

Spectrochimica Acta Part A 56 (2000) 2605-2616

SPECTROCHIMICA ACTA PART A

www.elsevier.nl/locate/saa

Reactions of alkenes with ozone in the gas phase: a matrix-isolation study of secondary ozonides and carbonyl-containing reaction products

Emma J. Feltham, Matthew J. Almond *, George Marston, Vivienne P. Ly, Karen S. Wiltshire

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK

Received 3 April 2000; accepted 13 April 2000

Abstract

Gas phase ozonolysis reactions of the alkenes ethene, *cis*- and *trans*-but-2-ene, isoprene and the monoterpenes α -pinene, β -pinene, 3-carene, limonene and β -myrcene have been carried out and the reaction products have been trapped in O₂-doped-argon matrices onto a CsI window held at 12 K. Products have been identified by IR spectroscopy. Comparison with previous matrix spectra, where secondary ozonides have been generated either in situ by annealing or in solution reactions allows a positive identification of the secondary ozonides of ethene and of *cis*- and *trans*-but-2-ene to be made. These observations are backed up by experiments utilising the isotopes ¹³C and ²H (D). It appears that secondary ozonides have also been formed from isoprene and the range of monoterpenes studied; this hypothesis is based upon the similarity of spectral features seen in the products of these reactions within those of the simpler alkenes. A number of other primary and secondary products are also identified from these reactions. Ethene gives formaldehyde as a primary product and acetaldehyde as a secondary product; it is found that the yield of acetaldehyde compared to formaldehyde increases as the reaction times are increased. Formaldehyde, one of the expected primary products, is formed by ozonolysis of β -pinene, although the other expected primary product, nopinone, is not seen. A range of secondary reaction products have been identified from the ozonolysis of the monoterpenes studied. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Matrix-isolation; Atmospheric chemistry; Ozonolysis; Biogenic volatile organic compounds; Infrared spectroscopy

1. Introduction

There is much current interest in the chemical reactions of ozone with alkenes, in part because of

* Corresponding author. Fax: +44-1-189316332.

the importance of such reactions in the chemistry of the troposphere. In particular, reactions of the so-called biogenic volatile organic compounds (Bio-VOCs) are of particular interest [1,2]. The Bio-VOCs include methane, non-methane hydrocarbons (NMHCs) and other organic compounds including oxygen-containing species. The NMHCs

E-mail address: m.j.almond@rdg.ac.uk (M.J. Almond).

include isoprene (I) and a class of alkenes known as monoterpenes, (e.g. II-VI) which are emitted, in particular, by conifer trees [1].



Monoterpenes are destroyed in the troposphere by reaction with ozone (alongside other reactions such as those with the hydroxyl radical and the nitrate radical). Ozonolysis is known to proceed via a primary ozonide, which then decomposes to give a carbonyl product together with a so-called Criegee intermediate. The Criegee intermediate may react by one of several possible routes; it may react with the carbonyl product to give a secondary ozonide; it may be stabilised by a third body (M) to give a carbonyl oxide; last, it may decompose to give OH radicals. It may be noted that the formation of secondary ozonide is unlikely under tropospheric conditions [1,2]. The secondary ozonide or carbonyl oxide will, of course, themselves react further to yield other stable products. These reactions are summarised for the alkene ethene in Scheme 1.

The products of the reactions of BioVOCs with ozone are involved in global tropospheric chemistry and their effects are far-reaching [3]. Some products are involved in ozone formation and destruction, affecting the oxidising capacity of the atmosphere [3]. Others are involved in the formation of aerosols which may lead to clouds and



Scheme 1.

photochemical smogs. At present little is known about the detailed mechanism of BioVOC oxidation [4,5].

The aim of the work which we describe in this paper was to carry out the gas phase ozone reaction of ethene, cis- and trans-but-2-ene, isoprene (I) and the monoterpenes α -pinene (II), β-pinene (III), 3-carene (IV), limonene (V) and β -myrcene (VI), then to trap the products in a low-temperature matrix. We anticipated that we would not trap the primary ozonide products or Criegee intermediates: these have lifetimes in the gas phase which would be too short to allow trapping by our experimental procedures [6]. However, we hoped to find infrared spectroscopic evidence for the secondary ozonides, whose lifetimes are known to be much longer [6,7], and for other stable oxidised products. These include primary products (i.e. the aldehydes formed by simple ozonolysis of the double bond e.g. formaldehyde from ethene) and secondary products (i.e. those formed by secondary reactions, e.g. acetaldehyde from ethene). In this way we hoped: (i) to obtain evidence for the formation of secondary ozonides of these alkenes in the gas phase; (ii) to learn something of the product distributions from these reactions; (iii) to identify primary and secondary reaction products and hence to learn something of the reaction mechanisms.

