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Ozonolysis of Tetramethylethylene: Characterization of Cyclic and Open-Chain Oligoperoxidic Products

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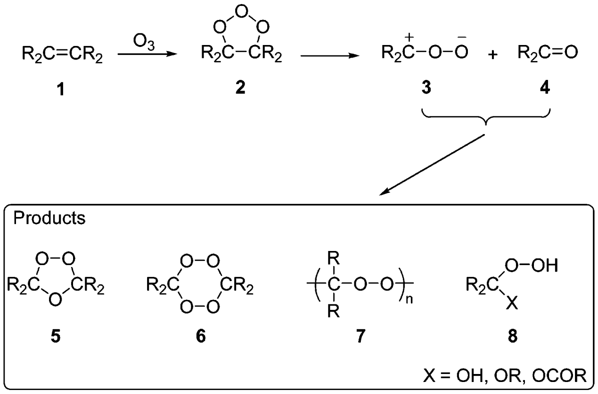
The ozonolysis of tetramethylethylene (TME) in solution to high conversion in *nonparticipating* solvents at −60 °C yields predominantly oligoperoxides. For the first time, these products have been characterized using electrospray ionization mass spectrometry (ESI-MS) under soft ionization conditions. The predominant structure formed in reactions carried out in pentane (up to 2.0 M TME) is shown to be the cyclic hexamer of acetone carbonyl oxide (oligocarbonyl oxide with degree of polymerization, $n = 6$), but cyclic structures with n up to 19 are observed. A small proportion of the oligoperoxides formed are open-chain compounds with end groups that suggest that chain termination of oligocarbonyl oxides can occur through reaction with either water or hydrogen peroxide. Ozonolysis in *dried* butyl acetate similarly produces mainly cyclic oligoperoxides. However, ozonolyses carried out in *undried* butyl acetate yield mainly open-chain oligoperoxides, confirming that propagating carbonyl oxide chains are readily terminated by water. Relative amounts of the open-chain oligomers so-formed suggest that *undried* butyl acetate contains ca. 0.1% w/w water. The ozonolysis of TME in the *participating* solvent, methanol, at −60 °C yields 2-methoxyprop-2-yl hydroperoxide via reaction of acetone carbonyl oxide with methanol; no oligoperoxidic products are formed in this case.

Introduction

Products of alkene ozonolysis, hereinafter termed “ozonates”, have been found by us to be useful as radical initiators of both solution and emulsion polymerizations of vinyl and acrylic monomers.[1,2] Evidence to date points to peroxidic products among the ozonates as being the species responsible for initiation. As a consequence, we have been interested recently in characterizing fully the products of alkene ozonolysis carried out to complete conversion.[3] We have chosen for our initial studies the products formed on ozonolysis of the symmetrical alkene 2,3-dimethylbut-2-ene (known also as tetramethylethylene and abbreviated here to TME). Preliminary studies suggested that ozonolysis of TME, especially at low temperatures, yielded a significant proportion of oligoperoxides, and it is the nature of these that we report on further here.

The reaction between O_3 and alkenes has been extensively studied;[4] the currently accepted mechanism of ozonolysis is outlined in Scheme 1. The initial adduct formed from the alkene **1** and O_3, termed the primary ozonide (1,2,3-trioxolane) **2**, is unstable and cleaves to a carbonyl oxide **3** and an aldehyde or a ketone **4**. It is further reactions of **3** and **4** that give rise to ozonates, in relative amounts that depend on reaction conditions, in the form of ozonides (1,2,4-trioxolanes) **5**, diperoxides (1,2,4,5-tetroxolanes) **6**, oligoperoxides **7**, and alkoxyalkyl hydroperoxides **8**. Compounds **8** are formed when ozonolysis takes place in the presence of a proton donor, HX.

SCHEME 1. Mechanism of Ozonolysis of Alkenes and Some Reported Products[4]



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(1) Cunliffe, D.; Lockley, J. E.; Ebdon, J. R.; Rimmer, S.; Palasz, P.; Emmett, S. *Polymer* **2001**, *42*, 9329.

(2) Lockley, J. E.; Ebdon, J. R.; Rimmer, S.; Tabner, B. J. *Macromol. Rapid Commun.* **2000**, *21*, 841.

(3) Lockley, J. E.; Ebdon, J. R.; Rimmer, S.; Tabner, B. J. *Polymer* **2001**, *42*, 1797.

(4) Bailey, P. S. *Ozonation in Organic Chemistry, Vol. 1: Olefinic Compounds*; Academic Press: New York, 1978.

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The degree and the nature of the substitution around the alkene double bond, the concentration of alkene present, the solvent used, and the temperature of ozonolysis all have a bearing on the product distribution.

