

Complete ozonolysis of alkyl substituted ethenes at $-60\text{ }^{\circ}\text{C}$: distributions of ozonide and oligomeric products†

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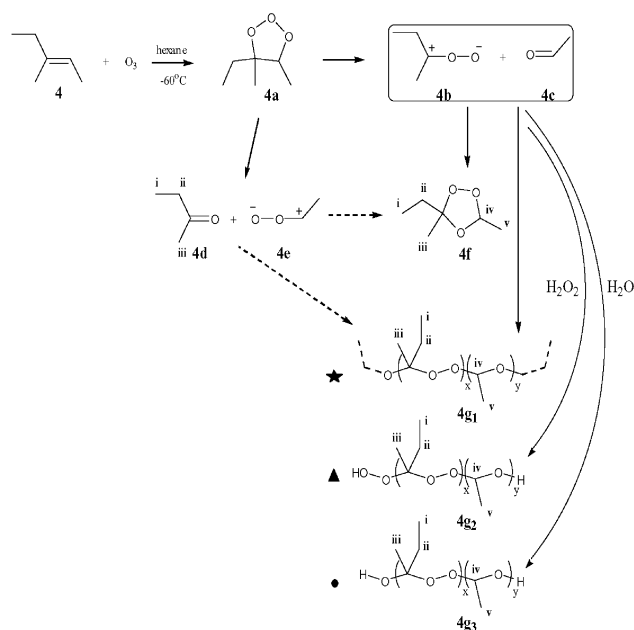
The distribution of ozonide and oligomeric structures formed on complete ozonolysis of alkenes in a non-participating solvent at $-60\text{ }^{\circ}\text{C}$ is governed by the alkyl substitution around the carbon-carbon double bond. The ozonolysis of a 1,1-alkyl substituted ethene generally favours the formation of an ozonide (a 1,2,4-trioxolane). Whereas the ozonolysis of a 1,1,2-alkyl substituted ethene also produces ozonide, a considerable amount of the ozonised products are oligomeric in nature.

For example, the ozonolysis of 3-methylpent-2-ene in solution to high conversion in pentane yields oligomers with structural units derived from the fragmentation products of the primary ozonide (a 1,2,3-trioxolane) which are namely butanone carbonyl oxide and acetaldehyde; these can be characterised by electrospray ionisation mass spectroscopy (ESI-MS) under soft ionisation conditions. The predominant oligomers formed are rich in carbonyl oxide units (80 + mol%) and are cyclic in nature. A small proportion of the oligomers formed are open chain compounds with end groups that suggest that chain termination is brought about either by water or by hydrogen peroxide. Residual water in the solvent will react with the carbonyl oxides to produce 2-methoxybut-2-yl hydroperoxide, which we propose readily decomposes generating hydrogen peroxide. A significant yield of oligomers also is obtained from the ozonolysis of a 1,2-alkyl substituted ethene. The ozonolysis of *trans*-hex-2-ene in pentane yields oligomers containing up to four structural units and are predicted to be mainly cyclic.

Introduction

The products obtained from the ozonolysis of alkenes, hereinafter termed 'ozonates', have been found by us to be usable as radical initiators of both solution and emulsion polymerizations of vinyl and acrylic monomers.¹⁻⁴ Consequently, the characterization of the ozonates formed in such reactions carried out to high conversion has been of interest.⁵ We have recently reported that the complete ozonolysis of 2,3-dimethylbut-2-ene, **1**, in pentane at $-60\text{ }^{\circ}\text{C}$ yields mainly oligomeric ozonates: the individual structures formed being readily identified by electrospray mass spectrometry (ESI-MS) run under soft ionisation conditions.⁶ The structure formed in the highest yield is the cyclic hexamer of acetone carbonyl oxide. The carbonyl compound (acetone) produced on decomposition of the primary ozonide (a 1,2,3-trioxolane) is not sufficiently polar to react with the carbonyl oxide to form a 1,2,4-trioxolane and is indeed shown not to be incorporated in these oligomeric structures. Here we explore further the effect the substitution around the double bond of the alkene has on the types of ozonate structures formed, oligomeric or otherwise, by ozonolysing 2,4,4-trimethylpent-1-ene, **2**, 2-methylpent-1-ene, **3**, a mixture of *cis* and *trans*-3-methylpent-2-ene, **4** and *trans*-hex-2-ene, **5**, the structures of which are presented in Scheme 1. The compounds were chosen because they allow us to examine in particular the effects of the alkyl substitution pattern on the structures of oligoperoxidic products (Fig. 1).

The reaction in solution of O_3 and alkenes has been extensively studied.⁷⁻⁹ The primary ozonide (1,2,3-trioxolane) initially formed upon ozonolysis is unstable and cleaves to a carbonyl oxide and a carbonyl compound. These two entities react in different ways to produce ozonates in the form of



Scheme 1 Mechanism and predominant products of the ozonolysis of 3-methylpent-2-ene, **4**, in pentane at $-60\text{ }^{\circ}\text{C}$.

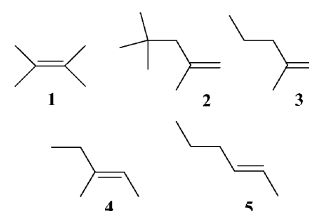


Fig. 1 Alkyl substituted ethenes ozonised at $-60\text{ }^{\circ}\text{C}$ in pentane.

ozonides (1,2,4-trioxolanes), diperoxides (1,2,4,5-tetroxolanes) and oligoperoxides. If the ozonolysis reaction is carried out in

† Electronic supplementary information (ESI) available: Figs. 1 and 2: proton NMR spectra from reactions A and B, DEPT carbon NMR spectra from reactions D and E; Tables 1–3: main oligomeric ozonate structures observed from ESI mass spectrometry. See <http://www.rsc.org/suppdata/ob/b4/b419174a/>

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the presence of a proton donor, alkoxyalkyl hydroperoxides are also produced. Generally ozonides are perceived to be the major ozonate product for reactions of mono-, di-, or trisubstituted ethenes in non-participating solvents. Diperoxides are formed in ozonolysis reactions of tetrasubstituted ethenes which do not generally yield ozonides.