There have been a number of previous matrix isolation studies of the ozonolysis of alkenes. These have focused upon the simpler alkenes and there has been no previous work on the monoterpenes. Moreover, the methods used to generate secondary ozonides in these experiments have centred upon two methods: (i) annealing of a solid matrix containing the alkene and ozone and (ii) prior formation of the ozonide by a solution reaction followed by trapping in a low-temperature matrix. Kohlmiller et al. investigated the ozonolysis of ethene in a xenon matrix warmed to 80-100 K and hence isolated the primary and secondary ozonides of ethene alongside a range of other products including formaldehyde and ethylene oxide [8]. Samuni et al. have carried out similar experiments in argon and carbon dioxide matrices [9]. These workers found that while an argon matrix evaporated before any reaction between ethene and ozone was observed, the primary and secondary ozonides of ethene could be formed in a CO_2 matrix at temperatures of 25 K or above. Andrews et al. have extended this work to the alkenes propene, *trans*-but-2-ene and methylpropene (isobutene) where primary and secondary ozonides are formed upon annealing ozone-doped xenon matrices to 80-100 K [10]. In a separate series of experiments Hawkins et al. [11] and Kuehne et al. [12] have generated isotopomers of the ethene secondary ozonides incorporating the isotopes ¹⁸O and D. These species were prepared in solution prior to trapping in argon matrices.

Previous gas phase studies of alkene ozonolysis have not been linked to matrix isolation with the exception of studies carried out by Kuehne et al. to investigate the ozonolysis of both ethene and cis-but-2-ene using microwave spectroscopy of the gas phase mixture and subsequent matrix isolation. The secondary ozonides of ethene and cisbut-2-ene were successfully isolated in these experiments and a range of primary and secondary products were seen [13-15]. Other gas phase ozonolysis studies have mainly concerned the kinetics of reaction and investigation of products. Atkinson has written several comprehensive reviews of the current available kinetic data of such reactions [16,17]. Several reports focus on the generation of hydroxyl radicals [6,7,18-21]. Examples of other recent product studies include the gas-phase ozonolysis of trans-but-2-ene, carried out by Fajgar et al. [22], where the secondary ozonide was detected by GC-MS, and a study of the products formed in the gas-phase ozonolysis of cis- and trans-but-2-ene carried out by Horie et al. [23].

The strategy in our experiments was, therefore, to isolate the secondary ozonides of ethene and *cis*- and *trans*-but-2-ene where we could compare our spectroscopic data with spectra previously obtained for ozonides produced by solution reactions or by annealing. Once we had found the correct conditions to isolate ozonides of these simple alkenes we could then move on to consider the monoterpenes, where no previous spectroscopic data for the secondary ozonides exists.

2. Experimental

The matrix isolation apparatus used at Reading has been described elsewhere [24,25]. Matrices were deposited onto a CsI window which was cooled to ~12 K by an Air Products 2020SP 'Displex' closed-cycle helium refrigerator. Pressures of ~1 × 10⁻⁷ Torr were maintained by means of an Edwards model E02 oil-vapour diffusion pump backed by an Edwards model ED100 oil-sealed rotary pump. Infrared spectra were recorded using a Perkin–Elmer 983 spectrometer with a typical resolution of 2 cm⁻¹ or better.

Gaseous samples of ethene (purity 99.5 + %) and *cis*- and *trans*-but-2-ene (purities 99 + %) were obtained from Aldrich and were used as supplied. Liquid samples of isoprene (99%), αpinene (98%), β-pinene (99%), 3-carene (90%), limonene (97%), β -myrcene (85%), methyl vinyl ketone (99%), methacrolein (95%) and nopinone (98%) were obtained from Aldrich and were degassed by the 'freeze-pump-thaw' method prior to use. The isotopically-labelled compounds C_2D_4 (99 at.% D) and ${}^{13}C_2H_4$ (99 at.% ${}^{13}C$) were obtained from Aldrich and CKGas Products respectively. The matrix gases argon (99.998 + %) and oxygen (99.6 + %) were purchased from Aldrich. Ozone was generated by an electric discharge in a flow of oxygen using a Fischer Ozone Generator model 502. Ozone was obtained as a 5% mixture in O_2 .

