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Polymerization of methyl methacrylate initiated by ozonates of tetramethylethene

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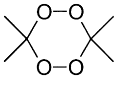
Abstract

It is confirmed that the major products of ozonolysis of tetramethylethene (TME) in butyl acetate at temperatures between −60 and 20°C are the cyclic peroxides, acetone diperoxide and acetone triperoxide plus, at low temperatures, species which may be open-chain oligoperoxides. Solutions of ozonized TME are able to initiate polymerizations of methyl methacrylate at temperatures above 60°C. ESR spectroscopy has shown that acetone diperoxide does not generate significant concentrations of radicals below 140°C, so that the chief initiating species below this temperature must be acetone triperoxide and the oligoperoxides. Despite the fact that these species have different structures, indicated by their differing retention times in GC and also their different mass spectra, they behave kinetically as one species, i.e. conversions to polymer after polymerization times of 1 h in the presence of ozonized TME are identical regardless of ozonolysis temperature. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ozonolysis; Tetramethylethene; Radical

1. Introduction

Ozonolysis of alkenes has attracted a great deal of attention from both a mechanistic and synthetic view point, such that our understanding of the course of the reaction is now quite advanced [1–22]. However, the thermal decomposition of the products from these ozonolyses is less well studied. Many of the species present in an ozonolysis mixture are peroxidic and are expected to generate radicals on thermolysis [23–25]. Reports on the nature of these radicals are few but several ESR studies have been published [26–28]. To our knowledge no reports on the thermolysis products of the ozonolysis of tetramethylethylene (TME) have appeared despite a large amount of data on the identities of these products. Also, radical polymerization of vinyl monomers is a well-known procedure so that radicals produced from the thermolysis of ozonolysis mixtures could be potential initiators of chain growth polymerization. Furthermore, alkene double bonds can easily be introduced into a variety of polymer chains so that ozonolysis and thermolysis of these ozonates should lead to macroradicals that may initiate polymerization and ultimately lead to block copolymer formation [29]. We were therefore interested in investigating the utility of using the peroxidic products from the ozonolysis of alkenes as a source of radicals in radical polymerization. Since the product distribution is known to be dependent on several variables (such as temperature, alkene concentration, solvent, etc.), in order to test this hypothesis, it was necessary to conduct an analysis of the product distribution using reaction conditions suitable for a polymerization process. Initially we have chosen to investigate reaction mixtures derived from the ozonolysis of the alkene, TME. The ozonolysis of TME is well studied and also TME is symmetrical, which simplifies the expected product distribution. The product distribution upon ozonolysis of TME can contain varying amounts of the epoxide of TME, **1**, Acetone cyclic diperoxide, **2**, acetone cyclic triperoxide, **3**, other oligomers of the acetone carbonyl oxide, **4**, and other minor products [1,14,15].



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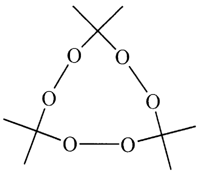

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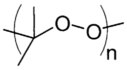

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Murray et al. reported that, at low conversions and low concentrations of TME, **2** was the only product. In this work

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we have examined the full product mixture from our reactions using GC-MS. Compounds **2**, **3** and **4**, on thermolysis, would all be expected to be capable of initiating radical polymerization. Compound **2** is known to be a stable solid with two possible thermolytic decomposition pathways: radical and concerted, non-radical routes. Much of the data on the thermolysis of cyclic diperoxides is due to the work of Cafferata et al. [30–35]. In particular these workers studied the high temperature thermolysis of **2** and reported that introducing styrene can enhance the rate of thermolysis.

2. Experimental

Materials: All chemicals were obtained from Aldrich unless otherwise stated. Methyl methacrylate (MMA) was dried by stirring over calcium hydride and purified by distillation under reduced pressure. Butyl acetate and all other solvents were distilled prior to use.

Ozonolysis: Tetramethylethene (TME) was ozonized at either −60, 0 or 20°C. In a typical procedure, TME (0.18 g, 2.2 mmol) was added to butyl acetate (25 cm^3) and then brought to the required temperature. A dry ice/acetone bath was used for the −60°C reaction temperature or an ice bath was used for the 0°C reactions. Ozone generated by passing an oxygen stream through an electric discharge-type ozone generator was then bubbled through the solution at a rate of 0.35 g h^{-1} for 8 min, until the solution turned blue, indicating the presence of excess ozone. Nitrogen was then bubbled through the solution for 20 min to remove the residual ozone. Butyl acetate was also ozonized as a control reaction.

Polymerizations initiated by ozonized TME solutions: In a typical procedure, MMA (18.00 g, 0.18 mol) was dissolved in butyl acetate (10 cm^3) and the resulting solution added to an ozonized TME solution (15.00 cm^3) in an ampoule. This procedure was repeated with two more ampoules. The ampoules were then sealed under vacuum following the usual freeze-pump-thaw degassing technique, which was repeated three times for each ampoule. The ampoules were then heated at 60, 80 or 100°C for 2 h after which they were cooled in ice. The products obtained were precipitated into petroleum spirit, filtered through sinters, dried overnight in a vacuum oven and weighed.

Polymerizations were also carried out at 120 and 140°C. Polymerizations at these temperatures were performed in three round-bottomed flasks under nitrogen. MMA (18.00 g, 0.18 mol) was dissolved in butyl propionate (10 cm^3) and added to an ozonized TME solution, in butyl propionate solvent, (15.00 cm^3) in a flask. This procedure was repeated with a second flask. The contents of each flask were then heated under a blanket of nitrogen at 120 or 140°C for 2 h. The products obtained were precipitated into petroleum spirit, filtered through sinters, dried overnight in a vacuum oven and weighed. In order to investigate the possibility of initiation from oxidized compounds derived from the reaction of ozone with the solvent the above procedures were repeated in the absence of TME.

*Synthesis of ACDP (**2**):* The method used was similar to that of Qi et al. [25]. Thus concentrated sulphuric acid (5.40 cm^3) was added dropwise to a solution of 70% v/v hydrogen peroxide (2.40 g, 70.5 mmol) in acetonitrile (20 cm^3) at −10°C in an acetone–dry ice bath with vigorous stirring. Acetone (3.00 g, 52 mmol) in acetonitrile (10 cm^3) was added dropwise over 20 min to the vigorously stirred mixture. After a short while, a white solid began to precipitate out of solution. Stirring was continued at −10°C for1 h. The product was collected by filtration and washed thoroughly with water before being dried on a sinter and then in a vacuum oven overnight. ACDP (2.04 g, yield 69%) was obtained. The product was recrystallized from warm ethyl acetate before being filtered once again and dried overnight in a vacuum oven.