Oligomers have long been recognized as significant products of the ozonolysis of alkenes in solution.[5] The nature of the repeat units found in such structures has prompted many discussions. Early studies speculated on whether *both* the carbonyl oxide and the carbonyl compound (the potential monomer units formed upon cleavage of the unstable primary ozonide) were incorporated in the oligomeric structures.[6,7] Greenwood and Rubinstein[8] suggested other oxygen linkages in the structures, including linkages of three contiguous oxygen atoms. Their work also confirmed the absence of carbon−carbon bonds in the oligomer backbones. Ozonolyses of a range of alkenes have yielded oligomers containing between 3 and 12 monomer units which are described as either open-chain[9] or cyclic structures.[10,11] Milas and Belic[12] have reported on oligomers derived from the ozonolysis of TME in nonparticipating solvents. They believed these to contain peroxidic structures derived from acetone carbonyl oxide and/or structures with hydroperoxide end groups. Their results suggested that water and hydrogen peroxide might also participate in the reaction.

More recently, Murray et al.[13] have studied the ozonolysis of TME to low conversion (about 2%) at different concentrations and temperatures. The ozonolysis of neat TME yielded mostly tetramethylethylene epoxide. Reducing the concentration of TME and the ozonolysis temperature increased the yield of acetone diperoxide until, eventually, it became the major product. These workers also noted the production of a significant amount of 3-hydroperoxy-2,3-dimethyl-1-butene. This was produced, they assumed, from the reaction of singlet oxygen with TME. Our own work has shown that the major products of ozonolysis of TME, at either 0 or 20 °C and at high conversion, are the epoxide, acetone cyclic diperoxide, and acetone cyclic triperoxide.[3] However, we have also shown, by GC−MS, that at lower temperatures other peroxidic species with boiling points higher than acetone triperoxide become the major products of ozonolysis.

Since the initial products of TME ozonolysis are acetone carbonyl oxide, **9**, and acetone, a major product of ozonolysis might be expected to be the recombination product (and conventional ozonide) 3,3,5,5-tetramethyl-[1,2,4]trioxolane, **10**. However, neither previous workers nor we have found any evidence for this product in TME ozonates. We thus assume that acetone is too thermodynamically stable to react with acetone carbonyl oxide to form a conventional ozonide.

TABLE 1. Ozonolysis of TME in Different Solvents at −60°C

	TME concd/M	solvent	yield/g (%)[b]	SEC (M_w, M_n)[c]	ESI MS max *m/z*
A	0.102	pentane	0.33 (88)		444 (+18)
B	0.411	pentane	1.38 (91)	776, 426	444 (+18)
C	1.647	pentane	5.25 (86)		444 (+18)
D	0.340	butyl acetate	1.02 (81)		330 (+18)
E	0.411	butyl acetate[a]	1.15 (76)	278, 217	444 (+18)
F	1.647	butyl acetate		276, 215	330 (+18)
G	0.411	methanol	1.48 (68)	117, 111	-

[a] Distilled butyl acetate was placed in 4 A molecular sieves for 2 days prior to use in ozonolysis reaction. [b] Percentage yield recovered related to the theoretical amount of acetone carbonyl oxide formed in each case; the yield quoted for ozonates generated in methanol is relative to the theoretical amount of 2-methoxyprop-2-yl hydroperoxide, **16**, formed. [c] Molecular weights quoted relative to polystyrene standards.

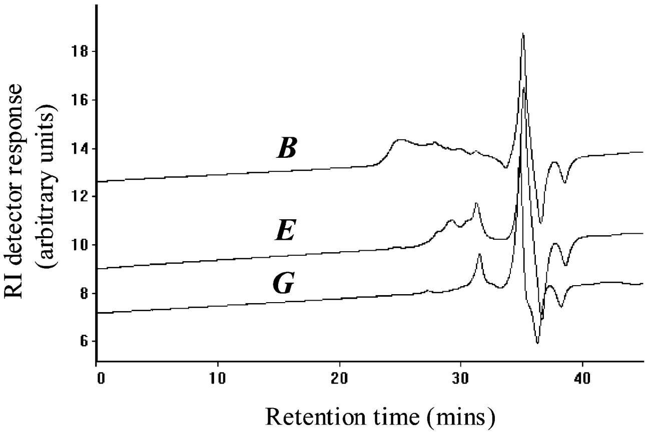
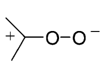


FIGURE 1. SEC chromatograms of the products of ozonolysis of TME at −60 °C in pentane (***B***), *dried* butyl acetate (***E***), and methanol (***G***) (reactions in Table 1).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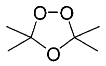
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In this paper, we report application of electrospray ionization mass spectrometry (ESI-MS) to the characterization of the oligomeric products of TME ozonolysis at −60 °C, at which temperature they are the predominant species in the ozonate. As will be seen, ESI-MS is able to provide, for the first time, a complete picture of the structures and distributions of these oligomers.

Results and Discussion

Ozonolysis of TME in Pentane. The complete ozonolysis in pentane at −60 °C of TME, at various concentrations, yielded white viscous residues upon removal of the solvent. A theoretical yield for the reaction can be calculated if we assume that only half the original TME molecule forms acetone carbonyl oxide, **9** (with the other half forming acetone), and that this is the only species involved in producing ozonates. This assumes that the acetone does not react with carbonyl oxide to form

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(5) (a) Harries, C.; Seitz, R. *Ann.* **1915**, *410*, 21. (b) Harries, C.; Wagner, H. *Ann.* **1915**, *410*, 29.

(6) Rieche, A.; Meister, R.; Sauthoff, H. *Ann.* **1942**, *553*, 187.