Gaseous mixtures were prepared on an all-glass vacuum line fitted with Young's greaseless taps. The line was maintained at a pressure of $\sim 1 \times 10^{-5}$ Torr by means of a water-cooled mercury vapour diffusion pump backed by an oil-sealed rotary pump. Pressures of gaseous samples were measured using a mercury manometer. For liquid samples the temperature was adjusted to give a vapour pressure of 1 Torr, the vapour was transferred on the line to a 1 1 Pyrex bulb and an excess of argon gas was added.

Samples were deposited onto the cooled matrix window by slow spray on. The Pyrex spray on tube was fitted with a needle valve; this could be closed to allow gaseous samples to mix in a mixing chamber for a fixed period of time, then opened to deposit the sample.

3. Results and discussion

There were two major aims of the work described in this paper. First, to identify the secondary ozonides from a range of alkenes including isoprene and a number of monoterpenes, generated by the gas phase reaction of the alkene with ozone and trapped in a low-temperature matrix. Second, to identify reaction products and hence to learn something of the mechanisms of these reactions. These two areas will be considered in separate sections.

3.1. Formation of secondary ozonides

Mixtures of ozone (5%) in oxygen and ethene (1%) in argon were allowed to mix for a period of 1 h, then deposited onto a CsI window held at 12 K via a Pyrex tube fitted with a needle valve which was opened to 1/3 of its maximum opening to allow a slow rate of deposition. A number of bands were observed in the infrared spectrum of the resulting condensate which are not seen in the spectra of either of the starting materials. In order to identify which bands result from ozonides the deposit was subject to broad-band UV-vis photolysis. It is known that such ozonides are photolabile [8,11]; thus their concentration will decrease upon photolysis. In Fig. 1 is illustrated the region 1250-900 cm⁻¹ of the infrared spectrum of the matrix generated in our experiments before and after 20 min broad-band UV-vis photolysis. The decay in intensity of bands assigned to the secondary ozonide can clearly be seen. As mentioned in the introduction it is unlikely that primary ozonides could be isolated in this way. Thus, it seems most likely that the observed bands arise from the secondary ozonide. Further confirmation that these bands do indeed belong to the secondary ozonide comes from a comparison with literature data for this matrix-isolated species. In these previous studies the ozonide was generated in situ in argon matrices containing ethene and ozone by annealing of the matrix. In our experiments the ozonides were generated in the gas phase and were trapped in a mixed argon/oxygen matrix (oxygen was necessarily an ingredient of our matrices as we



Fig. 1. The region $1250-900 \text{ cm}^{-1}$ of the transmission infrared spectrum of a matrix initially containing products of the gas phase reaction of ethene and ozone: (a) after mixtures of ethene (1%) in argon and ozone (5%) in oxygen had been allowed to mix for 1 h and the resulting mixture deposited onto a CsI window held at 12 K; (b) after the condensate had been subject to 20 min broad-band UV-vis photolysis.

obtained O_3 as a dilute mixture with O_2). In Table 1 are listed the bands that we assign to the secondary ozonide of ethene in our experiments. Here these bands are compared with literature data from three previous experiments [8,11,13]. It may be seen that there is a good correlation between the different sets of data. The maximum observed shift in position of any of the bands is 3%; most bands show shifts of 1% or less. These modest shifts may be accounted for by the change in matrix material from pure argon to mixed argon/oxygen.

This is good evidence that we have indeed isolated the secondary ozonide of ethene from a gas phase reaction. Further evidence is supplied by the results of isotopic substitution experiments. We have generated the same ozonide product from ${}^{13}C_{2}H_{4}$ and from $C_{2}D_{4}$. The bands observed in these experiments are listed in Tables 2 and 3 where they are compared with previous work on

the same species [8,11,12]. Again a very good correlation with the literature spectra is obtained with discrepancies in band position from one experiment to another of 3% or less; for most bands less than 1%.

We then moved on to study the reactions of *cis*and *trans*-but-2-ene with ozone. These compounds are expected to be more reactive towards ozone than is ethene. The rate constants for the gas phase reactions of ethene and *cis*- and *trans*but-2-ene with ozone [17] are: k_{ozone} (cm³ molecule⁻¹ s⁻¹): ethene 1.59×10^{-18} ; *cis*-but-2ene 1.25×10^{-16} ; *trans*-but-2-ene 1.90×10^{-16} . Indeed some reaction occurred if mixtures of ozone (5%) in O₂ and *cis*- or *trans*-but-2-ene (1%) in argon were codeposited via a tube fitted with a constriction ~ 0.5 mm in diameter. However, a larger yield of the secondary ozonide was seen if the same procedure as used for ethene was adopted, i.e. that the reagents were allowed to mix

ostions of infrared bands (in chi) assigned to the secondary ozonide of ethene			
This work	Kuehne et al. [13]	Kohlmiller et al. [8]	Hawkins et al. [11]
1126	1129	1130	1129
1090	1078	1079	1078
1021	1029	1030	1029
1002	1001	_	_
915	926	_	_
833	808	806	808

