was observed. Also, a high NO_2 concentration would lower the concentrations of peroxy radicals by promoting the formation of R–OONO$_2$ and HO_2NO_2. This trapping phenomenon for peroxynitrate was observed as a prolonged time of high concentration of R–OONO$_2$ and HO_2NO_2 in the experiments. Formation of organic nitrates through reaction between alkoxy radicals and NO_2 according to reaction (7) is also possible.

$$\text{R–O}^{\cdot} + NO_2 + M \rightarrow RONO_2 + M \qquad (7)$$

The total organic nitrate yield at the end of experiment for the low NO_2 case indicates 2-NAA to be the only nitrate left in the gas phase. However, high NO_2 experiments showed a small but significant increase of about 10%, in organic nitrate end concentration. This could be due to formation of dinitrates that have about twice the nitrate band absorption cross section of mono-nitrates (*cf.* Table 2).

MBO232

Acetone was produced in a yield of 63(±6)% with no significant difference between "low" and "high" NO_2 experiments. The only way of obtaining acetone is *via* path 1a in Fig. 5. 2-Nitrooxy-acetaldehyde is also a product from path 1a and was observed in a yield of 67(±8)%. Our acetone yield is in accordance with the value presented by Fantechi *et al.*[11] of 68.7(±7.1)%; however, their nitrate yield of 13% is significantly lower than ours. Acetone and 2-NAA are only produced in path 1a (Fig. 5), and this confirms bond rupture next to the double bond as the dominant process. 3(±2)% of formaldehyde was observed, showing that paths 2a and 2b are not very active. Analogous to allyl alcohol and 3-butene-2-ol, 2-NAA is the most abundant organic nitrate of the measured total alkyl nitrates at the end of the reaction. It is thus concluded that paths 3a and/or 3b account for a maximum of ~30% of the alcohol lost. Again, products from paths 3a and 3b are suspected to have properties such that would make them disappear from the gas phase with time. Mechanistic studies of MBO232 reacting with OH, Cl, or NO_3 indicated the possibility of multifunctional compounds being produced.[11,14] However, there is so far, no direct evidence for the formation of triply substituted compounds. The high NO_2 concentration experiments did not show a significant difference in product distribution.

2-Butene-1-ol

The main carbonyl products were 10(±3)% of formaldehyde, 12(±2)% of acetaldehyde, and 7(±2)% of 2-hydroxy-1-acetaldehyde (glycolaldehyde). The reaction scheme presented in Fig. 6 thus demonstrates that paths 2a and/or 2b are active. However, it is only possible to identify ~20% of the reacted alcohol as gas phase products. Logically, it follows that paths 3a and/or 3b could account for the remaining 80%. The total organic nitrate observed in these experiments initially reached a maximum of ~40% and then it decayed to ~30% at the end of the experiments. The total organic nitrate at the end stage is suspected to be 2-nitrooxy propanelaldehyde (*via* path 1a). This compound is equivalent to the 2-NAA formed in experiments with allylalcohol, 3-butene-2-ol and MBO232 *via* path 1a. This possible product, 2-nitrooxy propanelaldehyde, absorbs at slightly lower wavenumbers compared to 2-NAA (Fig. 9).

The use of a mixture of *cis* and *trans* isomers as starting material will not influence the product distribution since the

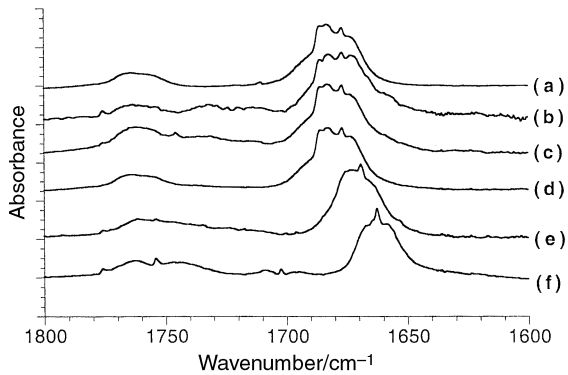


Fig. 9 Comparison of the reference spectrum of 2-NAA (a) with organic nitrate absorption resulting from oxidation of the five unsaturated alcohols. All spectra are scaled, offset and subtracted with unsaturated alcohol, HCHO, acetone, HNO_3, N_2O_5, NO_2, H_2O and HO_2NO_2. (b) Allyl alcohol, (c) 3-butene-2-ol, (d) MBO232, (e) 2-butene-1-ol, (f) MBO321.

initial attack by the NO_3 radical will break up the double bond and subsequently give the same radical [*cf.* reaction (3)].

