

# Formation of secondary ozonides in the gas phase low-temperature ozonation of primary and secondary alkenes

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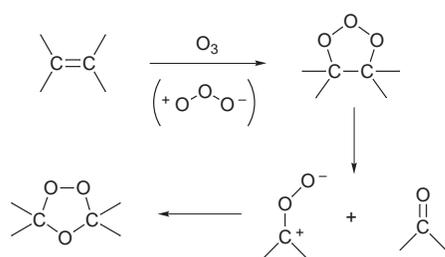
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The gas-phase ozonation of a series of alkenes  $RCH=CH_2$  ( $R = Et, Hex$ ),  $trans-RHC=CHR$  ( $R = Me, Et, Pr^i$ ) and  $Me_2C=CMe_2$  at  $-40$  to  $20$  °C, and that of ethene  $H_2C=CH_2$  at  $-120$  to  $0$  °C at  $10^{-4}$  v/v concentrations in  $N_2$  at atmospheric pressure have been studied. Using complementary product analysis by means of GC-FTIR and GC-MS techniques, we present conclusive evidence for the formation of secondary alkene ozonides as high-yield products in all instances except  $Me_2C=CMe_2$ . It is shown that the stereoselectivity for the conversion of  $trans-RHC=CHR$  ( $R = Me, Et, Pr^i$ ) to  $trans$ -secondary ozonides in the gas phase is similar to that observed earlier in solution, and that the yields of secondary ozonides from  $RHC=CH_2$ , but not those from  $RHC=CHR$ , significantly decrease with increasing temperature.

## Introduction

Gas-phase ozone-alkene reactions have attracted early,<sup>1</sup> continuing<sup>2</sup> and recent<sup>3</sup> attention, since simple alkenes are important constituents in the urban atmosphere<sup>4</sup> and over tropical forests<sup>5</sup> and detailed knowledge about their reaction with ozone would help to model the tropospheric chemistry that leads to photochemical smog and to characterize the harmful effects<sup>6</sup> of the reaction products on vegetation. Despite a large number of studies, complete understanding of the mechanism of this complex reaction is still awaiting further effort.

In analogy with the corresponding ozone-alkene solution-phase reactions (Criegee mechanism,<sup>7</sup> Scheme 1), the gas-phase



Scheme 1

ozonations of alkenes are believed<sup>8</sup> to be initiated by the formation of a primary ozonide (POZ) followed by its unimolecular dissociation into a carbonyl compound (CC) and a carbonyl oxide (COX), often referred to as the Criegee intermediate (CI). Considerable uncertainties persist, however, concerning the next steps, particularly the reactions of the Criegee intermediates. As shown in the energy level diagram, Fig. 1, the CC + COX pair is formed with a large excess of internal energy. In solution (or in a cryogenic matrix) they are rapidly vibrationally relaxed, leading to the formation of secondary ozonides (SOZ), the latter being easily isolated. As shown in recent theoretical work,<sup>9</sup> the POZ rearranges to form an electrostatically held dipole complex (DC), which subsequently forms the SOZ. In the gas phase many competing processes are possible, such as dissociation or rearrangement of the COX, followed by

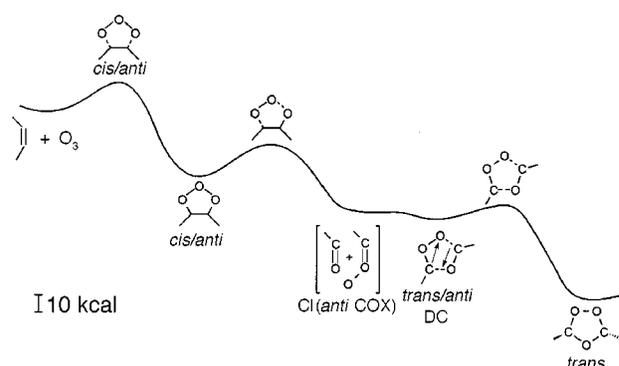
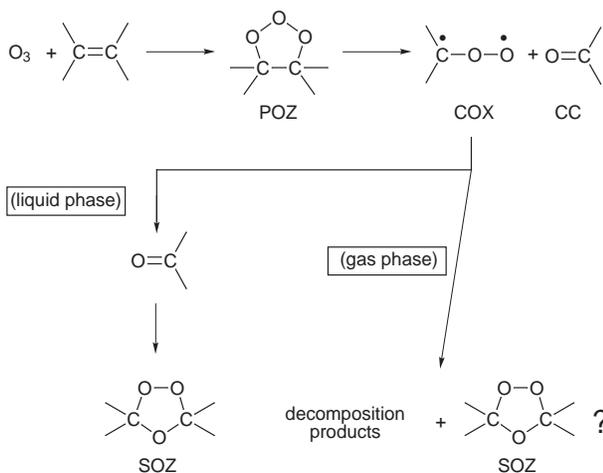


Fig. 1 Computed energy profile for *cis*-but-2-ene ozonation [ref. 9(b)].

bimolecular reactions of the fragment with the CC (or with residual COX) leading to a fairly complex sequence of events. The unimolecular decomposition of the vibrationally excited COX is currently considered to take place *via* several distinct routes, such as the ester, O-atom, hydroperoxide<sup>10</sup> and other<sup>11</sup> channels. The relevance of these is ascribed to the occurrence of unique indicator products and is dependent on the COX structure and ozonation conditions.<sup>10,11</sup> The hydroperoxide channel (the COX rearrangement into hydroperoxyalkene) is preferred over the ester channel (the COX rearrangement into dioxirane) with COXs possessing a CHR or  $CH_2R$  groups in the *syn* position<sup>12</sup> and it is followed by O-O bond cleavage to yield an OH radical, the species detected in ozonation of alkenes at both low<sup>13</sup> and atmospheric<sup>2d</sup> pressure.

These radicals are thought to play a pivotal role as reactive intermediates in ensuing processes. The lack of solvent stabilization of a highly energy-rich POZ and COX, as well as the absence of the solvent effect (holding CC and CI in close proximity) is believed to suppress the formation of SOZ *via* association of the CC and the COX, and enhance various decomposition/isomerization modes of the COX and other subsequent reactions (Scheme 2).

Although the parent dioxirane  $CH_2OO$ <sup>14</sup> and the POZ of ethene<sup>15</sup> have been identified by microwave spectroscopy in the gas phase after the warm-up of the cooled products of



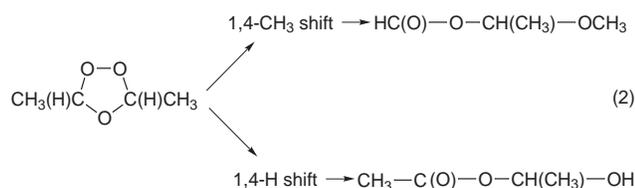
Scheme 2

ethene ozonation carried out in the solid phase at  $-196\text{ }^\circ\text{C}$ , none of the COX, dioxirane (the product of the ring closure of the COX) and the POZ have ever been detected as intermediate products of the alkene ozonation conducted truly in the gas phase.<sup>7,16</sup>

At low pressure (4–8 Torr<sup>17</sup>), the occurrence of the SOZ in the gas phase ozonation of alkenes has been suggested in earlier studies of the ozonation of several linear and branched-chain alkenes  $\text{R}_n\text{H}_2-n\text{C}=\text{CH}_2-n\text{R}_n$  ( $n=1, 2$ ;  $\text{R}=\text{CH}_3$  and  $\text{C}_2\text{H}_5$ ). Photoionization mass spectrometry revealed stable products which are characteristic of a CI decomposition, of reactions of alkenes with OH, and of other free radical reactions. With propene, 2-methylpropene, *cis*-but-2-ene and *trans*-pent-2-ene, but not with ethene, *trans*-but-2-ene and 2,3-dimethylbut-2-ene a very minor peak at *m/e* (alkene + 48) has been detected and tentatively assigned<sup>17</sup> to the SOZ. This assignment was believed to be supported by the observation of an increase of the signal at *m/e* 104 upon addition of  $\text{CH}_3\text{CHO}$  to *cis*-but-2-ene +  $\text{O}_3$  mixture, which was deemed<sup>17</sup> to reflect a “titration” of the COX [ $\text{CH}_3(\text{H})\text{C}^{\bullet}\text{OO}^{\bullet}$ ] with  $\text{CH}_3\text{CHO}$  [eqn. (1)].