(7) (a) Criegee, R.; Lohaus, G. *Justus Liebigs Ann. Chem.* **1953**, *583*, 1. (b) Criegee, R. *Record Chem. Prog.* **1957**, *18*, 111.

(8) Greenwood, F. L.; Rubinstein, H. *J. Org. Chem.* **1967**, *32*, 3369.

(9) (a) Fliszar, S.; Gravel, D.; Cavalieri, E. *Can. J. Chem.* **1966**, *44*, 67. (b) Fliszar, S.; Gravel, D.; Cavalieri, E. *Can. J. Chem.* **1966**, *44*, 1013. (c) Fliszar, S. *Can. J. Chem.* **1966**, *44*, 2351. (d) Fliszar, S.; Chylinska, J. B. *Can. J. Chem.* **1967**, *45*, 29. (e) Fliszar, S.; Chylinska, J. B. *Can. J. Chem.* **1968**, *46*, 783.

(10) (a) Razumovskii, S. D.; Berezova, L. V.; Gil′chenok, N. D.; Oranskaya, O. M.; Yur'ev, Y. N.; Tsyskovskii, V. K. *J. Gen. Chem. USSR (Engl. Transl.)* **1966**, *2*, 1910. (b) Razumovskii, S. D.; Niazaschvili, G. A.; Tutorskii, I. A.; Yur'ev, Y. N. *Polym. Sci. USSR (Engl. Transl.)* **1971**, *13*, 217.

(11) Murray, R. W.; Ramachandran, V. *J. Org. Chem.* **1983**, *48*, 813.

(12) Milas, N. A.; Belic, I. *Vestn. Sloven. Kem. Drustva* **1963**, *10*, 37.

(13) Murray, R. W.; Kong, W.; Rajadhyaksha, S. N. *J. Org. Chem.* **1993**, *58*, 315.

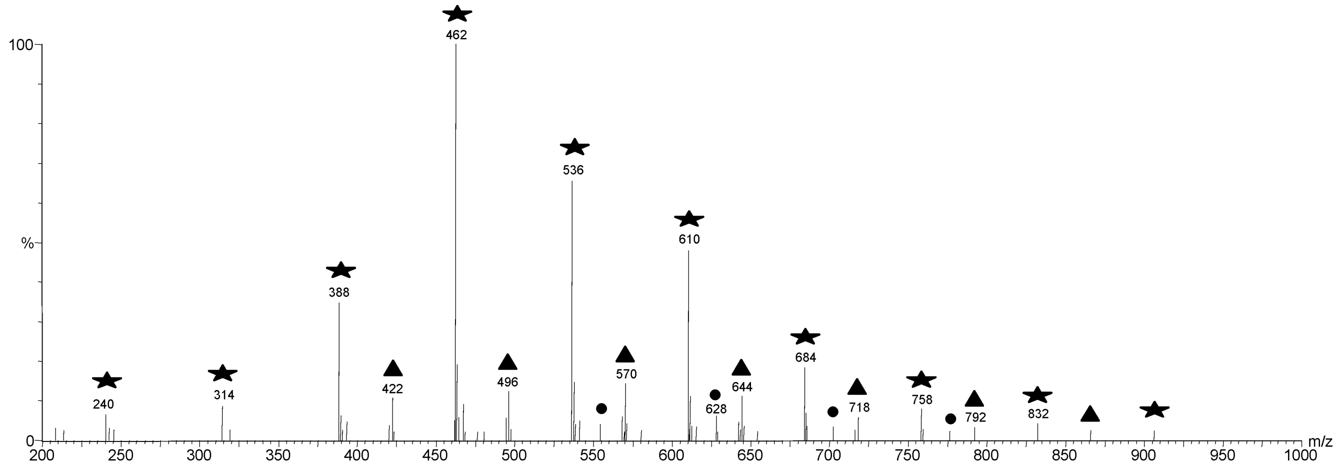


FIGURE 2. ESI mass spectrum of the products of ozonolysis of TME at −60 °C in pentane (reaction ***B***, Table 1): cyclic oligomers of acetone carbonyl oxide denoted with ★, with linear oligomers terminated with hydrogen peroxide denoted with ▲, and those terminated with water denoted with ●.

SCHEME 2. Possible Route to the Formation of Hydrogen Peroxide in Ozonolysis Reactions of TME[14-16]

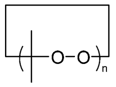
$$(CH_3)_2\overset{+}{C}OO^- + H_2O \longrightarrow (OH)(CH_3)_2COOH$$

$$(OH)(CH_3)_2COOH \longrightarrow (CH_3)_2CO + H_2O_2$$

ozonide, **10**, but rather is removed with the solvent in the workup. The calculation makes allowances neither for end groups present on the oligomers nor for any fragmentation products. However, the yields of almost 90% recorded on this basis in each case suggest that the majority of the ozonolysis products were recovered after removal of the solvent. Table 1 gives the yields of ozonolysis products from all the ozonolysis reactions carried out on TME together with other data which will be discussed in due course.