MBO321

The measurements with MBO321 were technically more difficult to make because this compound has a lower vapour pressure. For MBO321, a yield of 21(±6)% acetone and 29(±10)% glycolaldehyde indicate that paths 2a and/or 2b in Fig. 7 are the products forming pathways. 11(±3)% of formaldehyde shows that path 1a is also active. About 64% of the alcohol reacted is thus unaccounted for. One remaining route is path 3a that would form 3-nitrooxy-3-methyl-2-butanon-1-ol. Since the tri-substituted compound would most likely be lost from the gas phase, most of the total alkyl nitrate at the end of the experiments should be 2-nitroxy-2-methyl-propenelaldehyde, which is produced from path 1a in Fig. 7.

Oxidation of MBO321 gave the clearest case of aerosol formation that was observed in this investigation (Fig. 8). It is not immediately obvious why the triply substituted products from MBO321 should have properties favouring aerosol formation when similar products from some of the other alcohols do not form any visible aerosol. The answer is likely to be found in the fact that MBO321 reacts very fast with NO_3. Condensing products formed at a high rate may not have sufficient time to reach the walls, but will cause high supersaturation in the gas phase followed by homogeneous nucleation.

The apparent yield of total organic nitrates has a strong dependence on time. From the experiments, one can derive the total organic nitrates as two different yields, one at short reaction time and one at long reaction time, the latter only corresponding to nitrates with high enough vapour pressure. The values obtained for the initial and final total organic nitrates yield were 60(±39)% and 29(±6)%.

General trends

According to previous studies[28] the most likely primary target for the NO_3 attack on a double bond is the carbon atom that is less alkyl substituted. Table 4 indicates the number of carbon atoms adjacent to the α, β and γ carbon atom for the investigated compounds. The atom with the OH group is assigned to be the α carbon. For the first series, allyl alcohol, 3-butene-2-ol, and MBO232, the γ carbon atoms only have 1 adjacent carbon atom compared to 2 for the β carbon atom. NO_3 is here expected to preferentially add to the γ carbon atoms. The number of carbon atoms adjacent to the α-carbon atom plays a minor role for the initial attack of the NO_3 radical. From the experimental data, no evidence for addition to the β carbon atom was seen, *i.e.* case b in Figs. 3–5 and all identified products are explained by degradation following addition to the γ carbon atom, case a in Figs. 3–5.

Table 4 Number of adjacent carbon atoms attached to α, β and γ carbon atoms for the investigated compounds. The double bond is located between the β and γ carbon atoms

	Number of neighbouring carbon at position		
Compound	α	β	γ
Allyl alcohol	1	2	1
3-Butene-2-ol	2	2	1
MBO232	3	2	1
Allyl alcohol	1	2	1
2-Butene-1-ol	1	2	2
MBO321	1	2	3

Comparing the distribution between paths 1–3 within case a (initial addition to γ carbon atom) for the first series, there are at least two observations that can be made. Firstly, there is only a few percent of products *via* path 2. This is interpreted as breakage of the α–β bond in the alkoxy radical being more favoured than breakage of the β–γ bond. The second observation is that the relative importance of path 1 increases with the number of methyl groups in the α position. The change is in accordance with suggestions from the literature stating that increasing decomposition yield is related to an increasing stability of the produced fragments.[32] The stability of the radical leaving group $C(CH_3)_nH_{(2-n)}$ increases as n increases from 0 to 2 while the remaining fragment is identical in the series.