Oligomers have also been reported as significant products of the ozonolysis of alkenes in solution, although, prior to our work,⁶ identifying the precise structures has proven difficult. Early work proposed peroxidic and ether linkages in oligomers formed from the ozonolysis of but-2-ene.¹⁰ Criegee¹¹ thought that oligomers from tetrasubstituted ethenes resulted from the polymerization of the dipolar carbonyl oxide. The stereochemistry of the alkene has been reported to have an effect on the distribution of products from ozonolysis: *trans* isomers gave mostly oligomers, whereas *cis* isomers yielded mainly ozonides.¹² The reduction of the oligomers with lithium aluminium hydride yielded alcohols, including a small amount of α -diol, proving that there were no carbon-carbon bonds in the backbones of the oligomers. It was also suggested that there were a variety of different oxygen linkages present in the oligomers, including linkages of three contiguous oxygen atoms. Other studies of the ozonolysis of a range of mono and di-substituted alkenes proposed oligomers containing between three and twelve monomer units, derived from either the aldehyde or the carbonyl oxide.¹³ The oligomers were defined as cyclic structures on the basis of the absence of a carbonyl absorption in IR spectra. Fliszar *et al.*¹⁴ studied oligomers from the ozonolysis of phenyl-substituted ethenes and found that carbonyl oxides, which do not react to form an ozonide, form oligomers instead. These workers also found that only oligomers formed from tetra-substituted olefins were stable at room temperature and postulated that they were open chain polymeric peroxides. Oligomers derived from the ozonolysis of **1** in non-participating solvents were believed to contain peroxidic structures derived from acetone carbonyl oxide and/or structures with hydroperoxide end groups.¹⁵ This suggested that water and hydrogen peroxide were also participating in the reaction, findings borne out in our studies of the alkene.⁶

Murray and Ramachandran¹⁶ identified oligomers as significant products from the ozonolysis of *trans*-di-*tert*-butylethene at $-90\text{ }^{\circ}\text{C}$ in different solvents. They concluded from elemental analysis and molecular weight data that the oligomers obtained in hexane were composed of 7 or 8 carbonyl oxide units in a cyclic arrangement. Further work on the ozonolysis of hex-3-ene derivatives¹⁷ revealed that the solvent affects the molecular weight of the ozonised products. Alkenes ozonised in hexane produced higher molecular weight oligomers than did reactions in *n*-butylaldehyde. However, the use of aldehyde as solvent led to the formation, overall, of more oligomer. The oligomers were characterized from cryoscopic molecular weight and elemental analysis data. Other work,¹⁸ which considered the ozonolysis of some partially brominated tetrasubstituted ethenes in acetone, indicated that ozonide formation could occur *via* a non-concerted reaction of a carbonyl oxide and a carbonyl compound. The products of these reactions also included acetone diperoxide and acetone triperoxide, which

could be formed if the dipolar intermediate decomposed to form dimethyldioxirane, which then broke up to form the peroxides. The findings implied that the inability of **1** to form any ozonide is not due solely to the lack of mutual reactivity of the malozonide fragments (acetone carbonyl oxide and acetone). Cyclic peroxides can also be prepared by methods other than ozonolysis and the main methods were recently reviewed.^{19,20} Also, the reactions of these compounds have been reviewed by Cafferata.²¹

Despite the previous reports, much of the work on the oligomeric products of ozonolysis has involved a degree of speculation since it was impossible to directly observe the oligomers. However, we showed recently that ESI-MS could be used to directly identify the oligomers formed from ozonolysis of **1**. The products produced are mixtures of the cyclic diperoxide, triperoxide and higher oligomers. In the absence of water, the major products are cyclic oligomers but open chain oligomers are also found if significant amounts of water are present. In this work we extend this study to a series of alkenes in which the substitution pattern around the double bond is changed.

Results and discussion

In this work we wished to study the production of oligoperoxides during the ozonolysis of several alkenes in which the carbon-carbon double bond was located in various places within the carbon skeleton. Thus, we first examined alkenes with terminal double bonds: **2** and **3**. As expected, for the ozonolysis of **2** neither size exclusion chromatography (SEC) nor ESI-MS produced evidence for oligomeric structures in the ozonates. Also ¹H NMR spectra of the reaction mixture were composed of sharp lines, characteristic of low molecular weight products, rather than the broader peaks observed in our previous study of the ozonates derived from **1**.⁶ On the other hand, some evidence for oligomeric peroxides was obtained from SEC, following the ozonolysis of **3**, but these compounds were produced in very low concentrations and we were unable to obtain mass spectra of these materials. The SEC chromatogram of the reaction mixture produced from **3** is shown in Fig. 2 and the molecular weight averages calculated using polystyrene standards are given in Table 1.

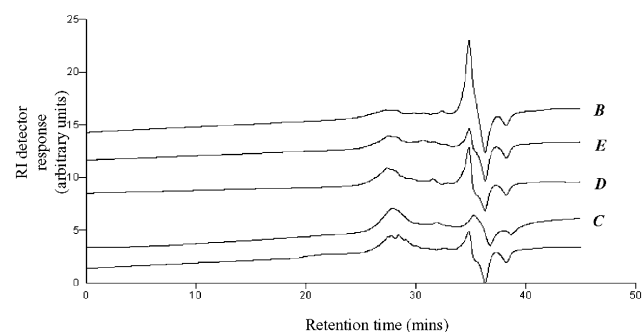


Fig. 2 SEC chromatograms of the products of the ozonolysis of 2-methylpent-1-ene, **2** (reaction *B*), 3-methylpent-2-ene, **4** (reactions *C* and *D*) and an equimolar mixture of 2,3-dimethylbut-2-ene, **1**, and 3-methylpent-2-ene, **4** (reaction *E*) in pentane at $-60\text{ }^{\circ}\text{C}$ (low molecular weight column, psty standards). Note: the bottom trace was obtained for the ozonates of **1** in previous work.⁶

Table 1 Results from ozonolysis of alkenes in pentane at $-60\text{ }^{\circ}\text{C}$

	Alkene conc./mol l ⁻¹	Alkene(s)	Yield/g (% ^b)	SEC ^c (M_w , M_n)	ESI MS max m/z
<i>A</i>	0.412	2	2.75(83)	—	—
<i>B</i>	0.411	3	1.76(65)	616, 508	—
<i>C</i>	0.396	4	1.28(82)	438, 123	528 (+18)
<i>D</i>	0.223	4	—	515, 379	528 (+18)
<i>E</i>	0.411	1 + 4^a	1.75(83)	448, 259	472 (+18)
<i>F</i>	0.411	5	1.80(64)	—	398 (+18)

^a Equimolar amounts. ^b Percentage yield recovered related to the theoretical amount the fragments of the primary ozonide (1,2,3-trioxolane) can contribute to the ozonates. Reaction *D* yield was not determined. ^c Oligomeric fraction molecular weights quoted relative to polystyrene standards.