A size-exclusion (SEC) chromatogram for ozonates formed in pentane at −60°C (reaction ***B*** in Table 1) is shown in Figure 1. The chromatogram shows that a large proportion of the ozonates are oligomeric, with a number average molecular weight, M_n, of 426 and a weight average molecular weight, M_w, of 776 (calibrated with polystyrene standards). The SEC chromatogram obtained for the oligomers after they had been heated at 60 °C for 5 h was very similar to the initial chromatogram, showing that the oligomers have reasonable thermal stability.

ESI-MS of the TME ozonates produced in pentane, obtained under soft ionization conditions, are shown in Figure 2. A distribution of oligomers, with a peak maximum at 462 Da, is obtained for each of the products within the concentration range explored (see Table 1). The spacing between each of the mass peaks in the series is 74 Da, which corresponds to the mass of acetone carbonyl oxide. The mass totals of the main series correspond exactly to the ammonium adducts (+18) of oligomers consisting solely of acetone carbonyl oxide repeat units, without any end groups (i.e., $m/z = 74n + 18$). The predominant ozonate structures formed in pentane can only, therefore, be cyclic oligomers of acetone carbonyl oxide, **11**. Note that the ESI-MS trace reveals only cyclic oligomers of acetone carbonyl oxide with $n \geq 3$. For example, the dimer, acetone diperoxide, was not generally observed by ESI-MS although it is known to be a significant reaction product under similar conditions.[3]



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There is a second minor distribution of mass peaks, with a spacing of 74 Da, evident among the main series. These peaks appear to correspond to open-chain oligomers of acetone carbonyl oxide, with end groups the mass of which total 34 Da. This end-group mass strongly suggests that these oligomers are terminated at both ends with −OOH groups, **12**. Such end groups may arise by reaction of oligocarbonyl oxides with hydrogen peroxide, which acts as a chain terminating agent. Hydrogen peroxide probably arises indirectly from the reaction of a trace amount of water in the ozonolysis solvent with a carbonyl oxide giving, 2-hydroxyprop-2-yl hydroperoxide. This hydroperoxide has been reported to be unstable and readily to decompose to acetone and hydrogen peroxide, at least in gaseous reactions (Scheme 2).[14,15] It has been reported also that hydrogen peroxide is a significant product in reactions of O_3 with aqueous emulsions of unsaturated fatty acids.[16]

There is also a third, minor, series of peaks in the ESI-MS traces, also spaced at intervals of 74 Da, with end group masses that total 18 Da. We suggest that these peaks correspond to open-chain oligomers of acetone carbonyl oxide directly terminated by reaction with adventitious water, giving structures with a hydroperoxy and a hydroxy group on the α and *ω* chain ends, **13**. The main oligomeric structures evident in the ESI-MS traces are listed in Table 2. The relatively high thermal stabilities of all these oligomeric structures are confirmed by the observation that there is no significant change in the

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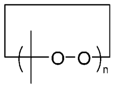
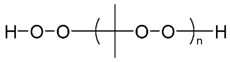
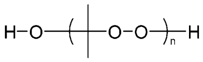
(14) Sauer, F.; Schafer, C.; Neeb, P.; Horie, O.; Moortgat, G. K. *Atmos. Environ.* **1998**, *33*, 229.

(15) Hasson, A. S.; Orzechowska, G.; Paulson, S. E. *J. Geophys. Res. [Atmos.]* **2001**, *106*, 34131.

(16) Pryor, W. A.; Das, B.; Church, D. F. *Chem. Res. Toxicol.* **1991**, *4*, 341.

TABLE 2. Main Oligomeric Ozonate Structures Observed from ESI-MS

Structure	Molecular ions (m/z) at n = x (NH_4^+ adducts)									
x	3	4	5	6	7	8	9	10	11	12
★  **11**	240	314	388	462	536	610	684	758	832	906
▲  **12**		348	422	496	570	644	718	792	866	940
●  **13**				480	554	628	702	776		

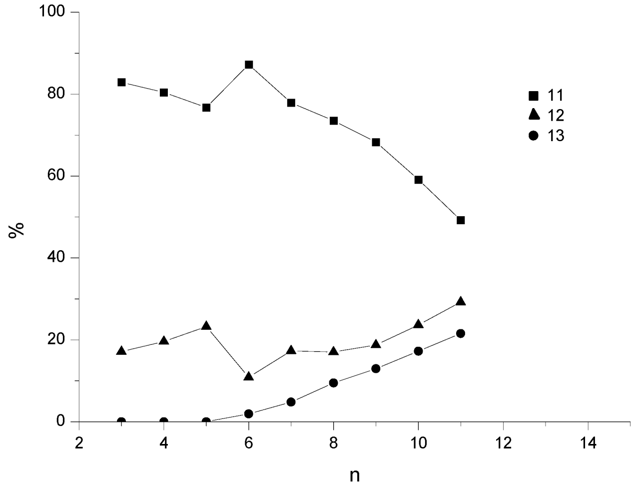
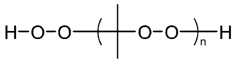


FIGURE 3. The relative proportions of cyclic (**11**) and open chain (**12**, **13**) oligomers in ozonates generated from the ozonolysis of TME in pentane at −60°C (reaction ***B***, Table 1).

distributions of mass peaks even after the ozonates have been refluxed in methanol for a few hours.