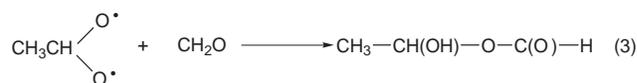


However, the MS signals assigned<sup>17</sup> to the SOZ can be equally well associated with the SOZ isomeric compounds which have been recently proved to originate from the secondary but-2-ene ozonide rearrangement [eqn. (2)].<sup>18</sup>



At atmospheric pressure, the SOZs were claimed to appear as minor products of the ozonation of but-2-ene<sup>3c</sup> based on the characteristic IR spectrum obtained by subtracting the IR spectral contributions of the other gaseous products, and also of the ozonation of pent-1-ene, hex-1-ene and hept-3-ene (but not of lower homologues) based on the observation of a strong IR absorption band near  $9\text{ }\mu\text{m}$ .<sup>1c</sup> Linear reactor-infrared Ar-matrix and microwave spectroscopy examination of the ozonation of *cis*-but-2-ene<sup>19</sup> and ethene<sup>20</sup> revealed the presence of absorption bands assignable to the SOZ present in a complex mixture of many products for the former but not for the latter reaction. This detection, suffering from concomitant occurrence of other products like esters, epoxides, hydroxyketones and oligomers

containing C–O–C and C–O–O–C linkages was, however, not confirmed in a similar matrix isolation FTIR spectral study of the ozonation of *trans*-but-2-ene in argon containing oxygen.<sup>21</sup> In this examination,<sup>21</sup> apart from other compounds, an unknown product was revealed and assigned as 1-hydroxyethyl formate. Its formation was explained by eqn. (3).



However, this type of association product, although observed in the gas phase ozonation of ethene,<sup>8,22</sup> was not found in the long path FTIR spectral study of the ozonation of *cis*-but-2-ene in air in the presence of methanal, when secondary propene ozonide was observed instead.<sup>23</sup> This observation was explained by eqn. (4).



It was later admitted<sup>24</sup> that the most probable structure of the unknown product is hydroperoxymethyl formate  $\text{HOO}-\text{CH}_2-\text{O}-\text{CHO}$ , which can be formed by association of the two COXs ( $\text{H}_2\text{C}^{\bullet}\text{OO}^{\bullet}$ ), or by reaction of the COX ( $\text{H}_2\text{C}^{\bullet}\text{OO}^{\bullet}$ ) with formic acid. This view was recently confirmed by comparing the IR spectrum of the unknown product to that of the synthesized hydroperoxymethyl formate.<sup>3e</sup>

Recently, secondary ozonides were observed in the low-concentration ozonation of some olefins by deliberately adding carbonyl compounds. Examples are the ozonation of ethene in an excess of  $\text{CH}_3\text{CHO}$  or  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$  yielding<sup>3d</sup> secondary propene and isobutene ozonide, respectively, and the ozonation of but-2-ene in an excess of  $\text{CH}_3\text{CHO}$  or  $\text{HCHO}$  affording<sup>3f</sup> secondary butene ozonide and secondary propene ozonide respectively. Although these experiments confirm that the COX can react with the CCs to yield the SOZs, they do not demonstrate the formation of the SOZs from the *geminate* pair of the COX and CC.

We have recently shown that a secondary butene ozonide can rearrange to the appropriate esters [eqn. (2)], and are therefore interested in possible reaction pathways leading to them. Previous work was mainly conducted at room temperature, at which some SOZs are fairly reactive. We have therefore set up a system allowing the measurement of gas phase reactions of some alkenes in the  $-40$  to  $+20\text{ }^\circ\text{C}$  range (and for ethene in the  $-120$  to  $0\text{ }^\circ\text{C}$  range).

In contrast with previous investigations, which relied on the application of just one spectroscopic technique to a mixture of ozonation products, we used two complementary methods, which enabled us to characterize ozonation products as separated entities: the ozonation products were separated by gas chromatography and identified by both infrared and mass spectroscopy.

In this paper, our previous work on the formation of the secondary butene ozonide in the gas phase<sup>25</sup> is extended to include several primary and secondary alkenes. Using GC–MS and GC–FTIR techniques, we unequivocally show that secondary ozonides are produced in the gas-phase ozonation of many alkenes. This finding confirms that the bimolecular coupling of the COX and the *geminate* CC can compete with the COX decompositions in the gas phase, and that the validity of the complete Criegee mechanism<sup>7,26</sup> can be extended to the gas phase.

## Experimental

### The ozonation set-up and analyses of ozonation products

The ozonation of  $\text{RHC}=\text{CHR}$  [ $\text{R}=\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  and  $(\text{CH}_3)_2\text{HC}$ ],

RHC=CH<sub>2</sub> (R = H, C<sub>2</sub>H<sub>5</sub>, and *n*-C<sub>4</sub>H<sub>9</sub>) and (CH<sub>3</sub>)<sub>2</sub>C=C(CH<sub>3</sub>)<sub>2</sub> alkenes was carried out by mixing ozone and the alkene (both in an excess of nitrogen). For that purpose, 45 Pa of alkene in 50 kPa of N<sub>2</sub>, and 135 Pa of ozone in 150 kPa of N<sub>2</sub> were prepared, each in a 2 l Pyrex round-bottom flask equipped with PTFE stopcocks. Both flasks were attached to a standard vacuum manifold and interconnected by a PTFE valve. The flasks were preconditioned by keeping them for 30 min either at room temperature, or at 0 to -40 °C by immersion in a box of 15 l volume containing a dry ice-ethanol bath. Thereafter, a quick opening and closing of the interconnecting valve equalized pressures in both flasks and led to the ozonation between 45 Pa of alkene and 45 Pa of ozone at 100 kPa of N<sub>2</sub>. The flask wherein the ozonation took place was immersed in the bath or kept at ambient temperature for a further 30 min. The progress of the ozonation within these 30 min intervals was checked by FTIR (a Nicolet, model Impact 400) spectrometry.

The ozonation mixture was then analysed by gas chromatography (a gas chromatograph Shimadzu 14A equipped with FID detector and coupled with a Chromatopac CR5A data processor), GC-MS (a Shimadzu, model QP 1000 quadrupole spectrometer, ionizing voltage 70 eV) and GC-FTIR (a Nicolet, model Impact 400 coupled to a laboratory-made chromatograph and a chromatograph interphase) techniques. The samples for the GC analysis were withdrawn by a gas-tight syringe directly from the ozonation flask *via* a septum. The GC-MS and GC-FTIR analyses were carried out on total amounts of the ozonation products concentrated in a 4 ml tube which was attached to the vacuum manifold and furnished with a septum and PTFE stopcock and which was cooled with liquid nitrogen.

Quantitative analyses were performed on a 3.3 m long column packed with SE-30 elastomer on a Chromosorb W. A column packed with 2,2'-oxydipropionitrile (3.3 m, 5% on Chromosorb G-HP) was used for the separation of the *cis*- and *trans*-isomers of SOZs. Other analyses were performed on a 50 m long SPIRA KI-5 capillary column. The chromatographic separation of the ozonation products was conducted at programmed column temperature. The FID response factors (*f*) of the ozonation products were determined from GC traces of a mixture of the authentic sample of the ozonation product (*o*) and of suitable hydrocarbon (*h*), both of which were prepared at determined partial pressures in a reservoir of a standard vacuum manifold. They were calculated by using the formulae  $f_o/f_h = (S_o M_h p_h)/(S_h M_o p_o)$  where *S*, *M* and *p* relate to the GC curve area, molecular weight and partial pressure respectively. The FID factors determined in this work are as follows: ethanal, 0.30; 3,5-dimethyl-1,2,4-trioxolane, 0.12; acetic acid, 0.24; propanal, 0.49; methanal, 0.05; 3-ethyl-1,2,4-trioxolane, 0.11; 3,5-diethyl-1,2,4-trioxolane, 0.14; pentanal, 0.64; butyl formate, 0.49; 2,3-diethylloxirane, 0.72; 3-methylbutanal, 0.66; and 3,5-diisopropyl-1,2,4-trioxolane, 0.15; others are taken from ref. 27.