Table 1 Positions of infrared bands (in cm^{-1}) assigned to the secondary ozonide of ethene

Table 2

Positions of infrared bands (in $\rm cm^{-1})$ assigned to the secondary ozonide of ${\rm ^{13}C_2H_4}$

This work	Kohlmiller et al. [8]	Hawkins et al. [11]
2845	_	2889
2710	_	2706
1119	1119	1119
1089	1059	1058
1000	1009	1008
893	_	912
800	805	805

Table 3

Positions of infrared bands (in $\mbox{cm}^{-1})$ assigned to the secondary ozonide of $C_2 D_4$

This work	Hawkins et al. [11]	Kühne et al. [12]
2175	2181	2181
2148	_	2161
2085	2091	2092
1158	1159	1160
1148	1142	1143
1112	_	1135
1053	1057	1059
1021	1020	1021
979	981	980
967	972	972
846	848	851

for 1 h then deposited via a needle valve. In these experiments we again saw bands arising from photolabile species and again these bands correlate well (Table 4) with bands seen in previous experiments [10,15] where the ozonides were gen-

Table 4

Positions of infrared bands (in cm^{-1}) assigned to the secondary ozonides of *cis*- and *trans*-but-2-ene

This work ^a	Kuehne et al. ^a [15]	This work ^b	Andrews et al. ^b [10]
1391	1393	1392	1392
1144	1147	_	1146
1116	1119	1115	1117
1076	_	1075	1075
889	893	_	895
852	_	852	847
523	522	523	_

^a Data from *cis*-but-2-ene experiments.

^b Data from *trans*-but-2-ene experiments.

erated by annealing of an argon matrix. We may therefore conclude that we have successfully generated the secondary ozonides of *cis*- and *trans*but-2-ene in these experiments.

Having established a method which clearly allows formation and trapping of secondary ozonides from alkenes we turned our attention to isoprene and a range of monoterpenes. The monoterpenes selected for study were α -pinene (II), β -pinene (III), 3-carene (IV), limonene (V) and β -myrcene (VI). The reactions of these compounds with ozone are of much interest in an atmospheric chemistry context [26-33] but they had not previously been studied by matrix isolation. In the current experiments the ozonides were generated by the gas-phase reaction between the alkene (1% in Ar) and ozone (5% in O_2). These ozonides were formed by allowing the two gaseous samples to mix for a period of one hour, then the resulting mixture was deposited onto

Table 5

Positions of infrared bands assigned to secondary ozonides of isoprene and the monoterpenes α -pinene, β -pinene, 3-carene, limonene and β -myrcene

Alkene	Ozonide band positions (cm ⁻¹)
Isoprene	1234(w), 1223(w), 1124(s), 998(w) and 930(m)
α-Pinene	1025(sh)
β-Pinene	1337(w), 1283(w), 1234(w), 1170(m), 1125(m),
	1020(m) and 1001(m)
3-Carene	1126(m), 1020(w) and 532(m)
Limonene	1181(m), 1126(m), 1112(m), 1021(m), 1001(w)
	994(w) and 930(m)
β-Myrcene	1234(m), 1125(m) and 1021(m)

a CsI window held at 12 K through a Pyrex tube via a needle valve. In each case infrared bands were seen in the condensate which decayed upon broad-band UV-vis photolysis and which occur in spectral regions where bands of the known secondary ozonides of ethene and of *cis*- and *trans*-but-2-ene appear. The positions of these bands are listed in Table 5; bands assigned to the secondary ozonide of isoprene are shown in Fig. 2.

Of course, these assignments to secondary ozonides must remain somewhat tentative, but the fact that these bands occur in spectral regions where secondary ozonides are known to absorb and that the species giving rise to the bands are clearly photolabile must point towards their formation. In many cases fewer bands are seen for these more complex alkenes which may be assigned to ozonides. This observation is accounted for by the complexity of the spectra of the starting materials which mean that large sections of the spectrum are obscured. With some of the compounds studied here there is more than one double bond present in the alkene and therefore more than one possible secondary ozonide product. An example is provided by isoprene (I), where there are two double bonds and therefore two possible secondary ozonide products (VII and VIII).