Melting point: 132–134°C (lit Ref. [25] 133–135°C); ^{1}H NMR: δ 1.35 (s) and 1.79 ppm (s). ^{13}C NMR: δ 20.32, 22.19 and 107.42 ppm; GC-MS(EI): — 101 (44), 73 (19), 59 (48), 58 (56) and 43 (100); IR: (Nujol) 2905 (s), 2845 (s), 1200 cm^{-1} (m).

*Polymerizations initiated by **2**:* Compound **2** (80 mg, 0.54 mmol) prepared as described above was dissolved in butyl propionate (6.4 cm^3) in an ampoule. MMA (4.50 g, 45 mmol) was added. This procedure was repeated for a further five ampoules. The ampoules were then degassed using the usual freeze-pump-thaw degassing technique and sealed under vacuum before being heated at 60, 80, 100, 120 or 140°C for 2 h. The products obtained were precipitated into petroleum spirit, filtered through a sinter, dried overnight in a vacuum oven and weighed. In the polymerizations initiated by acetone diperoxide the concentration of initiator was 0.045 mol dm^{-3} and that of the monomer was 3.90 mol dm^{-3}.

ESR experiments: ozonized TME solutions: Either *N-tert*-butyl-α-phenylnitrone (PBN) (9.00 mg, 0.1 mmol) or 2,4,6-tri-*tert*-butylnitrosobenzene (TTBNB) (34 mg, 0.25 mmol) were dissolved in an ozonized TME solution (2.50 cm^3). A sample was placed in an ESR tube and degassed with nitrogen for 5 min. Spectra were recorded over a period of 30 min at temperatures of either 60 or 80°C.

*ESR experiments, **2**:* Compound **2** (40 mg, 0.27 mmol) and TTBNB (34 mg, 0.25 mmol) were dissolved in butyl propionate (2.50 cm^3). A sample was placed in an ESR tube and degassed with nitrogen for 5 min. Spectra were recorded over 30 min at temperatures of either 120 or 140°C.

*ESR experiments, **2** and MMA:* Compound **2** (40 mg, 0.27 mmol) and TTBNB (34 mg, 0.25 mmol) were dissolved in butyl propionate (2.5 cm^3) together with MMA (0.20 g, 0.2 mol). A sample was placed in an ESR tube and degassed with nitrogen for 5 min. Spectra were recorded over a period of 30 min at a temperature of 140°C.

Instrumentation: ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX 400 MHz spectrometer using $CDCl_3$ as the

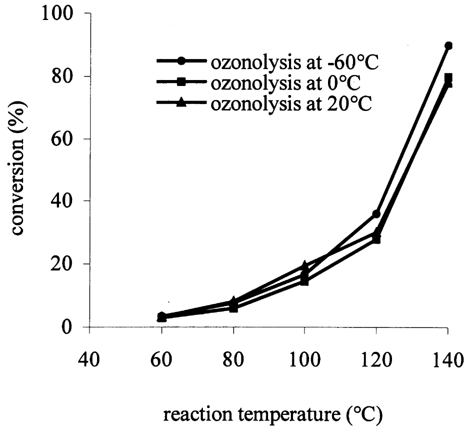


Fig. 1. Graph of conversion to polymer in 1 h against polymerization temperature for MMA initiated by ozonized solutions of TME.

solvent. IR spectra were recorded on a Nicolet 205 FT-IR instrument using a solution cell or a Nujol mull. GC-MS was performed on a Perkin–Elmer autosystem XL capillary gas chromatograph coupled to a quadrupole mass spectrometer and temperature pro-forming using a fused silica capillary column (30 m DB1 1.0 μm 0.32 nm). The following settings were used: injection temperature, 250°C; initial oven temperature, 50°C; final temperature, 250°C; ramp rate 15° $\min^{-1}$ and solvent delay, 2 min.

ESR spectra were recorded on a Bruker EMX X-band spectrometer operating with 100 kHz magnetic field modulation, a modulation amplitude of 0.02 mT and spectrum accumulation over four scans. Thermolysis was undertaken in situ employing the Bruker B-VT1000 variable temperature control system (accurate to ±1 K). PBN and TTBNB were employed as spin-traps at concentrations of 0.02 and 0.05 mol dm^{-3}, respectively. Thermolysis was undertaken for a period of up to 60 min and spectra were recorded, as required, at various times during this period. Spectral simulations were undertaken employing PEST WinSim (a NIEHS Public EPR Software Tool). The hyperfine splitting constants obtained from these spectral simulations are considered accurate to ±0.005 mT.

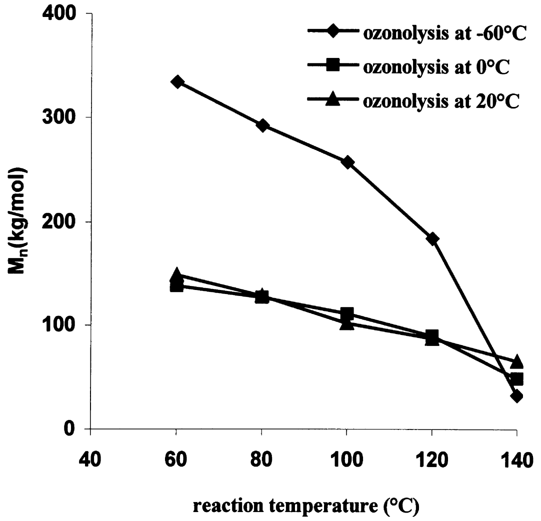


Fig. 2. Graph of M_n for low conversion polymerization of MMA initiated by ozonized solutions of TME.

GPC 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 gel mixed B; $3 \times 30\mathrm{cm}^2$ high-molecular-weight columns were used with a flow rate of 1 ml $\min^{-1}$. Sample concentrations were 2 mg dm^{-3}. Calibrations were with either PMMA or polystyrene standards from Polymer Laboratories (UK).