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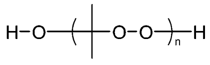

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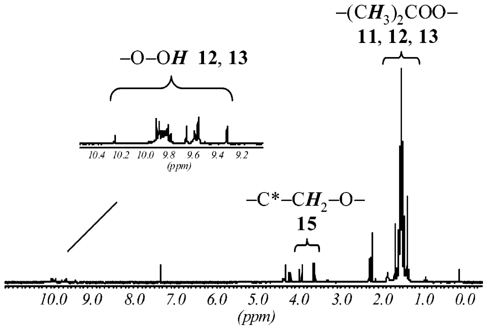


FIGURE 4. Proton NMR spectrum of ozonates generated in pentane (reaction ***B*** in Table 1) at −60°C with assignments.

Plotting the fraction of n-mers with cyclic structures against n, as shown in Figure 3, illustrates the increased significance of the open-chain oligomers at higher values of n. The fractions of open-chain oligomers with hydroperoxide and hydroxy α, ω or dihydroperoxide α, ω chain ends plotted against n also are shown in Figure 3. From these plots it is clear that the proportion of oligomers with open chain structures, for a given value of n, increases as n increases. Clearly, propagation of an oligocarbonyl oxide chain via addition of acetone carbonyl oxide is in competition with both capping and cyclization. Propagation ceases only when either a cyclization or chain capping event occurs. The data plotted in Figure 3 thus indicate that the rates of propagation of carbonyl oxides and of cyclization of the oligocarbonyl oxides so-formed are faster than the rates of chain capping by hydrogen peroxide and water. Since cyclization occurs at a faster rate than capping, it competes more effectively with propagation. Thus, the cyclic products dominate and they occur at lower degrees of polymerization than the open-chain oligomers. The data also indicate that the open chain oligomers are probably not derived from ring opening of cylics, since in the absence of further chain scission, ring opening should produce a distribution of open-chain oligomers that would be superimposable on the distribution of cyclics. Increasing the TME concentration in the reactions in pentane resulted in a marginal increase in the distribution of oligomeric lengths obtained, with the longer residue structures containing a higher proportion of cyclics.

Evidence in support of the oligomeric products of ozonolysis of TME in pentane being a mixture of cyclic and open-chain oligoperoxides is provided by proton NMR spectroscopy and by FT-Raman spectroscopy. The proton NMR spectra of these products consist mainly of a broad array of overlapped peaks centered at $\delta = 1.4$ ppm; these are assigned to the methyl protons of peroxidic units derived from the polymerization of acetone carbonyl oxide. The spectrum of the ozonates obtained in reaction ***B*** (Table 1) is shown in Figure 4. Tautomerization of the acetone carbonyl oxide is reported to give 2-hydroperoxypropene, **14**, which isomerizes to hydroxyacetone.[17] If the hydroxyacetone subsequently captures a carbonyl oxide

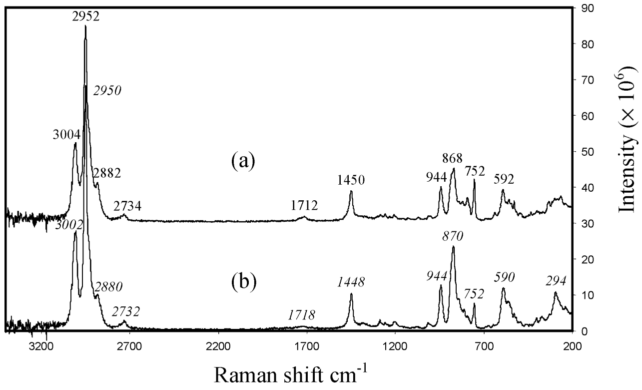
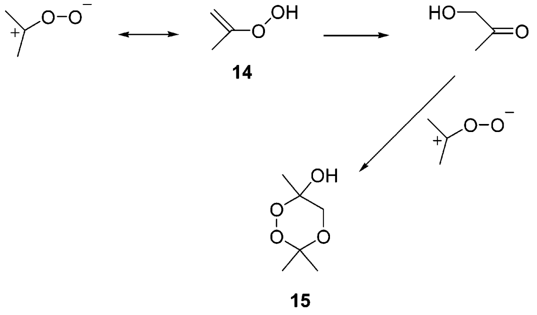


FIGURE 5. Raman spectra of the ozonates generated from (a) ozonolysis of TME in *undried* butyl acetate (reaction ***F***, Table 1) and (b) in pentane (reaction ***C***, Table 1) at −60°C.