Thus, as expected, the terminal alkenes studied here do not generate significant amounts of oligomeric peroxides probably because the formaldehyde generated on breakdown of the primary ozonide, reacts fast enough with the carbonyl oxide to prevent oligomerization of the latter. Next we examined the ozonolysis of some internal alkenes.

Complete ozonolysis of **4** in pentane at $-60\text{ }^{\circ}\text{C}$ gave colourless, viscous residues upon removal of the solvent (reactions *C* and *D*). A theoretical yield for the reaction can be calculated if we consider that the products from the decomposition of the unstable primary ozonide (a 1,2,3-trioxolane), **4a**, react with each other and as such are incorporated in the ozonate structures ultimately formed (Scheme 1). The percentage yield recovered on this basis in reaction *C* is thus estimated to be 82%. The SEC chromatograms obtained for ozonates formed in reactions *C* and *D* are shown in Fig. 2. Both chromatograms show that a large proportion of the ozonates are oligomeric, with a number average molecular weight of 379 g mol^{-1} (against polystyrene standards), comparable to that obtained from the ozonates of **1** (bottom trace⁶).

The proton NMR spectrum of the ozonates obtained in reaction *C* is shown in Fig. 3(a). The overall broadness of the resonances between 0.5 and 2.5 ppm suggests that oligomeric ozonates are the predominant products of this ozonolysis reaction. The resonance at 0.90 ppm is readily attributed to the terminal methyl group, *i*, but lacks the triplet fine structure resulting from coupling to the neighbouring methylene protons, *ii*. The resonance patterns between 5.0 and 6.0 ppm best distinguish the relative amounts of ozonide and oligomer formed on ozonolysis. The methine proton, *iv*, of the ozonide, **4f**, is represented by two partly overlapping quartets ($J = 4.9\text{ Hz}$) at 5.30 ppm from coupling to the neighbouring methyl group, *v*. We attribute the broad band centred at 5.50 ppm to the methine proton, *iv*, of acetaldehyde moieties (*y*) in oligomeric structures, **4g**. The resonances found between 9.0 and 10.0 ppm are assigned to hydroperoxy protons on the chain ends of open chain oligomers terminated with hydrogen peroxide, **4g**₂. Previous work with other alkenes has generally reported aldehyde groups to be under-represented in the oligomeric ozonate structures¹⁷ and in these reactions the percentage of acetaldehyde units,

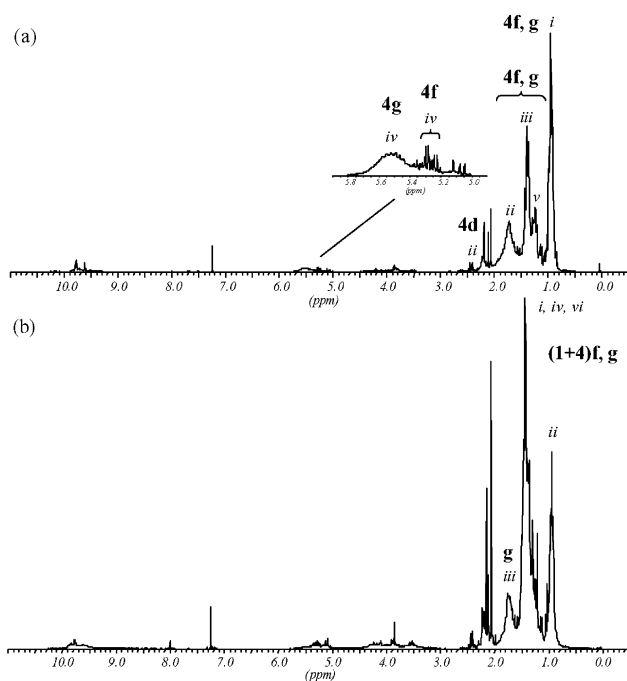


Fig. 3 Proton NMR spectra of the ozonates recovered from the complete ozonolysis of (a) 3-methylpent-2-ene, **4** (reaction *C*) and (b) an equimolar mixture of 2,3-dimethylbut-2-ene, **1**, and 3-methylpent-2-ene, **4** (reaction *E*).

relative to carbonyl oxide units, in the ozonate structures is 20–25 mol%.

ESI-MS of the ozonates of **4** made in pentane, obtained under soft ionisation conditions, provides the most direct evidence for the oligomeric peroxides. The spectra are shown in Fig. 4.

A distribution of ions derived from the oligomers is readily obtained for the products recovered from both reactions *C* and *D* (Table 1). The spacing between each of the ions in the main series is m/z 44. We expect the primary ozonide (a 1,2,3-trioxolane), **4a**, to decompose to yield butanone carbonyl oxide, **4b**, m/z 88 and acetaldehyde, **4c**, m/z 44. Therefore the spacing of m/z 44 confirms, in combination with the NMR data, that both carbonyl oxide and aldehyde units are included in the oligomeric ozonates. The mass totals of the ions correspond exactly to the ammonium adducts (+18) of oligomers, **4g**, produced from random copolymerization of butanone carbonyl oxide and acetaldehyde. The ions can be fully rationalized to these structures, which do not include any end groups. Thus, the oligomers are cyclic, **4g**₁. For example, the ions at m/z 458 and 546 correspond to the cyclic pentamer and hexamer of the carbonyl oxide, **4b**. There is a second minor distribution of ions that are also separated by m/z 44. These peaks appear to correspond to open chain oligomers of x butanone carbonyl oxide and y acetaldehyde repeat units, with end groups the mass of which total m/z 34, *i.e.* $m/z = 88x + 44y + 34$ overall. We suggest that these oligomers are predominantly terminated at both ends with $-\text{OOH}$ groups, **4g**₂. Such end groups may arise by reaction of oligocarbonyl oxides with hydrogen peroxide.⁶ There is also a third, minor, series of ions, also spaced at intervals of m/z 44. This group of ions has end group masses of m/z 18. We suggest that these ions correspond to open chain oligomers of the two structural units terminated directly by reaction with water, leaving structures with a hydroperoxy and a hydroxy group on the α and ω chain ends, **4g**₃.