The yields of the SOZs were ascertained on the basis of the GC and FTIR spectral analyses of the ozonation mixtures: the depletion of alkene was determined by gas chromatography, while the amount of the SOZ was revealed by FTIR spectral analysis of the ozonation mixture transferred under vacuum into either a standard IR cell (20 cm pathlength, 250 ml) or a multipath IR cell (1 m pathlength, 3 l) making use of the knowledge of extinction coefficients of the pure SOZs.

### Reactants and model compounds

Ozone was prepared in a 250 ml glass reactor furnished with PTFE stopcock by applying a high-voltage discharge to 3.5 kPa of oxygen (Technoplyn, purity 99%). The yield of ozone was determined by FTIR spectra using the diagnostic absorption band at 1053 cm<sup>-1</sup>.

*trans*-But-2-ene, hex-1-ene (both Fluka), but-1-ene, *trans*-

hex-3-ene, oct-1-ene (all Aldrich), ethene and 2,3-dimethylbut-2-ene (laboratory stock) were of purity higher than 96% and were distilled on a vacuum line prior to use.

Synthesis of 2,5-dimethylhex-3-ene (purity 97%) was accomplished<sup>28</sup> by the reaction of isobutyl bromide with triphenyl phosphine and subsequent treatment of the reaction product with *n*-butyllithium and isobutyraldehyde.

Compounds which were used as the standards for the analysis of the FTIR spectra of the ozonation mixtures were from laboratory stock (CO, CH<sub>3</sub>CHO, CH<sub>3</sub>COOH, CH<sub>3</sub>CH<sub>2</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>COOH, CH<sub>4</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>OH) or freshly prepared by standard techniques (H<sub>2</sub>CO, HCOOH). Their purity (higher than 96%) was checked by gas chromatography and FTIR spectroscopy.

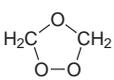
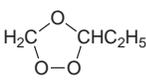
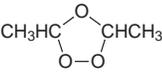
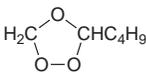
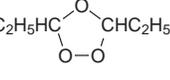
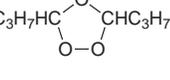
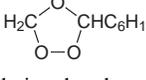
### Preparation of model SOZs

In order to identify the SOZs produced in the gas phase ozonation of alkenes at -40 to +20 °C, we prepared SOZs in advance at much lower temperatures in the liquid phase and measured their mass and FTIR spectra by applying GC-MS and GC-FTIR spectroscopy techniques to the ozonation mixtures.

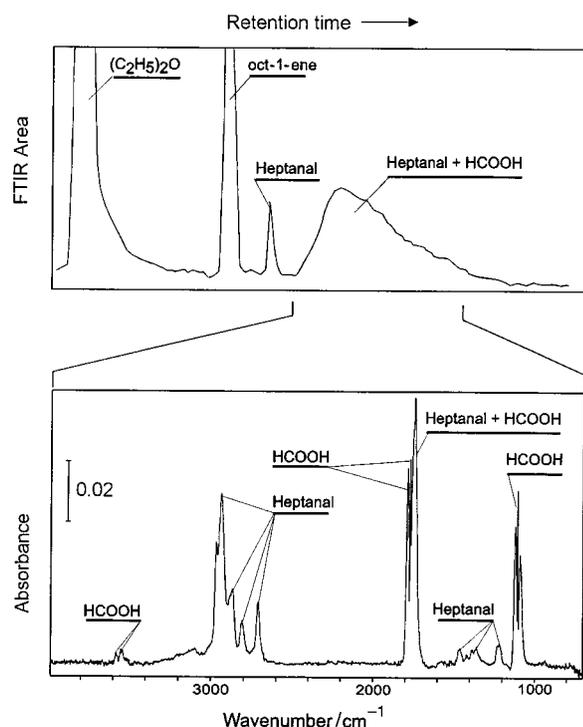
All secondary alkene ozonides, except for those of ethene, oct-1-ene and 2,3-dimethylbut-2-ene, were prepared by ozonation of alkenes in a 250 ml tube furnished with PTFE stopcock and connected to the vacuum manifold. 1–2 kPa amounts of alkene and then of ozone were repeatedly admitted into the tube which was immersed in the ethanol-liquid nitrogen bath and kept at -120 °C. Under these conditions the reaction takes place in either the solid or the liquid phase, depending on the alkene. Addition of fresh reactants was performed after the pressure of the previously added ozone decreased to less than 5% of its original value, indicating its complete reaction. The tube was left in the cooling bath overnight, during which period the temperature increased to -20 °C. During that time, the unstable POZ slowly reacted into mostly SOZ and only small amounts of decomposition products could be detected. The unreacted alkene was removed by pumping the sample at -20 °C.

The secondary octene ozonide was obtained by repeatedly admitting oct-1-ene and ozone into a 300 ml tube kept at -120 °C. The products of the ozonation were concentrated in a 4 ml condenser cooled by liquid nitrogen. After removing the liquid nitrogen bath, the products were slowly warmed up to room temperature and analysed. GC-MS and GC-FTIR analyses on an SE-30 column of the gaseous phase did not show any presence of secondary octene ozonide but only heptanal and methanal (major products). Analysis of the liquid phase was conducted, too: *ca.* 0.2 ml of diethyl ether was added to the droplets observed on the bottom of the 4 ml tube, and the resulting solution was analysed by FTIR, GC-FTIR and GC-MS spectroscopy. GC-MS analysis of the ethereal solution injected into an empty glass column, initially cooled by liquid nitrogen and later slowly warmed up to room temperature, showed a big peak of diethyl ether and a smaller peak whose mass fragmentation can be assigned to secondary oct-1-ene ozonide (Table 1). The FTIR spectra of the ozonation products after evaporation of ether showed characteristic absorption bands of ozonide (Table 1) and no ν(C=O) absorption band, which indicated that the secondary octene ozonide is a major ozonation product. However, GC-FTIR analysis of the ethereal solution revealed three major peaks (Fig. 2). The first two are due to oct-1-ene and heptanal. The third, unusually broad peak was found to represent a mixture of heptanal and formic acid, which indicates that the initially present secondary octene ozonide does not survive at the higher temperatures of the GC analysis (25–80 °C) and decomposes into these two compounds. Of the two pairs of the principle decomposition products<sup>18</sup> HCOOH + heptanal and H<sub>2</sub>CO + heptanoic acid, the latter is