SCHEME 3. Isomerization of Acetone Carbonyl Oxide Leading to 3,3,6-Trimethyl[1,2,4]trioxan-6-ol, 15

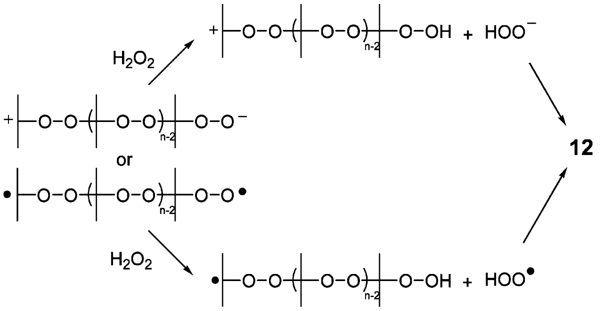


it will form 3,3,6-trimethyl[1,2,4]trioxan-6-ol, **15** (Scheme 3). Two sets of sharp resonances between 3.4 and 3.9 ppm resembling an AB quartet (J = 12.5 Hz) possibly arise from the methylene protons in this structure. These peaks are present regardless of whether the ozonolysis is carried out in pentane or in butyl acetate and indicate that ozonolysis products in pentane may contain up to 10% of 3,3,6-trimethyl[1,2,4]trioxan-6-ol. A minor series of peaks between 9 and 10 ppm are tentatively assigned to labile hydroperoxidic protons at the ends of open-chain oligomers, **12** or **13**, on the basis that the resonances disappeared upon shaking the solution with a small amount of D_2O. The fine structure, shown expanded in Figure 4, reflects the slightly different environments of the terminal hydroperoxidic protons in the distribution of oligomers. The sharp resonances evident at about 2.1 ppm indicate structures in which methyl protons are attached directly to carbonyl groups. An obvious assignment is acetone but the fine structure would suggest the presence of other related compounds in the ozonates.

The main features of the carbon NMR spectra of the ozonates are broad resonances centered at 21.5 and 108.0 ppm, which correspond to the methyl and backbone carbons of acetone carbonyl oxide residues in all oligomeric structures, respectively. Some other peaks evident between 60 and 70 ppm may be attributed to the methylene carbon in **15**.

The Raman spectrum of the mainly cyclic oligomeric ozonates obtained in pentane (in reaction ***C***, Table 1) is shown in Figure 5b. The intense band at 870 cm^{-1} is assigned mainly to the O−O stretching vibration in the peroxidic structures.[18] The methyl groups of the acetone carbonyl oxide units are readily identifiable from the strong CH stretch band between 2800 and 3000 cm^{-1} and the sharp CH_3 anti-symmetric deformation features at 1448 cm^{-1}. The sharp band at 752 cm^{-1} is assigned to the symmetrical v_s C−C vibration, while the sharp band present at 944 cm^{-1} is attributable to the CH_3 rocking mode.[19]

SCHEME 4. Reactions of Hydrogen Peroxide with a Propagating Polycarbonyl Oxide Chain



Ozonolysis of TME in Butyl Acetate. The complete ozonolysis of different concentrations of TME in butyl acetate at −60 °C yielded colorless viscous residues after removal of the solvent. The theoretical yields for the reactions are again determined on the basis that acetone carbonyl oxide is the predominant reactive species giving rise to the product. Percentage yields of 80−90% were recorded for these ozonolyses reactions in butyl acetate (see Table 1).

The SEC chromatogram of the ozonates obtained in *dried* butyl acetate (reaction ***E*****,** shown in Figure 1) shows that the oligomers formed in this solvent are of a marginally lower M_n (217 Da) than those formed in pentane. It should be noted that the SEC traces of the ozonates generated in *undried* butyl acetate (reactions ***D*** and ***F*** in Table 1) reveal similar mass distributions.

ESI-MS of the TME ozonates formed in *undried* butyl acetate (reaction ***D***), obtained under soft ionization conditions, are shown in Figure 6a. A distribution of oligomers, with a peak maximum at 348 Da, is obtained for each of the products within the concentration range explored (Table 1). There are two distributions observed, which are identified by the symbols ▲ and ★ in Figure 6a. The series, ▲, is the dominant one and is composed of peaks corresponding to $m/z = 74n + 18 + 34$. Therefore, this series can be assigned to oligomers with α-H and ω-OOH end groups. The predominant oligomeric structure formed in the *undried* solvent is thus the linear oligomer of acetone carbonyl oxide, with end groups resulting from H abstraction from H_2O_2 at the ω-COO chain end, which then liberates a hydroperoxyl species that reacts with the α-C chain end. The reaction pathway is shown in Scheme 4, which indicates reactions based on either radical or ionic propagation steps, both of which are feasible. At the current time it is not possible to

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[17] (a) Story, P. R.; Burgess, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 5726. (b) Storey, P. R.; Burgess, J. R. *J. Am. Chem. Soc.* **1968**, *90*, 1094.

[18] Vacque, V.; Sombret, B.; Huvenne, J. P.; Legrand, P.; Suc, S. *Spectrochim. Acta, Part A* **1997**, *53A*, 55.

[19] Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Organic Structural Spectroscopy*; Prentice Hall: Upper Saddle River, NJ, 1998.