VIII

VII

Limonene likewise has two double bonds, but here the double bonds are quite different in character. One forms part of the ring, the other is exocyclic. Gas phase studies [17] have shown that the double bond within the ring reacts $\sim 10 100 \times$ faster under similar conditions. It therefore seems likely that this ozonide (IX) would be formed preferentially over the alternative (X).



β-Myrcene has three double bonds so three secondary ozonides (**XI**–**XIII**) are possible. Of these the formation of **XIII** at the most substituted double bond would be most likely as this double bond would be expected to react ~ $100 \times$ faster [17] than the less-substituted bonds.



Seven bands, which may be assigned to secondary ozonides are seen for limonene and three bands for β -myrcene. However, it is not possible to state with certainty, on the basis of the experimental results alone, whether one or more ozonide has been formed.

3.2. Identification of other reaction products

The second aim of our experiments was to identify the other reaction products formed in

these experiments. In particular we wished to study the relative abundances of primary and secondary products. In this way we hoped to learn something of the reaction mechanism and, in the cases where more than one secondary ozonide product is possible, to decide which ozonide had been formed preferentially.

The simplest reaction studied was that of ethene with O_3 . Here the primary carbonyl product is expected to be formaldehyde. Indeed bands of formaldehyde can clearly be seen in the spectrum of the condensate at 2859(vw), 2794(vw), 1747(m),



Fig. 2. The region $1800-800 \text{ cm}^{-1}$ of the transmission infrared spectra of (a) a matrix formed by condensing (onto a CsI window at 12 K) the gaseous mixture formed by allowing isoprene (1%) in argon and ozone (5%) in oxygen to mix for 1 h in the gas phase, (b) of isoprene (1%) isolated in an argon matrix at 12 K, (c) of methyl vinyl ketone (1%) isolated in an argon matrix at 12 K and (d) of methacrolein (1%) isolated in an argon matrix at 12 K. Legend for spectrum (a): a = CH₃COOCHO, b = CH₃COOH, c = (HCO)₂O, d = CH₂O, e = CH₃CHO, f = H₂O, g = O₂, h = secondary ozonide, i = O₃.

1496(m), 1283(m) and 1174(m) cm⁻¹ [13–15,34, 35]. The other most abundant carbonyl product observed in these experiments is acetaldehyde, identified by bands at 2730(vw), 1725(m), 1395(w), 1350(m), 1120(m) and 750(w) cm⁻¹ [13–15,34,35]. Acetaldehyde has been observed as a secondary product of this reaction in previous gas phase and matrix isolation studies. In Fig. 3 are shown the regions 1800-1500 cm⁻¹ spectra of matrices formed by condensing gaseous mixtures of ethene (1%)/argon and ozone (5%)/oxygen which have been allowed to mix for (a) 1 h and (b) 3 h prior to deposition. It is clear that the relative yield of the secondary product (acetaldehyde) increases over the primary product (formaldehyde) as the mixing time is lengthened. Our experiments utilising ${}^{13}C_2H_4$ and C_2D_4 help to confirm the identities of formaldehyde and acetaldehyde as reaction products [35]. In Table 6 are listed the observed bands of the various isotopomers of these compounds.

Other secondary products to be identified more-or-less certainly are: H_2O [13–15,34], CO_2 [13–15,35], CO [13–15], the CO...CO₂ complex [36], HCOOH [13–15], (HCO)₂O [13–15], CH₃COOH [15,35] and ethylene oxide [35]. In

Table 6

Bands assigned to the ${}^{13}C_2$ and D_4 isotopomers of acetaldehyde [35] and of the ${}^{13}C$ and D_2 isotopomers of formaldehyde generated by ozonolysis of ${}^{13}C_2H_4$ or of C_2D_4

CH ₂ O	¹³ CH ₂ O	CD ₂ O	$\nu^{12}C/\nu^{13}C$	$\nu^1 H/\nu D$
2859(vw)	2789(w)	2068(w)	0.976	0.723
2794(vw)	_	_	_	_
1747(m)	1700(m)	1730(m)	0.973	0.990
1496(m)	1492(m)	1283(w)	0.997	0.858
1283(m)	-	955(m)	_	0.744
1174(m)	1151(m)	-	0.980	_
CH ₃ CHO	¹³ CH ₃ ¹³ CHO	CD ₃ CDO	$\nu^{12}C/\nu^{13}C$	$\nu^1 H/\nu D$
2730(vw)	_	_	_	_
1725(m)	1690(sh)	1700(m)	0.980	0.986
1395(w)	1390(m)	_	0.996	_
1350(m)	1340(w)	1025(w, sh)	0.993	0.759
1120(m)	1100(sh) ^a	950(w, sh)	0.982	0.848
750(w)	-	-	_	_

^a Partially obscured by secondary ozonide band.