In some synthetic procedures or industrial processes, ozonolysis may be conducted on mixtures of alkenes. This situation should generate mixtures of peroxy oligomers that are also amenable to analysis by joint application of ESI-MS and NMR. Therefore, we further extended our studies to a mixture of alkenes **1** and **4**.

The complete ozonolysis in pentane at $-60\text{ }^{\circ}\text{C}$ of an equimolar mixture of 2,3-dimethylbut-2-ene, **1**, and 3-methylpent-2-ene, **4**, yielded an inhomogeneous mixture of a white solid and colourless viscous residue upon removal of the solvent (reaction *E*). A theoretical yield for the reaction can be calculated if we assume that there are only three reactive species generated on ozonolysis capable of forming ozonate structures: acetone carbonyl oxide (from **1**), butanone carbonyl oxide, **4b**, and acetaldehyde, **4c** (both from **4**). The percentage yield recovered on this basis is 83%.

The SEC chromatogram obtained from these ozonates formed in pentane at $-60\text{ }^{\circ}\text{C}$ (reaction *E*) is shown in Fig. 2. The chromatogram shows that a large proportion of the ozonates are oligomeric, with a number average molecular weight of 259 g mol^{-1} (against polystyrene standards).

The proton NMR spectrum of the ozonates is shown in Fig. 3(b). The peak at 0.95 ppm is attributed to the methyl protons, *ii*, of butanone carbonyl oxide, **4b**, in all ozonate structures shown in Fig. 5. All resonances between 5.0 and 6.0 ppm are assigned to methine protons, *v*, in the different ozonate structures. The most intense band centred at 1.43 ppm is in turn attributed to the other four sets of methyl protons, designated *i*, *iv* and *vi* in the ozonate structures (**1 + 4**)**g**. Comparing the relative integrals of these three features allows an estimation of the proportions of the three main constituents to be found in the ozonate structures: 37% acetone carbonyl oxide, 46% butanone carbonyl oxide and 17% acetaldehyde units. The resonances found between 9.0 and 10.0 ppm are assigned to hydroperoxy protons on the chain ends of open chain oligomers terminated with hydrogen peroxide (**1 + 4**)**g**₂.

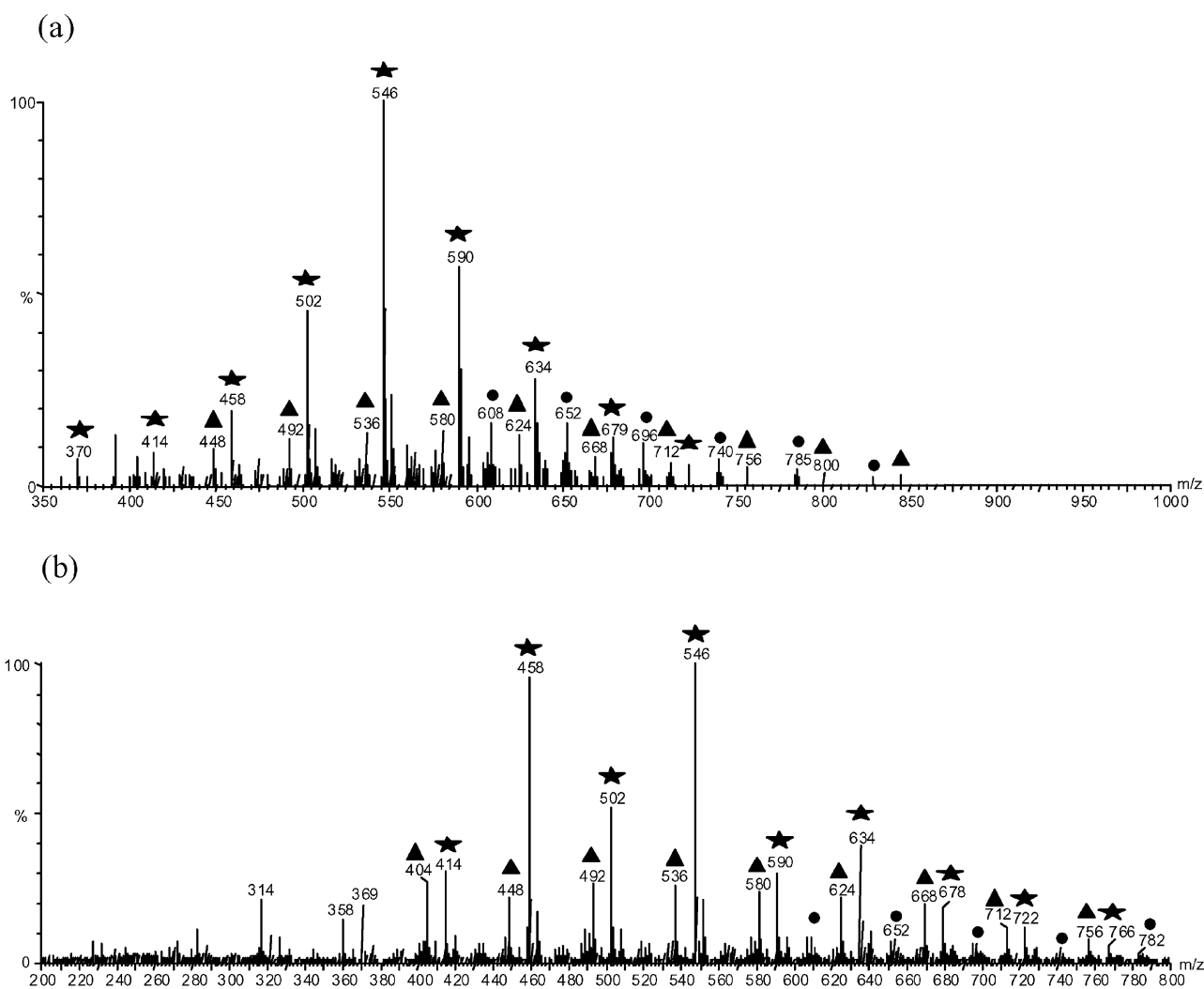


Fig. 4 ESI mass spectra of the products of ozonolysis of 3-methylpent-2-ene, **4**, in pentane at $-60\text{ }^{\circ}\text{C}$, part (a) reaction *C* and (b) reaction *D*: cyclic mixed oligomers of butanone carbonyl oxide and acetaldehyde denoted with ★, with linear mixed oligomers terminated by hydrogen peroxide denoted with ▲ and those terminated by water denoted with ●.