3. Results

3.1. Polymerizations of MMA initiated by the mixtures of peroxidic species derived from ozonolysis of TME

The following sections of this work were prompted by the observation that the ozonates formed from **1** were able to initiate polymerization of vinyl monomers. Thus, the vinyl monomer, MMA, was polymerized following heating in the presence of the ozonate mixtures. The degree of conversion after 1 h and values of M_n at a range of polymerization and ozonolysis temperatures are shown in Figs. 1 and 2.

Two rather unexpected features of these polymerizations came to light at this point. First, despite dramatic changes in the make-up of the product mixture following ozonolysis (see later), the nominal rates of polymerization are essentially independent of ozonolysis temperature. The other, and unexpected, observation is that the molecular weight average, M_n, is consistently higher for the polymerizations using the mixture ozonized at −60°C than in the other cases. Since the nominal rates of polymerization are not affected by changes in ozonolysis temperature the decrease in M_n must be due to a transfer event. The polydispersities of the molecular weight distributions, as expected decreased with increasing polymerization temperature. Thus, between 60 and 140°C M_w/M_n decreased from approximately 2.7 to 2.0 for polymers prepared following ozonolysis at either −60 or 0°C. Broader molecular weight distributions were, however, observed for polymerizations initiated by ozonates prepared at 20°C and at temperatures of polymerization of 60 and 80°C (typically $M_w/M_n \sim 4.0$–3.5). In order to further investigate these phenomena, and also to gain further insight into the initiation process, we then carried out a series of model experiments in which GC-MS was used to investigate changes in the product distribution following changes in ozonolysis temperature. ESR spectroscopy was also used to investigate the nature of the initiating radicals.

3.2. Analysis of the peroxy products derived from the ozonolysis of TME

In order to determine the sequence of events that lead to polymerization of vinyl monomers by the products of

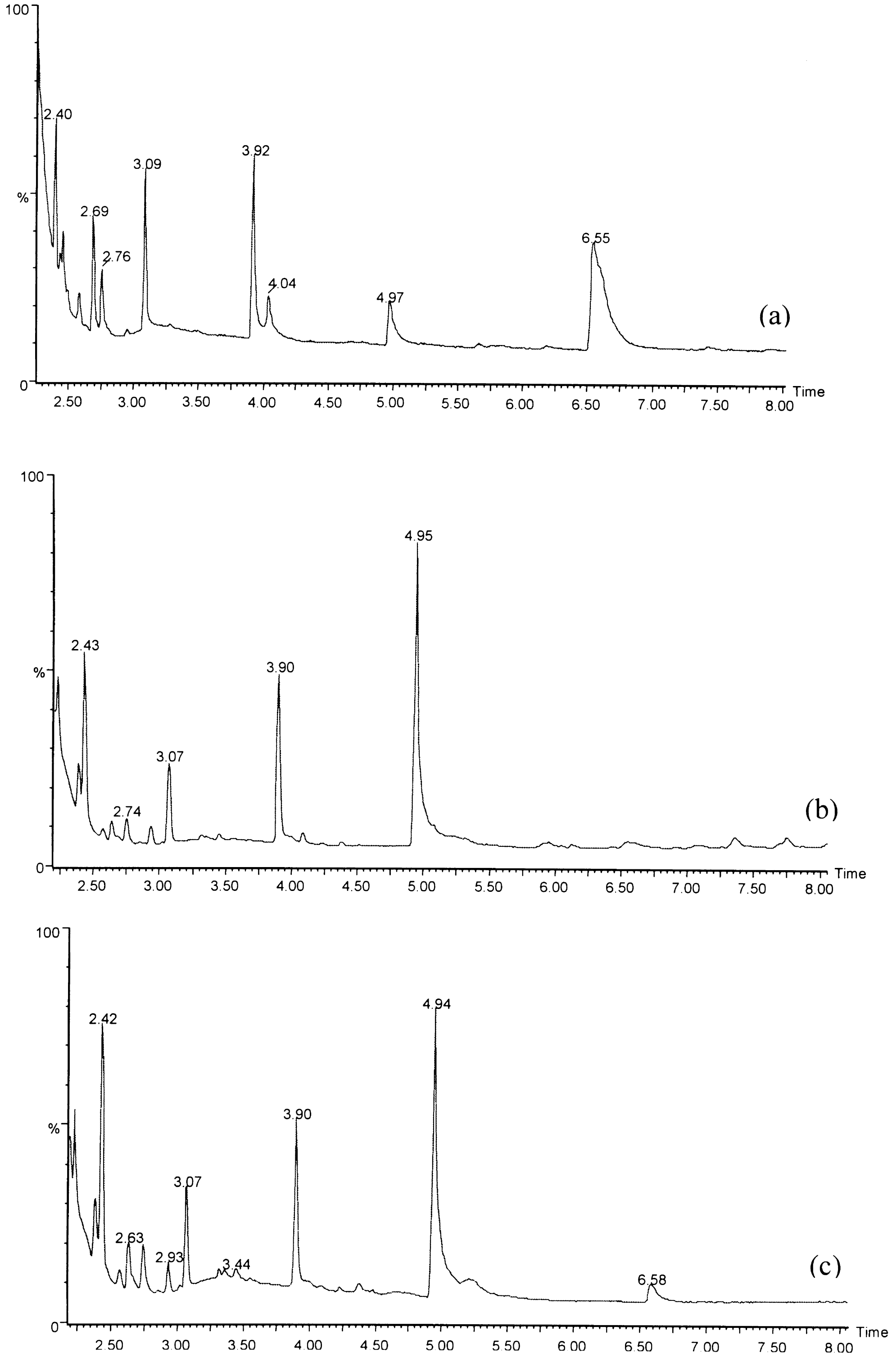


Fig. 3. Gas chromatograms of TME ozonized at: (a) −60, (b) 0, and (c) 20°C in butyl acetate.

ozonolysis of TME, it was vital that we determined the species present in the reaction mixtures after ozonolysis. In order to do this, we employed GC-MS as an analytical tool and have deduced the product distribution with the assistance of previously reported data. GC chromatograms of the products of ozonolyses carried out at −60, 0 and 20°C showed that several species were present and are shown in Fig. 3.