Fig. 3. The region 1800-1550 cm⁻¹ of the transmission infrared spectra of matrices formed by condensing (onto a CsI window held at 12 K) gaseous mixtures formed by allowing mixtures of ethene (1%) in argon and ozone (5%) in oxygen to react in the gas phase (a) for 1 h, (b) for 3 h.

general the following 'rules' were applied in assigning infrared bands.

1. There should be a good match between observed spectra and literature spectra for authentic samples (where possible for matrix-isolated samples) taking into account small shifts due to changes in phase or matrix material.

2. The strongest bands of a product should be visible unless they would obviously be obscured by bands of another ingredient of the matrix.

3. Ideally several bands, certainly more than one, should be seen for positive identification of a product.

The last four compounds listed above were obtained only in relatively low concentrations, however, and the bands assigned to these species were weak in intensity, so here the assignments are tentative.

Two further experiments were carried out. First a pure oxygen matrix was used to isolate the products. This was done in order to assess the influence of O_2 on the reaction. In this case very similar results to the mixed O_2/Ar matrices were obtained with only some minor shifts (typically much less than 1%) in band positions but a very similar product distribution. Thus, it may be concluded that the presence of O_2 in our reaction mixtures does not have a significant influence on the chemical route of the reaction. Second, a mixture of ethene $(1\%)/argon and O_3 (5\%)/O_2$ was deposited without mixing and the condensate was subject to broad-band UV-vis photolysis. The findings from this experiment reproduce those of a similar experiment previously carried out by Hawkins and Andrews using a pure argon matrix [35]. The main difference here is that in the photolysis experiment no secondary ozonides were seen, but higher concentrations of other products were obtained when compared with the gas-phase mixing experiments. A particular point is a much increased yield of ethylene oxide, which is likely to be formed by the reaction of O (³P) atoms with ethene [35], the atoms being generated by photolysis of O_3 . Other products seen in this photolysis



Fig. 4. The region $1800-800 \text{ cm}^{-1}$ of the transmission infrared spectra of (a) a matrix formed by condensing (onto a CsI window at 12 K) the gaseous mixture formed by allowing β -pinene (1%) in argon and ozone (5%) in oxygen to react in the gas phase for 1 h, (b) of β -pinene (1%) isolated in an argon matrix at 12 K and (c) of nopinone (1%) isolated in an argon matrix at 12 K. Legend for spectrum (a): $a=\beta$ -pinene, $b=O_3$, $c=(HCO)_2O$, $d=CH_2O$, $e=CH_3CHO$, $f=H_2O$, $g=O_2$, h=secondary ozonide.

experiment are: H_2O [13–15,34], CO [13–15], CO₂, [13–15,35] CH₂O [13–15,34,35], CH₃CHO [13,15,34,35], HCOOH [13–15] and (HCO)₂O [13–15].

Cis- and *trans*-but-2-ene both give a large number of products upon photolysis. Formaldehyde is clearly observed as a primary product. Amongst other secondary products the following are positively identified on the basis of their infrared spectra and applying the 'rules' outlined above. These are H₂O, CO, CO₂, CH₃CHO, CH₃COOH, CH₃CO₃H, (HCO)₂O and CH₄. All of these compounds have been observed in previous ozonolysis studies of these alkenes [10–15].

With isoprene two primary products alongside formaldehyde (which is observed) are possible. These are methyl vinyl ketone (XIV) (formed from the secondary ozonide VII) and methacrolein (XV) (formed from the secondary ozonide VIII).



Unfortunately we obtained no spectroscopic evidence for the existence of either of these products in our experiments. The spectra reproduced in Fig. 2, illustrating the reaction products of isoprene and O₃, show no correspondence to the spectra of authentic matrix-isolated samples of methyl vinyl ketone and methacrolein which are also reproduced. It is likely that this finding reflects the high reactivity of methyl vinyl ketone and methacrolein (both of which contain a C=C bond) towards O₃. In fact several secondary products are identified. These are CH₃COOCHO, CH₃COOH, (HCO)₂O, CH₃CHO, H₂O, O₂, CO and CO_2 . The primary product H_2CO is also seen. Bands at 1234, 1223, 1124, 998 and 930 cm⁻¹ are assigned to a secondary ozonide of isoprene on the basis of their disappearance upon photolysis.

In the ozonolysis of β -pinene formaldehyde is expected as a primary product and this compound is seen. The other primary aldehyde product is expected to be nopinone (**XVI**).