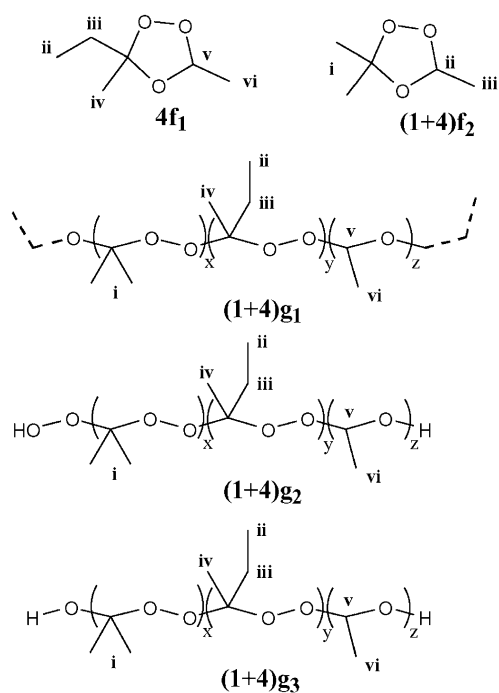


Fig. 5 Predominant products of ozonolysis of an equimolar mixture of 2,3-dimethylbut-2-ene, **1**, and 3-methylpent-2-ene, **4**, in pentane at $-60\text{ }^{\circ}\text{C}$.

ESI-MS of the ozonates of the alkene mixture made in pentane, obtained under soft ionization conditions, is shown in Fig. 6. A complex distribution of oligomers is obtained for the products recovered from reaction *E* (Table 1). We expect the oligomeric structures to be composed of x acetone carbonyl oxide, y butanone carbonyl oxide and z acetaldehyde units, with masses m/z of 74, 88 and 44, respectively. The predominant structures captured in the mass distribution correspond to ammonium adducts of mixed cyclic oligomers, $(\mathbf{1} + \mathbf{4})\mathbf{g}_1$, with $m/z = 74x + 88y + 44z + 18$. The larger oligomeric structures present, with masses of more than 600, correspond exclusively to open chain oligomers terminated with hydrogen peroxide, $(\mathbf{1} + \mathbf{4})\mathbf{g}_2$, with $m/z = 74x + 88y + 44z + 34 + 18$. This concurs with the findings for the ozonates obtained in the individual reactions of **1** and **4** in which the proportion of oligomers with open chain structures increased as the chain length increased. This latter feature of the mass spectra is a consequence of the cyclization process, which is an intramolecular termination reaction and occurs at lower degrees of polymerization than the intermolecular termination processes that lead to the open chain oligomers. That is, if the chain does not terminate by cyclization it grows by further addition of monomer until it is terminated in an intermolecular reaction. Thus, termination of the cyclic oligomers occurs earlier in the chain growth process than termination of the open chain oligomers and this leads to open chain oligomers with higher degrees of polymerization.

The complete ozonolysis in pentane at $-60\text{ }^{\circ}\text{C}$ of **5** yielded colourless viscous residues upon removal of the solvent

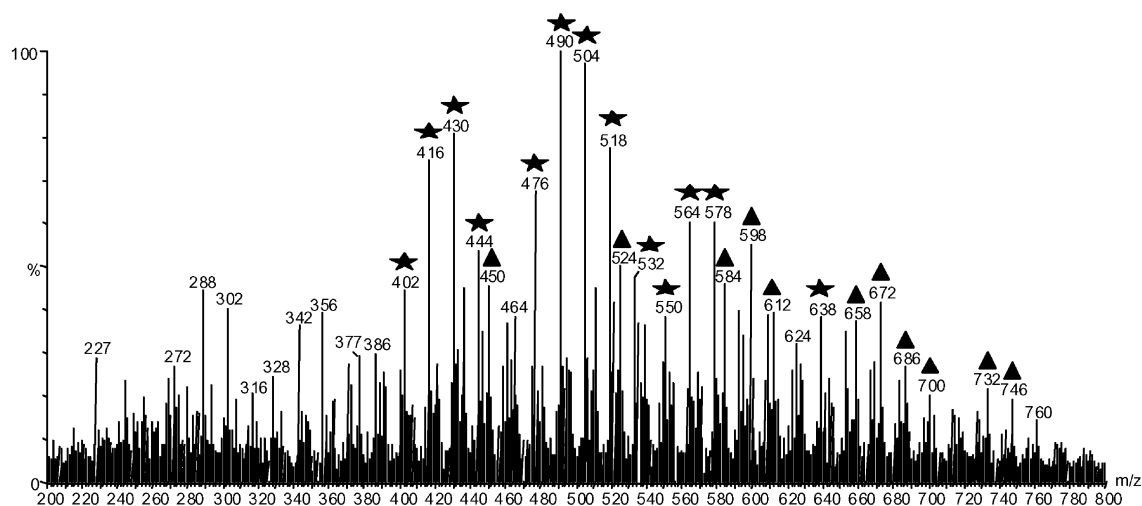
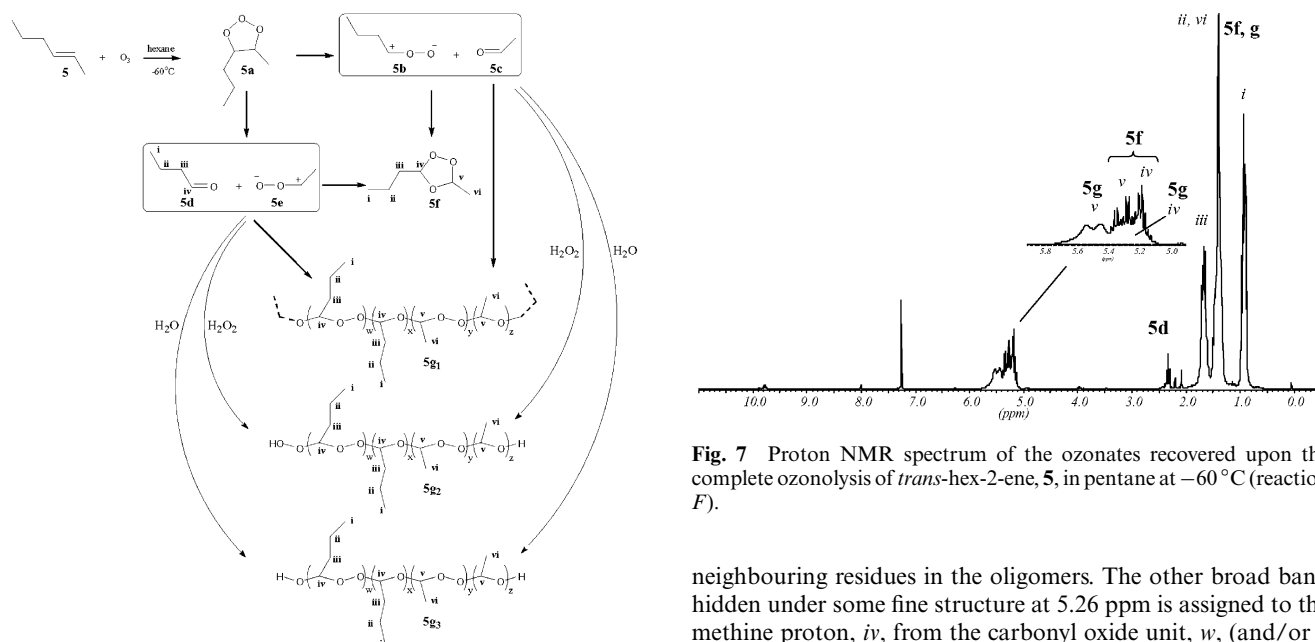