**Table 1** FTIR and mass spectral data of standard SOZs

SOZ	$\nu/\text{cm}^{-1a}$	$m/z$ (rel. intensity, %) <sup>b</sup>	
		Eight most intense peaks	Highest peak
	948, 0.45; 955, 0.45; 968, 0.46; 1082, 1.00; 1092, 0.80; 2887, 0.39; 2897, 0.74; 2908, 0.36; 2956, 0.11; 2970, 0.47; 2984, 0.26	29 (100); 30 (92); 28 (74); 46 (67); 45 (52); 44 (31); 18 (16); 76 (10)	76 (10), M <sup>+</sup>
	967, 0.39; 973, 0.42; 984, 0.41; 1066, 0.76; 1103, 0.87; 1117, 0.85; 1391, 0.29; 1470, 0.15; 2894, 1.00; 2963, 0.50; 2980, 0.193	29 (100); 27 (38); 28 (36); 31 (23); 30 (17); 57 (12); 26 (12); 75 (10)	104 (1.2), M <sup>+</sup>
	900, 0.14; 1128, 1.00; 1349, 0.12; 1386, 0.27; 1394, 0.28; 1452, 0.05; 2908, 0.28; 3005, 0.18	43 (100); 45 (41); 44 (34); 29 (34); 89 (16); 15 (15); 60 (11); 31 (10)	104 (5.0), M <sup>+</sup>
	984, 0.26; 1065, 0.62; 1107, 0.82; 1209, 0.04; 1325, 0.07; 1390, 0.24; 1466, 0.12; 2890, 0.85; 2967, 1.00	29 (100); 44 (60); 41 (57); 27 (41); 28 (26); 43 (25); 39 (23); 57 (23)	104 (0.8), M - 28
	896, 0.09; 959, 0.33; 1017, 0.29; 1122, 0.92; 1297, 0.09; 1386, 0.35; 1470, 0.27; 2894, 0.83; 2950, 0.55; 2979, 1.00	29 (100); 57 (43); 28 (33); 58 (31); 27 (27); 31 (23); 103 (17); 41 (11)	132 (1.5), M <sup>+</sup>
	957, 0.07; 993, 0.09; 1024, 0.11; 1088, 1.00; 1125, 0.19; 1191, 0.06; 1294, 0.06; 1364, 0.14; 1395, 0.23; 1476, 0.23; 2887, 0.50; 2938, 0.25; 2972, 0.65	43 (100); 41 (26); 27 (17); 29 (10); 72 (8); 73 (7); 39 (7); 55 (7)	117 (0.9), M - C <sub>3</sub> H <sub>7</sub>
	2953, 1.00; 2855, 0.82; 1463, 0.35; 1395, 0.28; 1380, 0.34; 1325, 0.16; 1225, 0.09; 1200, 0.12; 1103, 0.91; 1057, 0.82; 963, 0.49	43 (100), 41 (62); 29 (56); 44 (47); 55 (45); 70 (35); 57 (29); 45 (27)	132 (1.4), M - 28

<sup>a</sup> Relative absorbance. <sup>b</sup> At 70 eV.



**Fig. 2** GC-FTIR analysis of the mixture in diethyl ether obtained by ozonation of oct-1-ene at  $-120\text{ }^{\circ}\text{C}$ .

not seen due to low volatility of heptanoic acid and polymerization of H<sub>2</sub>CO.

The secondary ethene ozonide was prepared by admitting 10 kPa of ethene-N<sub>2</sub> (1:1) mixture, and then an O<sub>3</sub> (5 kPa)-N<sub>2</sub> (120 kPa) mixture into a 300 ml tube kept at  $-120\text{ }^{\circ}\text{C}$ . The reaction mixture was left overnight in the tube, whose temperature rose to  $-50\text{ }^{\circ}\text{C}$  over that period.

The preparation of the secondary tetramethylethene (2,3-dimethylbut-2-ene) ozonide was attempted by repeatedly admitting the olefin and ozone into the 300 ml tube kept at  $-120\text{ }^{\circ}\text{C}$ ,

or by carrying out the reaction in pentane at the same temperature. Both attempts failed; the reactions afforded mostly acetone and a mixture of *ca.* 20 minor products (tetramethyloxirane, tentatively diperoxyacetone and others).

### Characterization of model SOZs

All the raw SOZs were analysed by GC-FTIR and GC-MS providing IR and MS spectral data of their pure forms. The data agreed well with published previous work, when available. However, since many of the obtained SOZs have not been previously characterized, we have compiled both IR and MS spectral data for all the SOZs prepared in this work in Table 1.

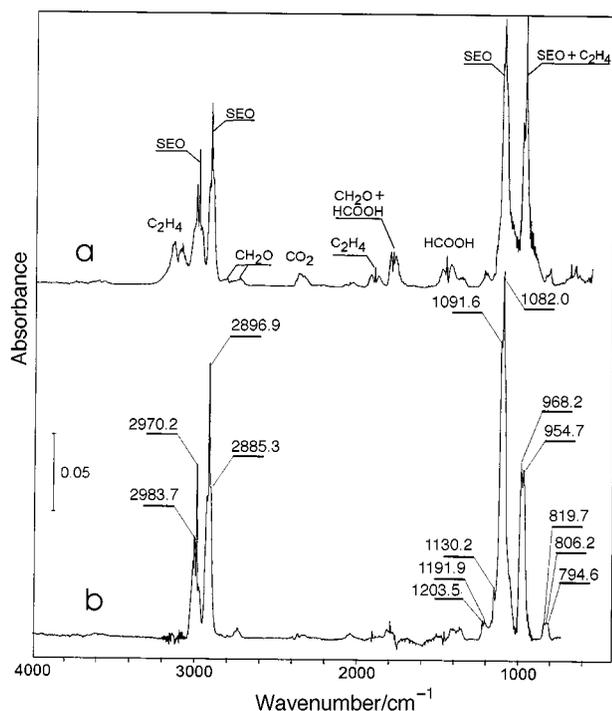
### Results and discussion

The formation of the SOZs in the gas-phase ozonation of (i) ethene, (ii) RHC=CH<sub>2</sub> (R = C<sub>2</sub>H<sub>5</sub> and *n*-C<sub>4</sub>H<sub>9</sub>), (iii) RHC=CHR [R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> and (CH<sub>3</sub>)<sub>2</sub>HC] and (iv) (CH<sub>3</sub>)<sub>2</sub>C=C(CH<sub>3</sub>)<sub>2</sub> will be dealt with separately due to some differences (yield, GC response factor of the SOZ) observed in each case.

The ozonation of alkenes under experimental conditions of this study can be partly affected by reactions of the OH radical.<sup>29</sup> (It is known that the yield of this radical is dependent on experimental conditions and the number of substituents attached to the alkene double bond.<sup>2d,12,13a</sup>) However, the significantly high yields of the SOZs, relating to the total amount of alkene reacted (see below), and the minor quantities of the detected products of the reactions of the OH radical (alcohols and diols<sup>13a,36</sup>) show that the formation of the SOZs under our conditions is a very important channel which competes successfully with the COX decomposition and also with the OH radical reactions.

#### (i) Formation of SOZ in the ozonation of ethene

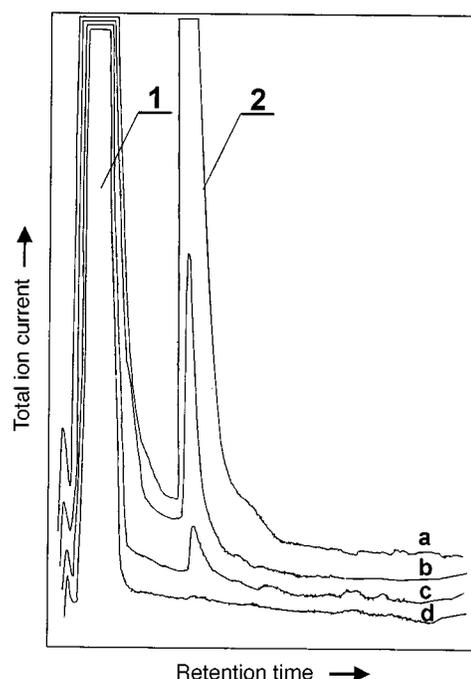
The gas phase ozonation of ethene at temperatures  $-120$ ,  $-50$ ,  $-20$  and  $0\text{ }^{\circ}\text{C}$  results in the formation of four observable products, namely methanal, formic acid, carbon dioxide and secondary ethene ozonide. Fig. 3 gives the FTIR spectrum of



**Fig. 3** FTIR spectrum of the mixture obtained by ozonation (a) of ethene at  $-120\text{ }^{\circ}\text{C}$  and (b) of secondary ethene ozonide attained by subtraction of the contributions of  $\text{CH}_2\text{O}$  and  $\text{HCO}_2\text{H}$ .

the gaseous ozonation mixture obtained at  $-120\text{ }^{\circ}\text{C}$  and the spectrum of secondary ethene ozonide (1,2,4-trioxolane) obtained by removing the contributions of ethene, methanal, carbon dioxide and formic acid. The derived spectrum shows a typical absorption pattern of secondary ethene ozonide (see Experimental section and ref. 30). The presence of secondary ethene ozonide is confirmed by GC-MS analyses of the ozonation mixtures which reveal a minor peak with fragmentation [ $m/z$  (rel. intensity, %): 76 (3), 46 (28), 45 (22), 44 (34), 30 (36), 29 (100), 28 (28)] assignable (see Experimental section and ref. 31) to secondary ethene ozonide and which show (Fig. 4) that the yield of secondary ethene ozonide diminishes with the increasing temperature. A quantitative estimate of the ozonation product yields by gas chromatography was not possible, since no secondary ethene ozonide peak was observed due to a very low FID response factor. However, both GC-MS and FTIR analysis provide unambiguous evidence that secondary ethene ozonide is formed in the gas-phase ozonation of ethene.