XVI

The infrared spectrum of the reaction products of β -pinene and O₃ are reproduced in Fig. 4 where they are compared with spectra of authentic matrix-isolated samples of β -pinene and nopinone. It may be seen that while some unreacted β -pinene remains there is no evidence for the presence of nopinone. Secondary products which are positively identified are (HCO)₂O, CH₃CHO, H₂O, O₂, CO and CO₂. Bands at 1337, 1283, 1234, 1170, 1125, 1067, 1020 and 1001 cm⁻¹ are assigned to a secondary ozonide on the basis of their disappearance upon photolysis.

Table 7

Secondary products generated by the ozonolysis of isoprene and the monoterpenes α -pinene, β -pinene, 3-carene, limonene and β -myrcene

Alkene	Secondary products
Isoprene	H ₂ O, CO ₂ , CO, CH ₃ COOCHO, CH ₃ COOH, HCOOH, (HCO) ₂ O, CH ₃ CHO and activated O. ^a
α-Pinene	H_2O , CO_2 , CO , $CH_3COOCHO$, CH_3COOH , HCOOH, $(HCO)_2O$, CH_2O , CH_3CHO and activated O_2^a
β-Pinene	H_2O , CO_2 , CO , $CH_3COOCHO$, CH_3COOH , HCOOH, $(HCO)_2O$, CH_3CHO and activated Ω_1^a
3-Carene	H_2O , CO_2 , CO , $CH_3COOCHO$, CH_3COOH , HCOOH, $(HCO)_2O$, CH_2O , CH_3CHO and activated O_2^a
Limonene	H ₂ O, CO ₂ , CO, CH ₃ COOCHO, CH ₃ COOH, (HCO) ₂ O, CH ₂ CHO and activated O ₂ ^a
β-Myrcene	H_2O , CO_2 , CO , $CH_3COOCHO$, CH_3COOH , (HCO) ₂ O, CH_3CHO and activated O_2^{a}

^a Activated O_2 ; O_2 trapped in a matrix cage in such a way that the O–O stretch becomes infrared active.

For α -pinene a ring-opening reaction to give a complex dialdehyde primary product is expected. It is not possible to say unequivocally whether this product is present or not in the reaction mixture because an authentic sample was not available. Limonene gives a significant yield of formaldehyde suggesting that there is some reaction at the exocyclic double bond. This double bond is expected to be the less reactive of the two double bonds in the molecule [17]. It is almost certain that reaction at the cyclic double bond leading to ring opening will also occur. 3-Carene, also must ozonolyse via ring opening. For both 3-carene and limonene infrared spectra of the possible larger aldehyde primary products, formed by ring opening, were not available. β-Myrcene has three double bonds. The less-substituted double bonds, which are also expected to be less-reactive [17], would give formaldehyde as a primary product. The more substituted double bond should yield acetone. Formaldehyde is positively identified as a product; acetone may well be present but the

complexity of the spectra make a definite assignment difficult. However, the evidence obtained suggests it is possible that, under the conditions of our experiments, reaction at all three double bonds takes place. The secondary products positively identified from each of these reactions are listed in Table 7.

4. Conclusions

The results which we report in this paper provide a clear indication that the secondary ozonides of ethene and *cis*- and *trans*-but-2-ene are generated by the gas-phase reaction of the appropriate alkene with O₃ in a gaseous mixture of argon and oxygen, followed by condensation at 12 K. This conclusion is reached by a comparison of our spectra with previously obtained spectra where the ozonides are generated by annealing of matrices containing the appropriate alkene and ozone. The other products of these reactions may be designated as primary or secondary products. Thus with ethene, formaldehyde is a primary product and acetaldehyde is a secondary product. An increased yield of acetaldehyde over formaldehyde is seen as the reaction time is increased showing the increased importance of secondary reactions at longer reaction times. Isoprene, β -pinene, limonene and β myrcene show formaldehyde as a product. This finding is entirely as expected. For isoprene and the monoterpenes we see no evidence for the larger primary aldehyde products presumably because these compounds are themselves highly reactive towards O₃. Several secondary products, however, are seen and are identified more-or-less certainly. These are listed in Table 7. Because of the difficulty in positively identifying primary reaction products it is difficult to assess the reactivity of different double bonds within the molecules studied towards ozone. For βmyrcene, however, it does appear that reaction occurs at all three double bonds. This conclusion is based upon the observation of formaldehyde as a product which may be formed by ozonolysis at the less-reactive double bonds.