The main products are **1** (2.40 min), **2** (3.92 min), **3** (4.97 min), and **4** (6.55 min). The presence of **2** was

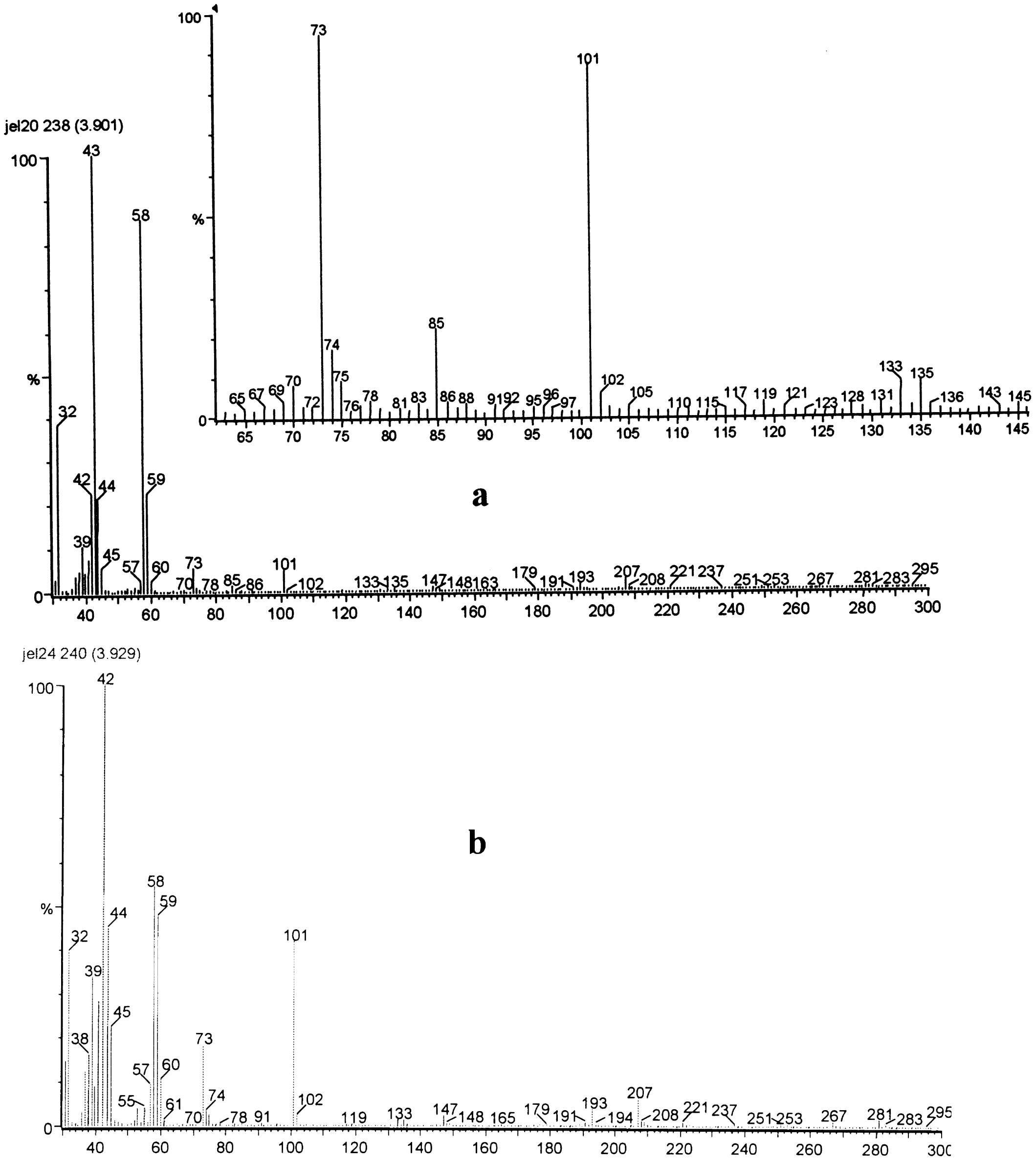


Fig. 4. Mass spectrum of: (a) **2** formed during the ozonolysis of TME at 0°C in butyl acetate (with insert showing expanded region *m*/*z* 60–145), and (b) **2** made by the non-ozonolysis method.

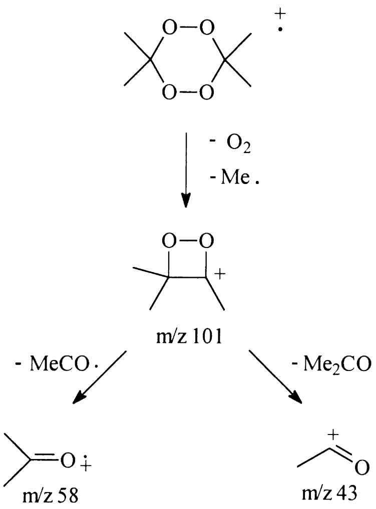
confirmed following synthesis of a genuine sample. The mass spectra obtained from this material and the product of the ozonolysis carried out at 0°C are shown in Fig. 4.

The spectra are almost identical: a result which mirrors previously reported data. The mass spectrum of **2** is rationalized, in part, in Scheme 1 (fragmentation pathways for **2**), which is fully consistent with the established literature [36].

However, the GC data clearly show that other species are also present. Thus we observed the production of large amounts of **1**. The presence of **1** was confirmed by the synthesis of the genuine compound and comparison of its mass spectrum with that derived from the GC peak at 2.40 min. Owing to the instability of **3** and **4**, reference compounds were not synthesized. However, the assignment of the peak at 6.55 min to **4** is supported first by its boiling point (i.e. in excess of those of both **2** and **3**) and also by its mass spectrum displayed in Fig. 5.

The results from Fig. 5 are rationalized in Scheme 2 (fragmentation pathways for **4**) in which each peak has been assigned ±1 *m*/*z* assuming a random set of homolytic and heterolytic scissions around the peroxide bond and a radical–radical coupling followed by further scission.

Compound **4** may in fact be cyclic or linear: both types of architecture could be inferred from the mass spectrum. The major peak at 6.54 was also accompanied by other high boiling fractions, which had very similar mass spectra (5.36 and 6.15 min). The mass spectra then imply that these fractions are also oligomeric peroxides (**4**), probably



Scheme 1.

with differing degrees of polymerization. Murray et al., have also noted the presence of these structures in their work [14]. The peak at 4.97 can be assigned to **3** by reference to its mass spectrum, shown in Fig. 6.