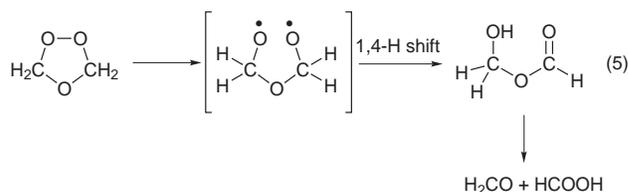
We note that in the previous studies of the reaction between ozone and ethene at low pressure<sup>17,32</sup> or in the ppm range in  $\text{O}_2\text{-N}_2$  mixtures at atmospheric pressure,<sup>11,20,22a,24,33</sup> all conducted at room temperature, only methanal, formic acid, formic anhydride,  $\text{CO}$ ,  $\text{CO}_2$  and a transitory  $\text{HOO-CH}_2\text{-O-CHO}$ <sup>24</sup> (or erroneously assigned  $\text{HOCH}_2\text{-O-CHO}$ <sup>11,22a,b,33</sup>) compound, but no secondary ethene ozonide, have been detected. The previously observed  $\text{H}_2\text{CO}$ ,  $\text{HCOOH}$ ,  $(\text{HCO})_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$  compounds, and also  $\text{H}_2\text{CO}$ ,  $\text{HCOOH}$  and  $\text{CO}_2$  observed under our low-temperature conditions are indicative of unimolecular decomposition of the energy-rich  $\text{COX}$  ( $\text{H}_2\text{C}^*\text{OO}^*$ ). The previous observation of peroxyethyl formate  $\text{HOO-CH}_2\text{-O-CHO}$ , but not of secondary ethene ozonide, at room temperature might indicate that (i) association of  $\text{H}_2\text{C}^*\text{OO}^*$  with  $\text{HCOOH}$  is preferred over that of  $\text{H}_2\text{C}^*\text{OO}^*$  with  $\text{H}_2\text{CO}$ , or that (ii) survival of hydroperoxymethyl formate needs less efficient collisional stabilization than that of secondary ethene ozonide. Our results do not allow us to discern between these alternatives. However, the most efficient formation of the secondary ethene ozonide at  $-120\text{ }^{\circ}\text{C}$ , the decrease in secondary ethene ozonide yield with temperature increasing to  $-20\text{ }^{\circ}\text{C}$  and no formation of secondary ethene ozonide at  $0\text{ }^{\circ}\text{C}$  (Fig. 4) seem to indicate that



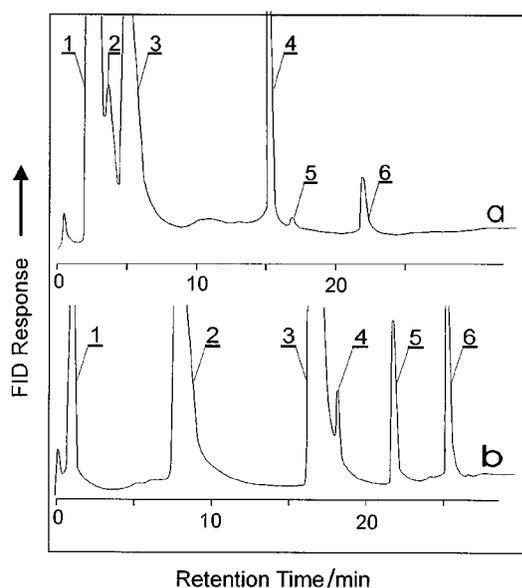
**Fig. 4** Comparison of GC-MS traces of the mixtures obtained by ozonation of ethene at (a)  $-120$ , (b)  $-50$ , (c)  $-20$  and (d)  $0\text{ }^{\circ}\text{C}$ . In the traces reflecting the same injected gaseous amounts of the ozonation mixture the first peak represents a blend of  $\text{N}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{CH}_2\text{O}$ , and the second relates to secondary ethene ozonide.

stabilization of the 'hot' SOZ or CI is indeed an important factor.

The above temperature dependence of the secondary ethene ozonide yield thus reveals that the observation of bimolecular reaction between  $\text{H}_2\text{C}^*\text{OO}^*$  and  $\text{H}_2\text{CO}$  to the SOZ is enabled by cooling the gaseous reaction mixtures to low temperatures which helps in preventing fragmentation of the reactants and/or of the nascent SOZ. The earlier proposed<sup>11,22a,b,33</sup> transient formation of hydroxymethyl formate has been now abandoned,<sup>3,24</sup> since this compound has not been yet observed. Nevertheless, we wish to note that hydroxymethyl formate formation can occur *via* the previously assumed<sup>11,22a,b,33</sup> reaction between the  $\text{COX}$  and  $\text{H}_2\text{CO}$ , or *via* the 'hot' secondary ethene ozonide decomposition involving the split of the ring  $\text{O-O}$  bond and 1,4-H shift [eqn. (5)], the route observed in the



laser-induced thermal decomposition of secondary butene ozonide.<sup>18</sup> We further note that the thermal gas-phase decomposition of secondary ethene ozonide affords<sup>34</sup> equimolar amounts of  $\text{HCOOH}$  and  $\text{H}_2\text{CO}$ , and even though it was postulated to occur *via*  $\text{HOCH}_2\text{-O-CHO}$ , this transient has never been directly detected. Also our FTIR spectral examination of secondary ethene ozonide decomposition at  $150\text{ }^{\circ}\text{C}$  confirmed  $\text{HCOOH}$  and  $\text{H}_2\text{CO}$  as two major products and did not reveal any  $\text{HOCH}_2\text{-O-CHO}$ . We believe, however, that  $\text{HOCH}_2\text{-O-CHO}$  must be the precursor<sup>18</sup> of the final  $\text{HCOOH}$  and  $\text{H}_2\text{CO}$  products and would like to confirm it by attempting its detection in laser-photosensitized<sup>35a,c</sup> (and heterogeneous contributions obviating<sup>35b</sup>) decomposition of secondary ethene ozonide which is under way.



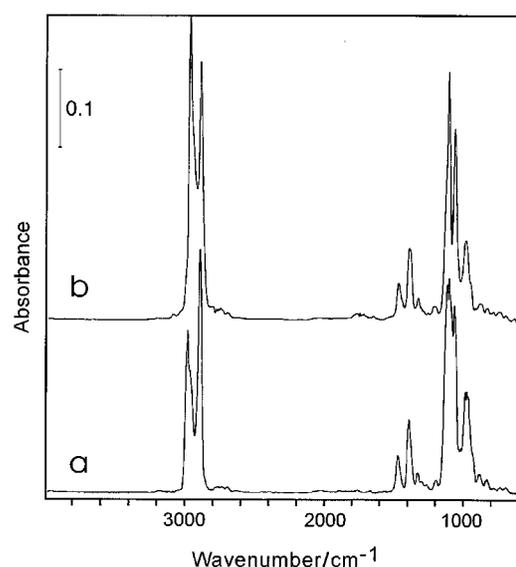
**Fig. 5** Typical GC-MS trace of ozonation mixtures. (a) But-1-ene- $O_3$  (SE 30 column, programmed temperature 25–75 °C). Peak identification: 1, air, CO,  $CO_2$ , but-1-ene; 2,  $CH_2O$ ; 3,  $CH_3CH_2CHO$ ; 4, secondary but-1-ene ozonide; 5,  $C_8H_{16}$ ; 6,  $CH_3CH_2COOH$ . (b) Hex-1-ene- $O_3$  (SE 30 column, programmed temperature 20–120 °C). Peak identification: 1, air, CO,  $CO_2$ ,  $n-C_4H_{10}$ ,  $CH_2O$ ; 2, hex-1-ene; 3,  $CH_3(CH_2)_3CHO$ ; 4,  $n-C_4H_9OC(O)H$ ; 5,  $n$ -butyloxirane; 6, secondary hex-1-ene ozonide.