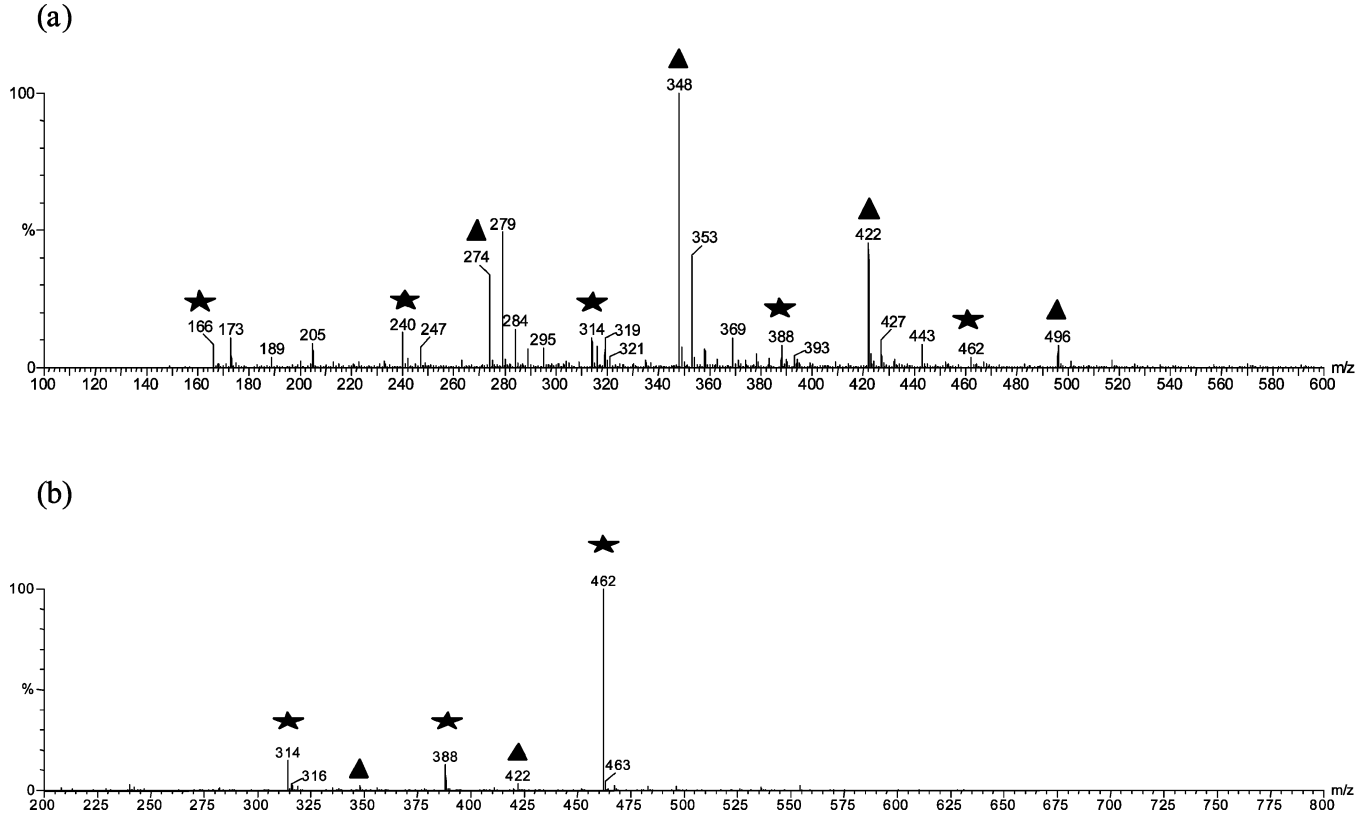

FIGURE 6. ESI mass spectra of the products of ozonolysis of TME at −60°C in (a) *undried* (reaction ***D***, Table 1) and (b) *dried* (reaction ***E***, Table 1) butyl acetate.

determine the relative importance of these two types of intermediate. Although these linear oligomers make up the majority of the products formed in butyl acetate, a series of mass peaks, ★, at 314, 388, and 462 Da, corresponding to the cyclic analogues ($m/z = 74n + 18$) are still observed. Also, some additional peaks can be assigned to the sodium adducts of the cyclic and linear oligomers.

Drying the distilled solvent with molecular sieves, type 4A, prior to the ozonolysis reaction (reaction ***E***), changed the oligomeric distribution of the ozonates formed with only the $n = 4$, 5, and 6 cyclics of acetone carbonyl oxide being clearly evident in the mass spectrum (see Figure 6b). This change was reflected also in the peak region attributed to methyl protons in the NMR spectrum of these ozonates which exhibited a broader group of peaks, not unlike that observed with the pentane generated ozonates, in which cyclic oligomers also predominate.

The proton NMR spectra obtained from the products generated in the *undried* solvent closely resemble those obtained from the ozonolysis products generated in pentane, although the main peak region attributed to the methyl protons of the acetone carbonyl oxide repeat unit is sharper. The collected hydroperoxidic proton peaks, between $\delta = 9$ and 10 ppm, are also twice as intense, with respect to the methyl protons resonance at $\delta = 1.4$ ppm, for these TME ozonates (reaction ***F***) than for those derived from ozonolysis of TME in a similar concentration of pentane (reaction ***C***). This suggests that there is a higher proportion of hydroperoxidic end groups on the oligomers formed in this solvent, i.e., that there are more open-chain oligomers (particularly of structure **12**) formed in *undried* butyl acetate than there are cyclic oligomers, **11**. Integration of the signals arising from the hydroperoxidic end groups in the proton NMR spectrum of the product from reaction ***D***, comparison with the areas of other proton signals, and assuming that hydroperoxidic end groups arise either directly or indirectly from reactions of propagating carbonyl oxide chains with water, suggests that the *undried* butyl acetate contained ca. 0.1% w/w water. This figure is not unreasonable given that the saturated solubility of water in butyl acetate is 1.2% w/w.[20] That the relative amounts of the linear oligomers are lower in reactions carried out in pentane is also to be expected given that the saturated solubility of water in this solvent is no more than 0.01% w/w.[20]