The fragmentation pattern (**3**) that this spectrum implies is then given in Scheme 3. The production of **1** and **2** is consistent with Murray et al.'s earlier report on the ozonolysis of TME in chloroform and hexane. However, in their work they found that, at concentrations of TME similar to those used here, **2** was the only product. An important difference between our work and that of Murray et al., is the extent of reaction at which the analysis was carried out. Thus, comparison of our results with those of Murray et al. [14,15] indicates that the product distribution is strongly affected by the extent of reaction.

The GC chromatograms in Fig. 3 clearly show that at −60°C the main peroxidic product is **4** along with substantial amounts of **2** and **3**. The other major product (2.69 min) is 2,3-dimethylbut-3-en-2-ol which can be identified as such from the mass spectrum, which includes the molecular ion at $m/z = 100$. The most important change that we observed on increasing the ozonolysis temperature to 0°C was that the concentration of **4** dramatically decreased. This material appears to have been almost completely replaced by an increase in concentration of **3** while the amount of **1** remained constant. Similarly, only small quantities of **4** were formed at 20°C. Therefore any observed changes in the ability of these mixtures to initiate the polymerization of vinyl monomers must be due to differences in the amounts of the two peroxidic species, **3** and **4**.

3.3. Ozonolysis of solvents

Since the major component in these ozonolyses was the solvent it also was ozonized at −60, 0 and 20°C. The products were then analysed by GC-MS. In each case, only one component was found to be present: i.e. the unchanged solvent. Therefore, the initiating peroxidic products must be derived from the added alkene.

3.4. Spin trapping of radicals

In order to examine the range of radicals produced upon the thermolysis of solutions of ozonized TME, we have employed two spin-traps, namely PBN and TTBNB. PBN

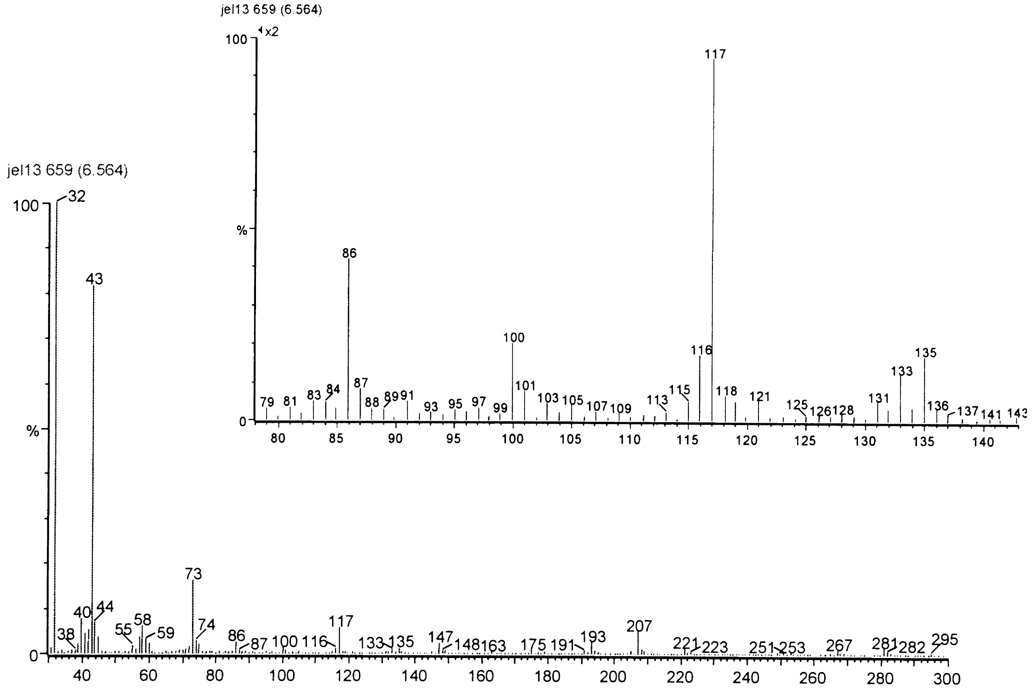
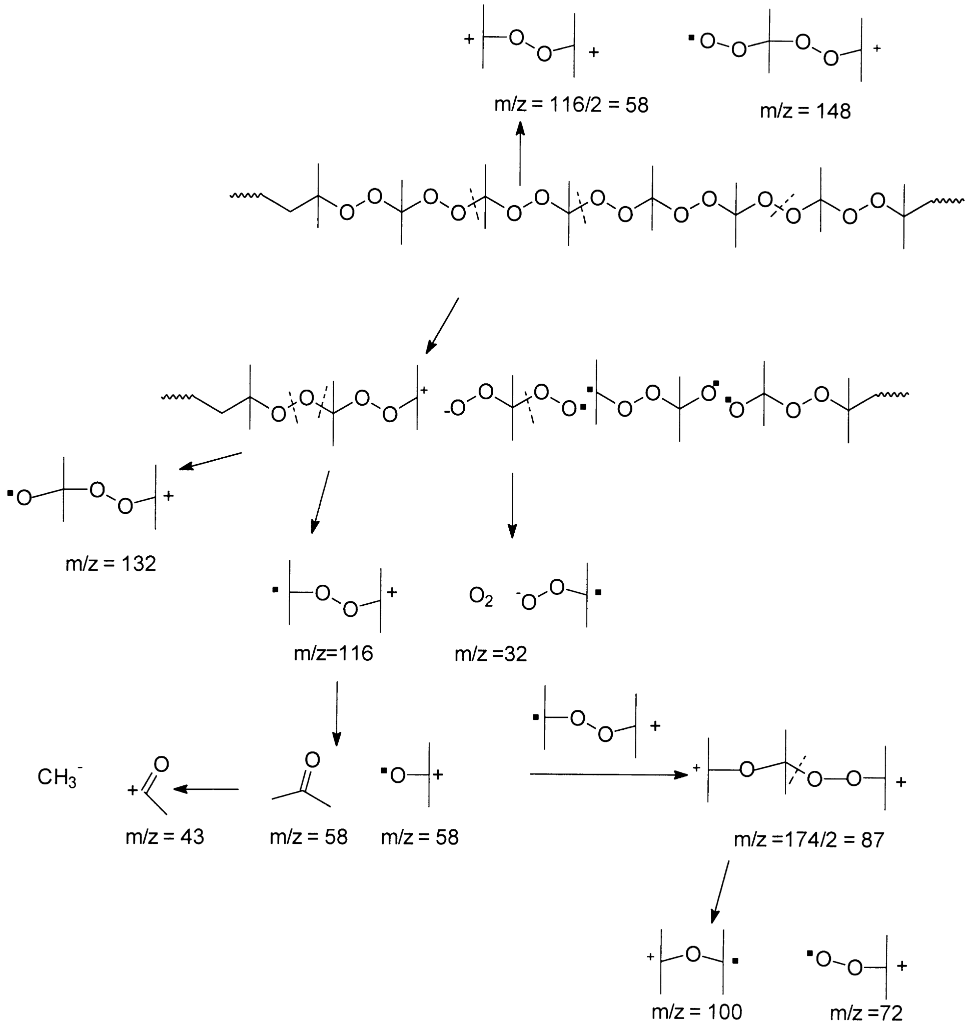