Fig. 6 ESI mass spectra of the products of ozonolysis of an equimolar mixture of 2,3-dimethylbut-2-ene, **1**, and 3-methylpent-2-ene, **4**, at $-60\text{ }^{\circ}\text{C}$ in pentane (reaction *E*).



Scheme 2 Mechanism and predominant products of ozonolysis of *trans*-hex-2-ene, **5**, in pentane at $-60\text{ }^{\circ}\text{C}$.

(reaction *E*). We can calculate a theoretical yield if we predict that both sides of the alkene form carbonyl oxide and carbonyl compounds **5b,c,d** and **e** on cleavage of the primary ozonide, **5a**, that are capable of contributing to ozonate structures (Scheme 2). A percentage yield of 64% was calculated on this basis.

The proton NMR spectrum of the ozonates is shown in Fig. 7. The overall broadness of the resonances again suggests the formation of predominantly oligomeric ozonates. Similar electronic substitution on each side of the double bond in the starting alkene makes it harder to speculate which carbonyl oxide and carbonyl compounds are expected to form upon ozonolysis from subsequent cleavage of the primary ozonide, **5a**.

The pattern of broad resonances between 5.0 and 6.0 ppm would suggest that methine protons exist in oligomeric structures in at least two forms. The split broad band centred at 5.50 ppm is assigned to the methine proton, *v*, of an acetaldehyde unit, *z*, (and/or the equivalent carbonyl oxide, *y*, derived from that side of the alkene) in oligomeric structures, **5g**. The resonance band is split in two by potential chiral centres on

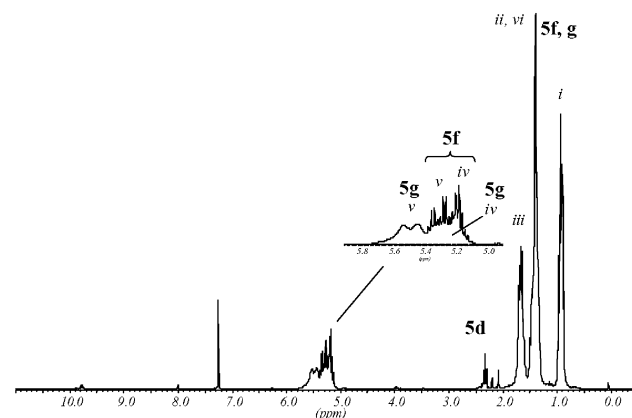


Fig. 7 Proton NMR spectrum of the ozonates recovered upon the complete ozonolysis of *trans*-hex-2-ene, **5**, in pentane at $-60\text{ }^{\circ}\text{C}$ (reaction *F*).

neighbouring residues in the oligomers. The other broad band hidden under some fine structure at 5.26 ppm is assigned to the methine proton, *iv*, from the carbonyl oxide unit, *w*, (and/or a butyraldehyde unit, *x*) formed from the larger side of the alkene in oligomeric structures, **5g**. Although the structures attributed to these broad peaks make up the majority of the ozonates, the fine structure is evidence for the formation of ozonide, **5f**; two overlapping quartets centred at 5.3 ppm are characteristic of the methine proton, *v*. The other methine proton, *iv*, present in the ozonide should be represented by a set of triplets from coupling to the neighbouring methylene protons, *iii*: unresolved fine structure is evident marginally upfield from the group of quartets. The proportions of each side of the ozonised alkene incorporated in the ozonate structures can be calculated by comparing the relative integral intensities of the broad peaks at 1.45 and 1.75 ppm. The peak at 1.45 ppm is attributable both to the methylene protons, *ii*, and the methyl protons, *vi*, in all ozonate structures, whilst the peak downfield at 1.75 ppm is due solely to the methylene protons, *iii*. Entities derived from the bulkier side of the double bond of the alkene contribute 57% to the ozonate structures. We again attribute multiple resonances between 9.0 and 10.0 ppm to hydroperoxy protons on oligomer chain ends. The low relative intensity suggests that a lower fraction of the open chain oligomers is derived from this alkene than is derived with either **1** or **4**. This may be connected with the stability of the predominant carbonyl oxide formed in each of the alkenes; both **1** and **4** form di-alkyl substituted carbonyl oxides on ozonolysis.