### (ii) Formation of SOZ in ozonation of $RHC=CH_2$

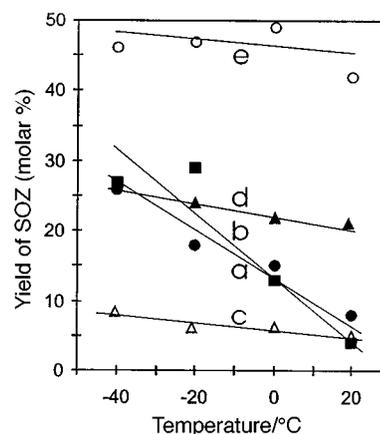
The gas-phase ozonation of  $RHC=CH_2$  ( $R = C_2H_5$  and  $n-C_4H_9$ ) at  $-40$ ,  $-20$ ,  $0$  and  $20$  °C yields a number of products, among which the secondary ozonides are the important ones.

Thus the ozonation of but-1-ene yields CO,  $CO_2$ ,  $H_2CO$ , secondary but-1-ene ozonide (3-ethyl-1,2,4-trioxolane), propanal, a  $C_8H_{16}$  hydrocarbon, whose origin is not clear, and propionic acid; that of hex-1-ene gives CO,  $CO_2$ ,  $H_2CO$ , pentanal,  $n$ -butyl formate, butyloxirane and secondary hex-1-ene ozonide (3-butyl-1,2,4-trioxolane) (Fig. 5). The ozonides separated by gas chromatography were characterized by their mass fragmentation [ $m/z$  (rel. intensity, %)] for secondary but-1-ene ozonide 104 (1,  $M^{+\cdot}$ ), 75 (10), 58 (9), 57 (12), 47 (8), 46 (6), 45 (10), 42 (11), 41 (7), 31 (23), 30 (17), 29 (100), 38 (35), 27 (37); for secondary hex-1-ene ozonide 104 (1,  $M - 28$ ), 90 (4), 75 (7), 73 (6), 71 (5), 60 (17), 58 (16), 57 (23), 55 (9), 45 (14), 44 (59), 43 (25), 42 (15), 41 (57), 39 (22), 31 (12), 30 (11), 29 (100), 28 (26), 27 (42)]. While a very small signal for the molecular ion is observed for secondary but-1-ene ozonide, the highest  $m/z$  signal for secondary hex-1-ene ozonide corresponds to a  $M - 28$  fragment. FTIR spectra of both chromatographically separated ozonides are given in Fig. 6; they are characteristic of secondary ozonides<sup>22e,23,30</sup> and contain no carbonyl absorption bands. We stress that both the FTIR and MS data of the ozonides chromatographically separated from the gaseous ozonation mixtures match those of the secondary ozonides prepared as standards (see Experimental section).

While there are several distinctive routes for the formation of the observed products and while CO and  $CO_2$  are regarded as formed by multistep reactions,<sup>8,10,11</sup> the aldehydes and carboxylic acids can be rationalized as formed, apart from other routes,<sup>8,10,11</sup> by direct SOZ decomposition.<sup>18,34</sup> Both secondary ozonides are stable in the gaseous mixtures and do not decompose at room temperature within several hours. The yields of secondary but-1-ene ozonide and secondary hex-1-ene ozonide steeply decrease with the increasing ozonation temperature and are at each temperature very similar (Fig. 7). The almost identical slopes of their yield vs. temperature plots indicate that the formation of the SOZ from the primary



**Fig. 6** FTIR spectra of (a) secondary but-1-ene ozonide and (b) secondary hex-1-ene ozonide as obtained by GC-FTIR spectroscopy.



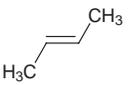
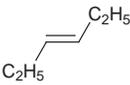
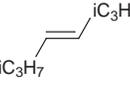
**Fig. 7** Yields of secondary ozonides as dependent on the ozonation temperature: a, but-1-ene; b, hex-1-ene; c, *trans*-but-2-ene; d, *trans*-hex-3-ene; e, *trans*-2,5-dimethylhex-3-ene.

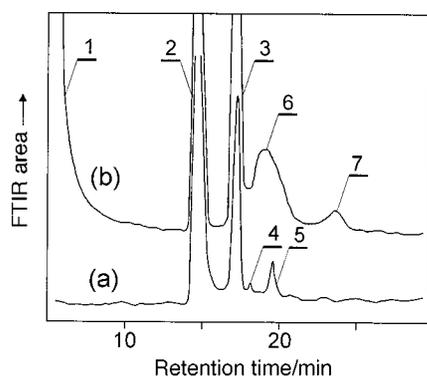
alkenes  $RHC=CH_2$  is not affected by the length of the R group. The significantly lower yields of both  $RHC=CH_2$  SOZs at higher temperatures may explain why the two SOZs can escape detection in studies conducted at ambient temperatures. It is known (ref. 29) that in the ozonation of alkenes at atmospheric pressure and room temperature yields of  $H_2C^{\cdot}OO^{\cdot}$  are significantly higher than the yields of  $RHC^{\cdot}OO^{\cdot}$  or  $RR^{\cdot}C^{\cdot}OO^{\cdot}$ . Table 2 shows that the yield of the rearranged products of  $H_2C^{\cdot}OO^{\cdot}$  ( $HCOOH$ ) and of  $RHC^{\cdot}OO^{\cdot}$  ( $RCOOH$ ) slightly decrease with higher temperature, while the yield of CO and  $CO_2$  (decomposition products of  $H_2C^{\cdot}OO^{\cdot}$ ) increase more profoundly. We thus believe that the steep yield vs. temperature plot seen with the primary but not secondary alkene SOZs (Fig. 7) indicates that  $H_2C^{\cdot}OO^{\cdot}$  is more efficiently stabilized at lower temperatures than  $RHC^{\cdot}OO^{\cdot}$  species.

The gas-phase ozonation of oct-1-ene ( $RHC=CH_2$ ,  $R = n-C_6H_{13}$ ) was carried out, due to the low volatility of this alkene at low temperatures, only at 20 °C and the obtained ozonation mixture was concentrated in the 4 ml tube cooled with liquid nitrogen and subsequently warmed up to room temperature. Both gas and liquid phase (droplets) were produced and analysed. GC-MS and GC-FTIR analyses on the SE 30 column of the gaseous phase revealed the presence of heptanal, methanal, hexane, hexyloxirane and hexyl formate, but no secondary oct-1-ene ozonide.

We note that hexyloxirane was observed<sup>36</sup> as a product of the

**Table 2** SOZ *trans/cis* ratio

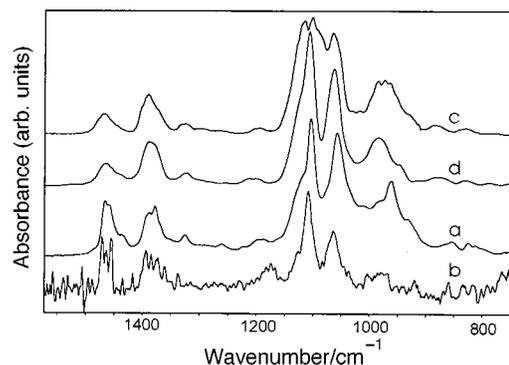
Olefin	<i>T</i> /°C			
	20	0	-20	-40
	2.32	2.51	2.25	2.32
	2.31	1.55	1.23	1.46
	1.30	1.30	1.47	1.83



**Fig. 8** GC-FTIR trace of (a) gas phase and of (b) ethereal solution of liquid phase resulting from ozonation of oct-1-ene carried out at 20 °C. Column SE 30, programmed temperature 20–120 °C. Peak identification: 1, diethyl ether; 2, oct-1-ene; 3, heptanal; 4, hexyl formate; 5, hexyloxirane; 6, heptanal, formic acid, hexyl formate and hexyloxirane; 7, heptanoic acid.