Fig. 5. Mass spectrum (with insert showing expanded region m/z 80–145) of **4** formed during the ozonolysis of TME at −60°C in butyl acetate.



Scheme 2.

was selected because of its superior ability to trap oxygen-centred radicals compared to carbon-centred radicals although, sometimes, it will also trap the latter. Unfortunately, PBN adducts provide limited information on the exact structure of the original radical as its atoms are remote from the unpaired electron in the adduct. TTBNB preferentially traps carbon-centred radicals and provides more information on the structure of the original radical owing to the proximity of its atoms to the unpaired electron in the adduct.

3.5. ESR spectroscopy during thermolysis of **2**

ESR experiments were undertaken, employing TTBNB as a spin-trap, on **2** synthesized by a non-ozonolysis method. No ESR signals were observed when **2** was thermolysed at 60, 80 and 100°C in butyl propionate. A spectrum was obtained, however, when **2** was thermolysed at 120°C, but the strongest spectra were obtained when **2** was thermolyzed at 140°C. The spectrum obtained at 140°C is shown in Fig. 7 together with its simulation. The trapping of TTBNB with alkyl radicals to give the TTBNB nitroxyl spin-adduct is shown in Scheme 4. In addition to the nitroxyl adduct, formed by attack at the nitrogen atom of the nitroso group, this spin-trap can also give an anilino adduct, by attack at the oxygen atom of the nitroso group, when the original radical is relatively bulky (as in secondary and tertiary carbon-centred radicals).

The spectrum indicates the presence of a mixture of four adducts with considerable overlapping of the hyperfine lines from each adduct. However, the simulation (Fig. 7b) clearly indicates the presence of the TTBNB adduct of a methyl radical (characterized by coupling to three equivalent β-protons). The methyl radical undoubtedly arises via β-scission of the alkoxy radical formed by cleavage of the O–O bond in **2**. The three remaining adducts are a nitroxyl adduct of a $^{\cdot}CH_2R$ radical (characterized by coupling to two equivalent β-protons) and a nitroxyl and an anilino adduct of a $^{\cdot}CHR_2$ radical (characterized by coupling to a single β-proton). All of these latter radicals are produced by hydrogen atom abstraction from the solvent by methyl (and possibly by also alkoxyl) radicals. The hyperfine parameters of all of the adducts are summarized in Table 1.

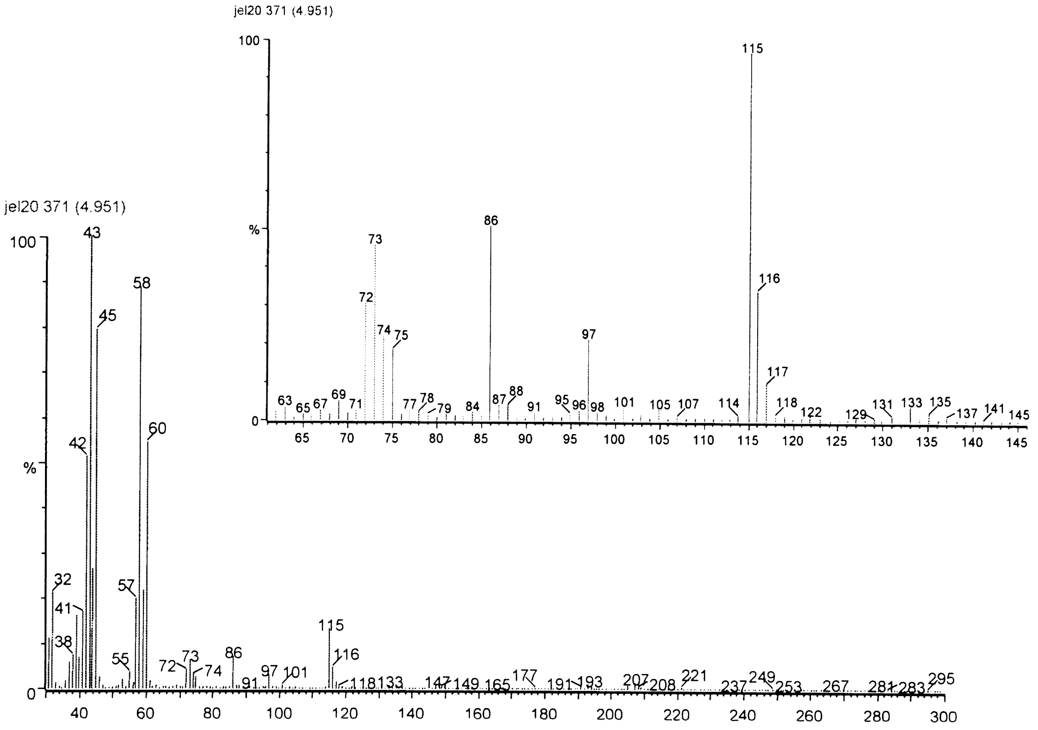
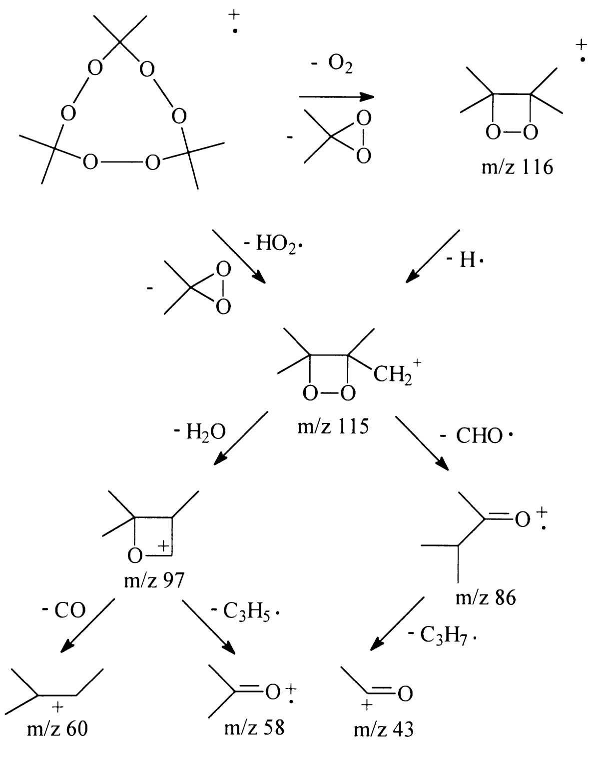