A similar type of analysis can be made for the second series, allyl alcohol, 2-butene-1-ol, and MBO321. In this series, the number of methyl group substituents increases at the γ position instead of the α position as was the case for the first series. As the number of methyl group substituents increases, it is more probable for the NO_3 attack to take place at the β carbon atom instead of the γ carbon atom (Table 4). This causes path 2b to be more active which increases the yield of products in path 2. However, the greater number of methyl group substituents at the γ carbon atom increases the stability of the radical leaving groups produced *via* path 2a. Analogous to the radical produced *via* path 1a it can be represented as $C(CH_3)_nH_{(2-n)}$ and its stability increases as the value of n increases. The absence of a clear trend in the second series may be explained by a combination of the effects discussed above.

Conclusions

This study showed that closed mass balances for the investigated unsaturated alcohols were impossible to achieve by just considering the products remaining in the gas phase. Strong evidence exists that products are lost from the gas phase. This is shown by the decrease of IR nitrate absorption with time to approach a value determined by the equilibrium between gas phase and the reactor wall. The change in nitrate peak size and shape with time is an indication of a selective loss of organic nitrates of low volatility. The formation of aerosol was positively observed in the reaction between NO_3 and MBO321. It is clear that the products lost must have a low vapour pressure. A plausible channel producing nitrated compounds with a molecular structure that is expected to give a low vapour pressure is that proceeding *via* hydrogen abstraction by molecular oxygen, *i.e.* path 3 above. Based on the arguments given above, it is suggested that the hydrogen abstraction from the oxy radical is an important pathway for all compounds except MBO232. In the case of MBO232, the bond cleavage between the α and β carbon atoms is the most important process as was shown by the >60% yield of acetone and 2-NAA. As expected, this bond breakage was more pronounced when the number of methyl substituents was increased from zero to two at the α carbon atom because the stability of the leaving group also increases.[32]

In the series with increasing number of methyl substituents at the γ carbon atom, the tendency for bond breakage between the β and γ carbon atom was increased. It is proposed that this is an effect of NO_3 attack occurring more frequently at the β carbon atom with increasing substitution at the γ carbon atom. This accordingly leads to an increased flow through path 2b with an increased number of γ carbon atom methyl substituents. The effect of increased stability of the leaving radical with additional methyl groups may also contribute to the increased bond breakage through path 2a.

Atmospheric implications

This study is concerned with the oxidation mechanisms of unsaturated alcohols, which are emitted to the atmosphere from biogenic sources. The oxidation produces aldehydes, ketones, and organic nitrates as major products. One of the strongly emitted compounds, MBO232, showed a large yield of 2-NAA and acetone. Since acetone has a significant role in the upper troposphere as a precursor for peroxyacetylnitrate (PAN), such a high yield should be regarded as an important fact to consider for upper troposphere and lower stratosphere chemistry. Production of nitrates converts NO_x into a form that could be subjected to long range transport before being released *via* photolysis. NO_2 can be formed either directly *via* path 2 or by oxidation of NO as result of the production of HO_2 from path 1. For all the investigated compounds except MBO232, path 1 was found dominant over path 2. Notable is also that the two degradation paths for the hydroxynitrooxy substituted alkoxy radical, *e.g.* from oxidation of allyl alcohol, give back different odd electron species as illustrated by reaction (8a) and (8b).

$$CH_2OH\text{–}CHO^{\bullet}\text{–}CH_2ONO_2 \rightarrow HO\text{–}CH_2ONO_2 + HCHO + HO_2 \quad (8a)$$

$$CH_2OH\text{–}CHO^{\bullet}\text{–}CH_2ONO_2 \rightarrow CH_2OH\text{–}CHO + HCHO + NO_2 \quad (8b)$$

The implications for the atmosphere will then be different. In the atmosphere, HO_2 could convert NO to NO_2 giving OH, which maintains the oxidative degradation cycle of organic compounds. The NO_2 can be formed either directly in path 2 or *via* oxidation of NO as a result of the production of HO_2 in path 1. For most of the investigated compounds path 1 is dominant over path 2.

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