ozonation of octene at atmospheric pressure together with isomeric octanal and octan-2-one and that our GC-FTIR technique shows that of these three products only hexyloxirane is formed under our experimental conditions. GC-FTIR analysis of the gas phase and that of the ethereal solution of the liquid phase are very different and are compared in Fig. 8. While the former indicates the presence of oct-1-ene, heptanal, hexyloxirane and hexyl formate, the latter reveals oct-1-ene, heptanal and a broad peak in the IR spectrum, which is composed of contributions of hexyl formate, heptanal, formic acid and hexyloxirane. Considering that retention times of formic acid and heptanal differ from that of the broad peak, we can assume that these two compounds are products of the secondary oct-1-ene ozonide (3-hexyl-1,2,4-trioxolane) decomposition. This decomposition is supported by the data in the Experimental section (Fig. 1). We assume that the secondary oct-1-ene ozonide  $\rightarrow$  HCOOH + C<sub>6</sub>H<sub>13</sub>CHO decomposition is facilitated at higher temperatures, since the FTIR spectrum of the crude liquified ozonation product (the ethereal solution of the droplets from which ether had evaporated) exposed only to room temperature is fully compatible with the FTIR spectrum of secondary oct-1-ene ozonide. This is proved in Fig. 9 showing the same FTIR spectral pattern of secondary but-1-ene ozonide and secondary hex-1-ene ozonide and of the crude product. We can thus conclude that secondary oct-1-ene ozonide escapes direct gas-phase observation due to its low volatility and stability, but it is an important product in the gas phase ozonation of oct-1-ene.

Up to now, studies of reaction products in the gas-phase ozonation of primary alkenes were restricted only to the ozonation of propene<sup>11,17</sup> and oct-1-ene<sup>36</sup> which revealed a number of products but no SOZ. Our results on the gas phase ozonation of the RHC=CH<sub>2</sub> (R = C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, and *n*-C<sub>6</sub>H<sub>13</sub>) prove



**Fig. 9** Comparison of the FTIR spectrum of the crude product (secondary oct-1-ene ozonide) from ozonation of oct-1-ene obtained at (a) -120 °C, (b) 20 °C and that of (c) secondary but-1-ene ozonide and (d) secondary hex-1-ene ozonide.

that secondary ozonides of these alkenes are produced in substantial amounts and that they are stable in the gas phase at room temperature.

### (iii) Formation of SOZs in the ozonation of RHC=CHR

The gas phase ozonation of RHC=CHR [R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> and (CH<sub>3</sub>)<sub>2</sub>CH] carried out at -40, -20, 0 and 20 °C yields, apart from other products, secondary ozonides in relatively high yields. Typical GC traces of the ozonation mixtures obtained by reacting ozone and alkene at the lowest temperature are shown in Fig. 10. It is found that the products of the ozonation of *trans*-but-2-ene are CO, CO<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>CHO, CH<sub>3</sub>OH and *cis*- and *trans*-secondary but-2-ene ozonides (*cis*- and *trans*-3,5-dimethyl-1,2,4-trioxolanes), the products of the ozonation of *trans*-hex-3-ene are CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>CH<sub>2</sub>CHO, diethyl-oxirane and *cis*- and *trans*-secondary hex-3-ene ozonides (*cis*- and *trans*-3,5-diethyl-1,2,4-trioxolanes), and the products of the ozonation of *trans*-2,5-dimethylhex-3-ene are CO, CO<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>CHCHO, C<sub>16</sub>H<sub>24</sub> and *cis*- and *trans*-secondary 2,2-dimethylhex-3-ene ozonides [*cis*- and *trans*-3,5-bis(2-propyl)-1,2,4-trioxolanes]. As in the previous instances [see (ii)], CO and CO<sub>2</sub> can be regarded as products of several reaction sequences, and RCHO (along with unobserved RCOOH) can arise, apart from other routes,<sup>8,10,11</sup> from decomposition of the SOZ.<sup>18,34</sup>

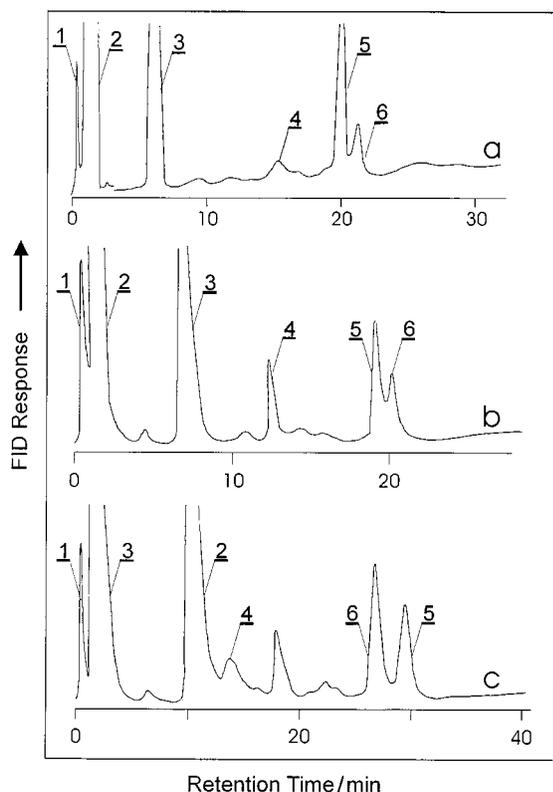
The secondary ozonides were identified using the GC-FTIR procedure through their FTIR spectra (Fig. 11) and characterized by mass fragmentation. The mass spectra of the SOZ are in agreement with those of the authentic samples (Table 1) and show that the molecular ion is observed only with secondary but-2-ene ozonides (*m/z* 104) and secondary hex-3-ene ozonides (*m/z* 132), while for the secondary 2,2-dimethylhex-3-ene ozonides the highest *m/z* fragment corresponds to M - R.

The total yields of the SOZs (combined yield of the *cis*- and *trans*-isomers) from the symmetric secondary RHC=CHR alkenes differ considerably depending on the R group size and are much less temperature dependent than in the case of the primary RCH=CH<sub>2</sub> alkenes (Fig. 7). The SOZ yields for R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> and (CH<sub>3</sub>)<sub>2</sub>CH noticeably increase in the given order at each temperature and reveal the stabilizing effect of bulkier substituents. The very small temperature dependence of the yields of SOZs from the RHC=CHR, together with a fairly significant temperature dependence of the yields of SOZ from the RHC=CH<sub>2</sub> is in line with the assumed different stability of the involved COXs at different temperatures. In other words, the reason for the increased yield at low temperatures of secondary but-1-ene ozonide and secondary hex-1-ene ozonide is more efficient stabilization of the H<sub>2</sub>C'OO' intermediate, a species not involved in the ozonation of RHC=CHR.

Previous studies on the gas-phase ozonation of RHC=CHR alkenes, which were aimed at the identification of ozonation products, dealt with *cis*-but-2-ene,<sup>2a,13a,17,19,23</sup> *trans*-but-2-

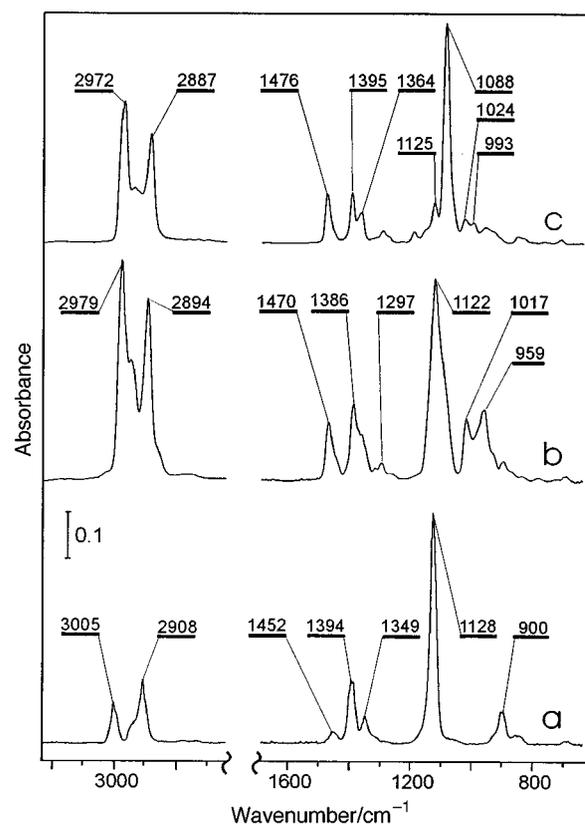
**Table 3** Yields of decomposition products in ozonation of RCH=CH<sub>2</sub> alkenes

R	T/°C	Yield <sup>a</sup>				
		CO	CO <sub>2</sub>	HCOOH	RCOOH	RH
C <sub>2</sub> H <sub>5</sub>	20	0.28	0.38	0.02	0.02	0.14
	0	0.24	0.35	0.01	0.09	0.13
	-20	0.17	0.28	0.02	0.10	0.11
	-40	0.17	0.28	0.05	0.12	0.12
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	20	0.15	0.09	0.00	0.05	0.19
	0	0.10	0.09	0.01	0.07	0.05
	-20	0.09	0.30	0.01	0.06	0.09
	-40	0.05	0.04	0.02	0.09	0.04

<sup>a</sup> In mole/mole of alkene reacted.