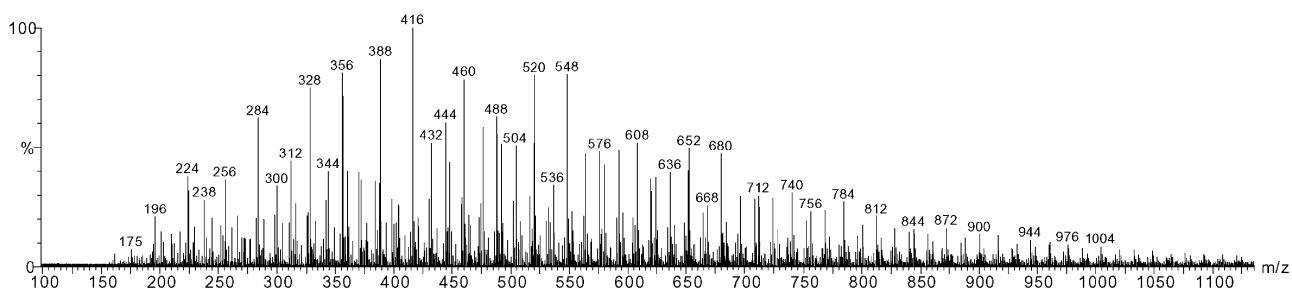


Fig. 8 ESI mass spectra of the products of ozonolysis of *trans*-hex-2-ene, **5**, in pentane at $-60\text{ }^{\circ}\text{C}$ (reaction *F*).

An ESI mass spectrum of the ozonates of **5** made in pentane, obtained under soft ionisation conditions, is shown in Fig. 8. A distribution of ions derived from the oligomers is readily obtained. If the oligomers were composed only of structural units derived from carbonyl oxide, **5b**, (m/z 88) and acetaldehyde, **5c**, (m/z 44) we would expect a mass distribution similar to that obtained for the ozonates of **4**, shown in Fig. 4. However the array of ions observed suggests that all four possible structural units, *w*, *x*, *y* and *z*, from the ozonolysis of **5** are present in the oligomeric structures. The masses of the *w*, *x*, *y* and *z* residues are m/z 88, 72, 60 and 44 respectively. The spacings between the most prominent peaks, notably m/z 12, 16, 28 and 32, in the distribution, correspond to the mass differences between these predicted residues. However, the ions captured do not, in almost all cases, directly conform to the ammonium adducts (+18) of the numerous cyclic oligomers that are possible. Instead the ions can be assigned to combinations of the four structural units existing as either fragmented cyclic oligomers or open chain oligomers terminated with hydrogen peroxide. All the combinations that make up the suggested oligomeric structures are included in the electronic supporting information.†

Conclusions

The complete ozonolysis of both **2** and **3** in pentane at $-60\text{ }^{\circ}\text{C}$ yielded predominantly their respective conventional ozonides (1,2,4-trioxolanes). Any oligomeric structures that form do so in yields that are too low to be detected by ESI-MS although some evidence for their presence in product mixtures was obtained by SEC analysis.

The viscous ozonates recovered from the complete ozonolysis of **4** in pentane at $-60\text{ }^{\circ}\text{C}$ (reactions *C* and *D*) are observed in the ESI-MS under soft ionisation conditions and are predominantly cyclic oligomers composed of butanone carbonyl oxide and acetaldehyde; proton NMR analysis shows that the ozonates are rich in repeat units derived from the carbonyl oxide (80 + mol%). The predominant cyclic structure captured has m/z 546, which we can speculate contains either six butanone carbonyl oxide units or five butanone carbonyl oxide units and two acetaldehyde units. Distributions of open chain oligomers containing the two structural units terminated with hydrogen peroxide are also readily observed in the ESI-MS. As before,⁶ we propose that hydrogen peroxide is generated from the reaction of carbonyl oxide with residual water in the solvent.

The ozonolysis of an equimolar alkene mixture of **1** and **4** in pentane at $-60\text{ }^{\circ}\text{C}$ (reaction *E*) generated oligomeric ozonates containing three structural units: acetone carbonyl oxide, butanone carbonyl oxide and acetaldehyde. The predominant ions in the ESI-MS are again attributed to cyclic structures, whilst most of the heavier ions (longer chain oligomers) are attributed to open chain structures terminated by hydrogen peroxide.

The complete ozonolysis of **5** in pentane at $-60\text{ }^{\circ}\text{C}$ (reaction *F*) revealed a complex array of oligomeric ozonate structures in the ESI-MS. Both proton NMR and ESI-MS analysis suggest that the primary ozonide cleaves in two ways to give four entities, butanal carbonyl oxide (*w*, m/z = 88), butanal (*x*, m/z = 72),

acetaldehyde carbonyl oxide (*y*, m/z = 60) and acetaldehyde (*z*, m/z = 44), which are included in the oligomeric ozonates. The stability of both ozonides and oligomers is influenced by the R substitution in the $-\text{O}-\text{C}(\text{R}_2)-\text{O}-$ linkages. Mono-alkyl substituted oligomers have been reported to decompose at room temperature whilst di-alkyl substituted oligomers, *i.e.* those from tetrasubstituted alkenes, were found to be stable at room temperature.¹⁴ The ESI-MS analysis of these ozonates captures the initial fragmentation products that are composed solely of mono-alkyl substituted carbonyl oxide and carbonyl structural units.

In summary, we present here for the first time unequivocal evidence for cyclic and open chain oligomeric ozonates containing structural units derived from both fragments, carbonyl oxide and aldehyde, generated upon the decomposition of the primary ozonide in ozonolysis reactions of 1,1,2-trialkyl and 1,2-dialkyl substituted alkenes. Cyclic structures are prevalent in reactions carried out in pentane, with the open chain oligomeric structures (best observed in the ozonates generated from 3-methylpent-2-ene) terminated with either water or hydrogen peroxide. The volatility of some of the ozonates generated may hinder their recovery from the solvent, particularly in the case of **5**, and we therefore avoid quoting absolute values for the relative quantities of ozonide and oligomers formed in each case. The yields recovered in each case would suggest that whereas the complete ozonolysis of 1,1-alkyl ethenes yields predominantly ozonides, 1,1,2-alkyl and 1,2-alkyl substituted ethenes yield considerably more oligomeric ozonates.