Fig. 6. Mass spectrum (with insert showing expanded region *m*/*z* 65–145) of **3** formed during the ozonolysis of TME at 20°C in butyl acetate.

A further ESR experiment was undertaken in which **2** was heated with MMA and TTBNB at 140°C in butyl propionate in an attempt to model polymerization conditions. The spectrum recorded after 15 min is shown in Fig. 8. The sharp (low intensity) lines at the low and high field extremities indicate the presence of the methyl radical adduct. The intense broad lines towards the centre of the spectrum are due to an anilino adduct of a $^{\cdot}CR_3$ radical [a(N) 0.999 and $a(2H_m)$ 0.199 mT], characteristic of the MMA propagating chain end [36]. The ESR spectrum recorded after 45 min is shown in Fig. 9. As expected, the intensity of the $^{\cdot}CR_3$ adduct increases with time, reflecting the increase in concentration of the trapped chain ends.



Scheme 3.

3.6. ESR spectroscopy during thermolysis of the products of ozonolysis

The ESR spectrum obtained when a solution of TME, ozonized at −60°C in heptane, was heated in the presence of PBN at 60°C increased in intensity with time. The ozonized TME solution was also heated with PBN at 80°C, which resulted in the more intense spectrum shown in Fig. 8. The spectrum has parameters [a(N) 1.512 and a(Hβ) 1.902 mT] typical of an oxygen-centred radical, [37,38] consistent with the trapping of the alkoxyl radicals formed following homolytic cleavage of the O–O bond.

An activation energy of 158 kJ mol^{-1} for the rupture of the peroxy bond in **2** has been reported together with a value of ln A equal to 31.8 [33]. Thus, at 80°C a value of 1.47×10^{-9} for the dissociation constant of **2** can be calculated. Therefore, the rate of thermolysis of **2** would appear to be too slow at 80°C to produce an ESR-observable concentration of radicals. Trapped radicals giving rise to the ESR spectrum probably arise from **3** and **4**, which are

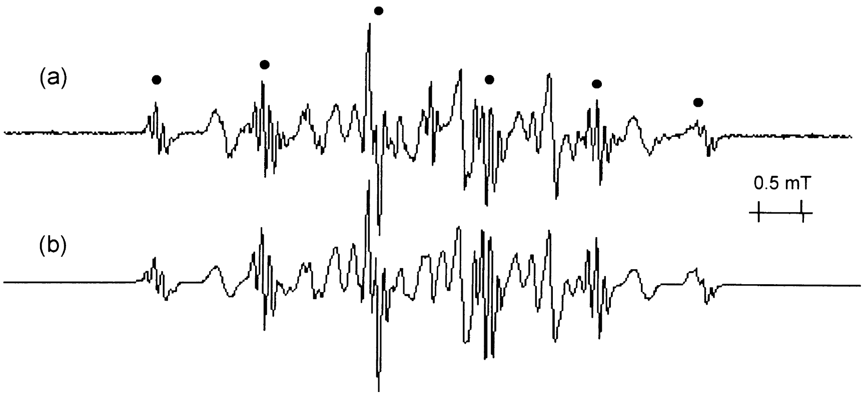
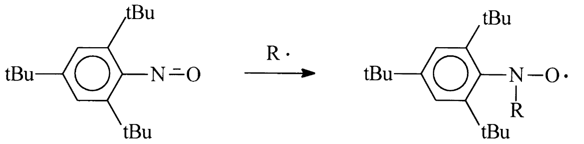


Fig. 7. ESR spectrum of the spin-adducts formed during thermolysis of **2** in the presence of TTBNB at 140°C in butyl propionate: (a) experimental spectrum and (b) simulated spectrum. The group of lines which include those arising from the methyl radical adduct are indicated by ● in (a).



Scheme 4.

known to be thermally much less stable than **2**. Thermolysis of **3** may form oxygen-centred radicals by initial rupture of peroxy bonds within the molecule. If the rate of spin trapping of oxygen-centred radicals, generated from peroxy bond cleavage, competes favourably with further decomposition of **3**, then an ESR spectrum such as the one shown in Fig. 10 would be observed. Thus the primary radicals generated upon heating a solution of TME ozonized at −60°C in heptane are oxygen-centred.

Next TTBNB was employed as a spin-trap for the presence of carbon-centred radicals. The ESR spectrum obtained upon thermolysis of ozonized TME at 80°C, in the presence of TTBNB, is shown in Fig. 11 together with its simulation.

The simulation of the experimental spectrum (see Fig. 11b) indicates the presence of the methyl adduct [*a*(N) 1.270, *a*(3Hβ) 1.194 and *a*($2H_m$) 0.087 mT] together with a TTBNB nitroxyl adduct of a $^{\cdot}CHR_2$ radical [*a*(N) 1.339, *a*(Hβ) 2.100 and *a*($2H_m$) 0.079 mT]. The $^{\cdot}CHR_2$ radical has almost certainly arisen following hydrogen atom abstraction from the solvent, which commonly occurs with radicals derived from scission of peroxides. The intensity of the spectrum is fairly weak indicating a low concentration of methyl radicals.