References

- P. Warneck, Chemistry of the Natural Atmosphere, International Geophysics Series, vol. 41, Academic Press, London, 1988.
- [2] R.P. Wayne, Chemistry of Atmospheres, Oxford University Press, Oxford, 1985.
- [3] A.M. Thomson, Science 256 (1992) 1157.
- [4] R.A. Atkinson, J. Arey, Acc. Chem. Res. 31 (1998) 574.
- [5] A. Calogirou, B.R. Larsen, D. Kotzias, Atmos. Environ. 33 (1999) 1423.
- [6] M. Olzmann, E. Kraka, D. Kremer, R. Gutbrod, S. Andersson, J. Phys. Chem. A 101 (1997) 9421.
- [7] W.C.D. Rathman, T.A. Claxton, A.R. Rickard, G. Marston, Phys. Chem. Chem. Phys. 1 (1999) 3981.
- [8] C.K. Kohlmiller, L. Andrews, J. Am. Chem. Soc. 103 (1981) 2578.
- [9] U. Samuni, R. Fraenkel, Y. Haas, R. Fajgar, J. Pola, J. Am. Chem. Soc. 118 (1996) 3687.
- [10] L. Andrews, C.K. Kohlmiller, J. Phys. Chem. 86 (1982) 4548.
- [11] M. Hawkins, C.K. Kohlmiller, L. Andrews, J. Phys. Chem. 86 (1982) 3154.
- [12] H. Kuehne, H.H. Guenthard, J. Phys. Chem. 80 (1976) 1238.
- [13] H. Kuehne, S. Vaccani, T.-K. Ha, A. Bauder, H.H. Guenthard, Chem. Phys. Lett. 38 (1976) 449.
- [14] H. Kuehne, S. Vaccani, A. Bauder, H.H. Guenthard, Chem. Phys. 28 (1978) 11.
- [15] H. Kuehne, M. Forster, J. Hulliger, H. Ruprecht, A. Bauder, H.H. Guenthard, Helv. Chim. Acta 63 (1980) 1971.
- [16] R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 2, 1 (1994).
- [17] R. Atkinson, J. Phys. Chem. Ref. Data 26 (1997) 215.

- [18] R. Atkinson, S.M. Aschmann, J. Arey, B. Shorees, J. Geophys. Res. 97 (1992) 6065.
- [19] S.E. Paulson, A.D. Sen, P. Liu, J.D. Fenske, M.J. Fox, Geophys. Res. Lett. 24 (1997) 3193.
- [20] N.M. Donahue, J.H. Kroll, J.G. Anderson, K.L. Demerjian, Geophys. Res. Lett. 25 (1998) 59.
- [21] G. Marston, C.D. McGill, A.R. Rickard, Geophys. Res. Lett. 25 (1998) 2177.
- [22] R. Fajgar, J. Vitek, Y. Haas, J. Pola, Tetrahed. Lett. 37 (1996) 3391.
- [23] O. Horie, P. Neeb, G.K. Moortgat, Int. J. Chem. Kinet. 29 (1997) 461.
- [24] M.J. Almond, M. Hahne, J. Chem. Soc. Dalton Trans. (1988) 2255.
- [25] E.J. Feltham, PhD Thesis, University of Reading, 2000.
- [26] S.E. Paulson, R.C. Flagan, J.H. Seinfeld, Int. J. Chem. Kinet. 24 (1992) 103.
- [27] A.R. Rickard, D. Johnson, C.D. McGill, G. Marston, J. Phys. Chem. A 103 (1999) 7656.
- [28] P. Neeb, F. Sauer, O. Horie, G.K. Moortgat, Atmos. Environ. 31 (1997) 1417.
- [29] R. Atkinson, J. Arey, S.M. Aschmann, E.C. Tuazon, Res. Chem. Intermed. 20 (1994) 385.
- [30] R.M. Kamens, M.W. Gery, H.E. Jeffries, M. Jackson, E.I. Cole, Int. J. Chem. Kinet. 14 (1992) 955.
- [31] K. Griesbaum, M. Hilss, J. Bosch, Tetrahedron 52 (1996) 14813.
- [32] K. Griesbaum, V. Miclaus, I.C. Jung, Environ. Sci. Technol. 32 (1998) 647.
- [33] M. Jang, R.M. Kamens, Atmos. Environ. 33 (1999) 459.
- [34] B. Schrader, Raman and Infrared Atlas of Organic Compounds, 2nd edn., VCH Publishers, New York, 1989.
- [35] M. Hawkins, L. Andrews, J. Am. Chem. Soc. 105 (1983) 2523.
- [36] V. Raducu, D. Jasmin, R. Dahoo, P. Brosset, B. Gauthier-Roy, L. Abouaf-Marguin, J. Chem. Phys. 102 (1995) 9235.