Experimental

Materials

2,3-Dimethylbut-2-ene (98%), 2,4,4-trimethylpent-1-ene (99%), 2-methylpent-1-ene (99 + %), a mixture of *cis* and *trans*-3-methylpent-2-ene (99%), *trans*-hex-2-ene (98 + %) and pentane (99 + %, HPLC grade) were obtained from the Aldrich Chemical Co. and were used as supplied. Sodium thiosulfate and potassium iodide were purchased from BDH Laboratory Supplies and also used as supplied.

Instrumentation

Proton and carbon NMR spectra were recorded on 250 MHz and 400 MHz spectrometers respectively, using deuterated chloroform as solvent. The chemical shifts quoted are relative to tetramethylsilane. SEC measurements were carried out with RI and UV (260 nm) detectors at ambient temperature using THF as the solvent and toluene as a flow marker. Polymer Laboratories PLGel, 5 μm , 500 \AA , and 2 \times 60 cm low molecular weight columns were used with a solvent flow rate of 1 ml min^{-1} . The chromatograms were calibrated against low molecular weight polystyrene standards (Polymer Laboratories). Sample concentrations were 5 mg/2 ml THF. The ESI-MS experiments were carried out on a Micromass "Platform LCZ" quadrupole mass spectrometer equipped with an atmospheric pressure ionisation (a.p.i.) source operated in the nebulizer-assisted

electrospray mode. The potential on the electrospray capillary was set to 2.0 kV and the extraction cone voltage was set to a value of 25 V, with the extractor at 4.0 V and a desolvation temperature of 150 °C. Samples were dissolved in methanol at 1 mg ml⁻¹. Aliquots of 10 µL were injected into a flowing solvent mixture (1 ml min⁻¹) composed of 10% aqueous ammonium acetate solution (10 mM) and 90% methanol by volume. A flow rate of 0.2 ml min⁻¹ of this mixture was diverted into the mass spectrometer.

Ozonolysis procedure

A flask containing a solution of alkene was placed in a dry ice-acetone bath at -60 °C for 20 min before starting ozonolysis. Ozone was generated by passing an oxygen stream through an electrical discharge-type ozone generator. The O₂ stream was set to 20 ml min⁻¹ and the electrical discharge was set at 150 V. The O₃ flow rate at these settings was measured by bubbling the O₂-O₃ mixture through an alkaline boric acid-buffered aqueous solution (50 ml) of potassium iodide (3.47 × 10⁻² M) for 2 min. The liberated iodine solution was then acidified before being titrated with sodium thiosulfate (6.94 × 10⁻² M) using starch indicator solution. The rate of evolution of O₃ was found to be 0.88 g hr⁻¹.

The O₂-O₃ mixture was bubbled through the stirred solution, with the outlet gas from this being passed directly into an ozone analyser (BMT Ozone Analyser 963, Berlin). Initially, almost all the O₃ in the gas was taken up by the solution, but eventually, as ozonolysis reaches completion, the increasingly positive reading on the analyser stabilised at about 40 g m⁻³. The completion of alkene ozonolysis can also be observed visually, as the solution turns blue from saturation with O₃. Typically the time required for ozonolysis was proportional to the concentration of alkene in the solution. For example, the ozonolysis reactions of 2,4,4-trimethylpent-1-ene and 3-methylpent-2-ene in pentane, *A* and *C*, were completed in 80 and 50 min respectively. This amounts to the respective solutions receiving 1.17 g (24.4 mM) and 0.73 g (15.3 mM) of O₃, which are approximately equivalent to the alkene concentrations in each of the solutions. After completion of ozonolysis, the contents of the flask were bubbled through with N₂ for about 20 min to remove free O₃. The solvent was then carefully removed under reduced pressure at room temperature in a rotary evaporator, and the yield of product recorded. The samples were then stored in a refrigerator at -10 °C with all subsequent analyses being completed within a few days. No safety problems were encountered during the ozonolysis reactions but we would advise appropriate caution in the preparation and handling of the ozonates, e.g. use of safety shields, given the potentially explosive nature of many of the products. The ozonates were always maintained and handled in solution by us and were never rigorously dried.

Preliminary analysis of the ozonates

Ozonolysis of **2** in pentane at -60 °C (reaction *A*): ozonates mainly in the form of ozonide and ketone, ¹H NMR (250 MHz, CDCl₃, 25 °C, TMS) δ 5.14 and 5.04 [2H, d, ((CH₃)₃CCH₂)-(CH₃)C(OO)OCH₂], 2.31 [2H, s, ((CH₃)₃CCH₂)(CH₃)CO], 2.12 [3H, s, ((CH₃)₃CCH₂)(CH₃)CO], 1.75 [2H, s, ((CH₃)₃CCH₂)-

(CH₃)C(OO)OCH₂], 1.47 [3H, s, ((CH₃)₃CCH₂)(CH₃)C(OO)OCH₂], 1.01 [9H, s, (CH₃)₃CC-].

Ozonolysis of **3** in pentane at -60 °C (reaction *B*): ozonates mainly in the form of ozonide and ketone, ¹H NMR (250 MHz, CDCl₃, 25 °C, TMS) δ 5.12 and 5.03 [2H, d, (CH₃CH₂CH₂)(CH₃)C(OO)OCH₂], 2.40 [2H, t, (CH₃CH₂CH₂)-(CH₃)CO], 2.20 [3H, s, (CH₃CH₂CH₂)(CH₃)CO], 1.80 [2H, br, (CH₃CH₂CH₂)(CH₃)C(OO)OCH₂], 1.40 [2H + 3H, br, (CH₃-CH₂CH₂)(CH₃)C(OO)OCH₂], 0.90 [3H, t, (CH₃CH₂CH₂-)].

The other ozonolysis reactions *C-F* in pentane at -60 °C produced mainly oligomeric ozonates, the ¹H NMR (250 MHz, CDCl₃) spectra of which are discussed elsewhere in the paper.

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