Table 1
Hyperfine splitting constants (in mT) for the TTBNB spin adducts formed during thermolysis of **2** in the presence of TTBNB at 140°C in butyl propionate

Adduct	*a*(N)	*a*(Hβ)	*a*(H_m)	Assignment
1	1.301	1.212 (3H)	0.090 (2H)	methyl (nitroxyl)
2	1.360	1.690 (2H)	0.080 (2H)	$^{\cdot}CH_2R$ (nitroxyl)
3	1.352	2.064 (1H)	0.075 (2H)	$^{\cdot}CHR_2$ (nitroxyl)
4	1.019	0.202 (1H)	0.180 (2H)	$^{\cdot}CHR_2$ (anilino)

4. Discussion and conclusions

We have shown that radicals generated from the products of ozonolysis of TME are useful in the polymerization of vinyl monomers such as MMA. Under the conditions used in this work, the major products of the ozonolysis are the cyclic species acetone diperoxide, **2**, and acetone triperoxide, **3**, plus, at low temperatures, peroxidic species, which may be open-chain oligomers, **4**. Below 140°C, acetone diperoxide does not generate radicals in sufficient concentration to reach the detection limit of the ESR spin-trapping technique, so we conclude that the chief initiating species below this temperature are **3** and **4**. Methyl radicals were detected using TTBNB as the spin trap but the major alkyl radical component was a radical derived from

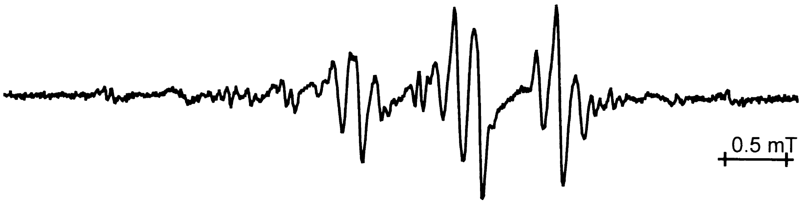


Fig. 8. ESR spectrum of the spin adducts formed after 15 min upon heating **2** in the presence of TTBNB with MMA at 140°C in butyl propionate.

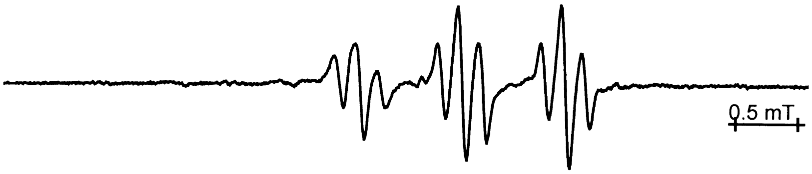


Fig. 9. ESR spectrum of the spin adducts formed after 45 min upon heating **2** with MMA and TTBNB at 140°C in butyl propionate.

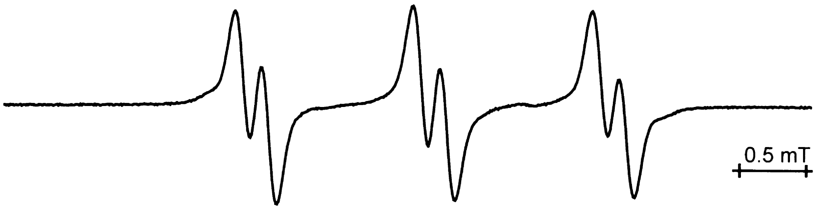


Fig. 10. ESR spectrum of the spin adduct formed upon heating a solution of TME ozonized at −60°C with PBN in heptane at 80°C.

abstraction of hydrogen from the solvent. PBN was also used to trap oxygen-centred radicals. Thus we have been able to show that the primary radicals generated on thermolysis of the ozonates of TME are oxygen-centred. The observation that these species can be trapped by PBN indicates that radical trapping competes favourably with decomposition to alkyl radicals and oxygen. It is therefore reasonable to assume that reaction of vinyl monomers with these oxygen-centred radicals, from the primary scission process, will also compete favourably with decomposition: that is initiation by the primary scission products will contribute significantly to the initiation process.

Following on from the GC-MS results, the main differences that have been observed in the product distribution of the ozonates on changing temperature were in the relative ratio of **3** to **4**. This observation can now be used to provide insight into the behaviour of the ozonates as initiators. Since the temperature of ozonolysis does not appear to affect the nominal rate of polymerization, but does affect the distribution of **3** and **4** in the ozonate, **3** and **4** must be equally able to initiate polymerization (i.e. the rate constants for homolytic scission to give radicals, k_d, for both species are similar). Despite the fact that these species have different structures, indicated by their differing retention times in GC and also their differing mass spectra, they behave kinetically as one species.

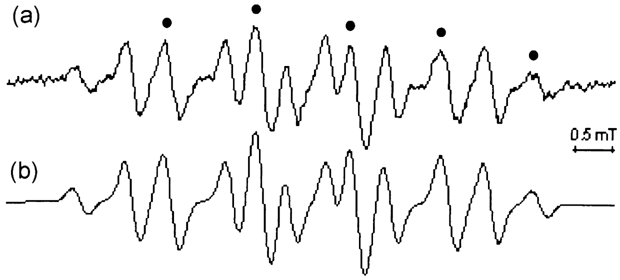


Fig. 11. ESR spectrum of the spin-adducts formed during the thermolysis of ozonized TME in the presence of TTBNB at 80°C, (a) experimental spectrum and (b) simulated spectrum. The lines due to the methyl radical adduct are indicated by ● in (a); the remaining lines arise from a $^{\cdot}CHR_2$ adduct.

The GC-MS results also allow us to offer an explanation for the increase in molecular weight in polymers produced using the ozanate produced at −60°C rather than the two higher temperatures. The main difference between this ozonate and the mixtures produced by ozonolysis at 0 and 20°C, is the presence of substantial amounts of **4**. Since this increase in the concentration of **4**, at the expense of **3**, has resulted in increased molecular weight, while the rate of polymerization remained constant, **4** must have a lower transfer constant than **3**. At the current time no data are available that would allow us to provide a molecular explanation for this statement but it seems to be an unavoidable conclusion from these results.

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