**Fig. 10** GC trace of ozonation products of (a) *trans*-but-2-ene, (b) *trans*-hex-3-ene and (c) *trans*-2,5-dimethylhex-3-ene obtained at -40 °C. (a) (2,2'-Oxydipropionitrile column, temperature programmed between 25–50 °C). Peak identification: 1, air, CO, CO<sub>2</sub>, CH<sub>4</sub>; 2, *trans*-but-2-ene; 3, CH<sub>3</sub>CHO; 4, CH<sub>3</sub>OH; 5, secondary but-2-ene ozonide (*trans*-isomer); 6, secondary but-2-ene ozonide (*cis*-isomer). (b) (2,2'-Oxydipropionitrile column, temperature programmed between 30–70 °C). Peak identification: 1, air, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>; 2, *trans*-hex-3-ene; 3, CH<sub>3</sub>CH<sub>2</sub>CHO; 4, diethyloxiran; 5, secondary hex-3-ene ozonide (*trans*-isomer); 6, secondary hex-3-ene ozonide (*cis*-isomer). (c) (2,2'-Oxydipropionitrile column, temperature programmed between 30–70 °C). Peak identification: 1, air, CO, CO<sub>2</sub>; 2, (CH<sub>3</sub>)<sub>2</sub>CHCHO; 3, *trans*-2,5-dimethylhex-3-ene; 4, C<sub>16</sub>H<sub>24</sub>; 5, secondary 2,5-dimethylhex-3-ene ozonide (*cis*-isomer); 6, secondary 2,5-dimethylhex-3-ene ozonide (*trans*-isomer).

ene<sup>2a,10a,11,21,37</sup> and *trans*-pent-2-ene.<sup>17</sup> In these studies the SOZs have been suggested but not unambiguously identified. Similarly to the reaction in solution,<sup>7d,38</sup> the ozonation of *trans*-RHC=CHR alkenes in the gas phase is stereospecific. The ratios of the *trans*- and *cis*-SOZ isomers (given in Table 3) reveal the preference of the *trans*-SOZ forms, which is also true for the solution ozonation where the *cis/trans* ozonide ratio depends on the solvent, the presence of complexing agents, and the warm-up rate of the ozonation reaction mixture.<sup>7d,38</sup> The deviations



**Fig. 11** FTIR spectra of (a) secondary but-2-ene ozonide, (b) secondary hex-3-ene ozonide and (c) secondary 2,5-dimethylhex-3-ene ozonide as obtained by GC-FTIR spectroscopy.

from stereo randomization in the solvent-phase ozonation of *trans*-RCH=CHR alkenes carried out in non-polar hydrocarbons is greater for R = (CH<sub>3</sub>)<sub>3</sub>C (*trans/cis* ratio 2.6 and higher) and smaller with less bulky R [*trans/cis* ratio ca. 1.2–1.5 for (CH<sub>3</sub>)<sub>2</sub>HC, CH<sub>3</sub>CH<sub>2</sub> and CH<sub>3</sub> groups].<sup>7d</sup> Our data show that the preference for the *trans*-isomer in the gas phase is comparable to that observed in solution with R = (CH<sub>3</sub>)<sub>2</sub>HC and CH<sub>3</sub>CH<sub>2</sub> and somewhat higher with R = CH<sub>3</sub>.

The observed ratios of SOZs can be qualitatively explained in terms of the original Criegee mechanism<sup>26</sup> and of its recent refinement<sup>9a</sup> by adopting the view that the COX and CC formed upon the dissociation of the POZ are not separated but form the DC that subsequently transforms to the SOZ. The recent view on the POZ-SOZ transformation<sup>9b</sup> involves two types of rotation of the CC with respect to the COX, the one taking place in the plane of heavy atoms and maintaining the steric structure, and the other taking place in a perpendicular plane and inverting it. The explanation of the higher preference of the *trans* isomers of secondary but-2-ene ozonide and secondary hex-3-ene ozonide in the absence of solvent can be thus related to an easier 'in plane' rotation, even though the reasons for promoting this type of rotation by absence of solvent are not clear. In any case, this stereospecificity is a strong indication of geminate pair recombination. Reactions between randomly oriented reactants may lead to smaller selectivity, although the AM1 calculations of ref. 9(b) indicate a smaller barrier for the preferred route, making it possible that selectivity will be observed also for secondary reactions. This point may be tested by adding intentionally excess carbonyl compounds and analysing the *cis/trans* ozonide ratio. We are aware that the presented interpretation involving the DC is not in keeping with the observation<sup>23,40</sup> that the SOZ formation at higher dilutions of alkene and ozone is suppressed in the presence of SO<sub>2</sub> or HCOOH, which is in support of the COX and CC being separated in the course of ozonation.

This makes us surmise that the degree of separation of the

COX and CC is affected by the amount of the internal energy of a COX...CC agglomerate, and that the mechanism of ozonation involving the DC operates under our conditions of low temperatures while it might not be operative at higher temperatures.

#### (iv) Failed formation of SOZ in the ozonation of 2,3-dimethylbut-2-ene

The gas phase ozonation of  $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$  carried out at  $-40^\circ\text{C}$  does not yield secondary tetramethylethene ozonide but only acetone (major product) and acetone diperoxide together with a  $\text{C}_4\text{H}_8\text{O}$  and two other minor products. These findings are in keeping with other unsuccessful attempts to prepare secondary tetramethylethene ozonide in the gas phase at low<sup>6,39</sup> or atmospheric<sup>41</sup> pressure, in solution,<sup>7c</sup> in silica gel<sup>42</sup> and in cryogenic matrices.<sup>43</sup> We note, however, that the successful formation of secondary tetramethylethene ozonide occurs on the surface of polyethene particles, when restricted migration of the adsorbed CC and COX is believed<sup>44</sup> to overwhelm low reactivity of the CC in intramolecular cyclization with COX. The absence of secondary tetramethylethene ozonide among the products of the gas-phase ozonation of tetramethylethene is thus confirming the failure of secondary tetramethylethene ozonide formation in the solution phase.

## Conclusions

The use of complementary combination of GC-FTIR and GC-MS techniques provides unequivocal evidence that secondary ozonides are products of ozonation of alkenes in the gas phase.

The SOZ yields from primary alkenes ( $\text{RHC}=\text{CH}_2$ ) decrease as the temperature is increased from  $-40$  to  $20^\circ\text{C}$ , while those from secondary alkenes (*trans*- $\text{RHC}=\text{CHR}$ ) are almost unaffected within this temperature range. The stereoselectivity for the formation of *trans*-secondary ozonides from *trans*- $\text{RHC}=\text{CHR}$  possessing Me, Et and  $\text{Pr}^i$  is similar to that earlier observed for the ozonation in solution. The data show that the geminate CO and COX components can bimolecularly react into SOZ without the stabilizing effect of solvent and they give definite support to earlier held opinions that the complete Criegee mechanism can be extended to the gas-phase.

The unambiguous determination of the SOZs as products of alkenes ozonation in the gas phase reported in this work also adds more light to many open questions<sup>45</sup> regarding bimolecular reactions of the COX.

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