The Raman spectrum of the ozonates obtained in *undried* butyl acetate (reaction ***F***) is shown in Figure 5a. No significant differences in the bands are observed between this spectrum and that obtained for the ozonates generated in pentane: for example, the O−O stretch is clearly evident, although it is not as intense, at 868 cm^{-1}. The reduction in intensity may be attributed to the splitting of the peroxy band due to increased contributions from hydroperoxy structures on the chain ends of the open-chain oligomers obtained in this ozonate mixture.

Ozonolysis of TME in Methanol. The complete ozonolysis of TME in methanol at −60 °C yielded a colorless liquid following removal of the solvent. As expected, the product distribution obtained in methanol

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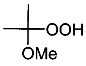
(20) Whin, B. P. J., P. G. *Directory of Solvents (Part 2)*; Kluwer: Dordrecht, 1996.

(reaction ***G***) is quite different to those obtained in pentane and butyl acetate, as illustrated by the SEC trace for this product shown in Figure 1: i.e., oligomers were *not* formed in this case. Proton NMR analysis of the products of reaction ***G*** confirm the sole product to be 2-methoxyprop-2-yl hydroperoxide, **16**, with sharp peaks evident at 1.38 and 3.28 ppm, attributable to methyl and methoxy protons, respectively. A broad band centered at 8.5 ppm is assigned to the hydroperoxy proton. A theoretical yield for this reaction can be estimated if we assume 2-methoxyprop-2-yl hydroperoxide to be the sole reaction product and on this basis the yield is calculated to be 68% (Table 1). That no oligomeric ozonolysis products are obtained in methanol is also evident from the absence of their characteristic mass peaks in ESI mass spectra.



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Conclusions

The work reported here provides, for the first time, *unequivocal* evidence for the presence of both cyclic and open chain oligoperoxides in the product mixtures derived from the ozonolysis of TME in nonparticipating solvents. The cyclic oligoperoxides arise from intramolecular reactions of the α and ω chain ends of propagating oligocarbonyl oxide chains, while the open chain oligoperoxides are produced when the propagating chain is terminated by either adventitious water or by hydrogen peroxide.

The analyses show that the complete ozonolysis of TME in pentane at −60 °C yields mainly cyclic oligomers of acetone carbonyl oxide. The cyclic hexamer is the predominant structure, but structures with degrees of polymerization up to 19 are also observed. Small amounts of linear oligomers are also formed with hydroperoxy end groups that may originate from reaction with hydrogen peroxide.

The competitive formation of cyclic and linear oligomers is more clearly reflected in the results of complete ozonolysis of TME in butyl acetate at −60 °C. An open chain tetramer of acetone carbonyl oxide, terminated with end groups derived from hydrogen peroxide, is the main oligomeric species formed in all reactions involving what we consider to be *undried* butyl acetate. However, when special precautions are taken to dry the solvent, the cyclic series of oligomers once again becomes the main product, with the tetramer, pentamer, and hexamer being the dominant constituents.

The product obtained from the ozonolysis of TME in methanol at −60 °C was predictably 2-methoxy-prop-2-yl-hydroperoxide, **16**; no oligomers were observed by ESI-MS in these product mixtures. The proton donor solvent thus reacts directly with the active carbonyl oxide species, as expected, preventing oligomer formation.

Experimental Section

Ozonolysis Procedure. A flask containing a solution of TME 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 O_2 stream was set to 20 mL min^{-1}, and the electrical discharge was set at 150 V. The O_3 flow rate at these settings was measured by bubbling the O_2/O_3 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 O_3 was found to be 0.88 g h^{-1}.

The O_2/O_3 mixture was bubbled through the stirred solution, with the outlet gas from this being passed directly into an ozone analyzer. Initially, almost all the O_3 in the gas was taken up by the solution, but eventually, as ozonolysis reaches completion, the increasingly positive reading on the analyzer stabilized at about 40 g m^{-3}. The completion of alkene ozonolysis can also be observed visually, as the solution turns blue from saturation with O_3. Typically the time required for ozonolysis was proportional to the concentration of TME in the solutions. For example, the ozonolysis reactions of the three different concentrations of TME in pentane, ***A***, ***B***, and ***C***, were completed in 25, 70, and 280 min, respectively. This amounts to the respective solutions receiving 0.37 g (7.71 mM), 1.03 g (21.5 mM), and 3.96 g (82.5 mM) of O_3, which are approximately equivalent to the TME concentrations in each of the solutions. After completion of ozonolysis, the contents of the flask were bubbled through with N_2 for about 20 min to remove free O_3. 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 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 fully dried.

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Supporting Information Available: Materials, instrumentation used, and further spectral data for the ozonates (^{1}H NMR, ^{13}C NMR, ESI-MS). This material is available free of charge via the Internet at http://pubs.acs.org.

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