Detection of Free Radicals from Low-Temperature Ozone–Olefin Reactions by ESR Spin Trapping: Evidence That the Radical Precursor Is a Trioxide

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Abstract: Free radicals are detected from the low-temperature ozonation of a series of olefins by using an electron spin resonance (ESR) spin-trap method. The technique involves ozonation at -78 °C in Freon-11, blowing out the ozone with an inert gas, adding the spin trap at -78 °C, and then warming the solution while in the probe of the ESR spectrometer. A series of small olefins was examined, and tetramethylethylene (TME) and 2-methyl-2-pentene (2-MP) gave the highest yield of radicals. However, even these two olefins give yields of radicals that are less than 1% on the basis of ozone consumed. Thus, our data indicate that while the nonradical Criegee ozonation process is the principal reaction for monoolefins, radical production is a significant side reaction. The temperature dependence of the appearance of spin adducts from both TME and 2-MP shows that the radical precursor in this case is a trioxidic species; specifically, we suggest that it is an alkyl hydrotrioxide, ROOOH. We propose that ROOOH is formed by allylic hydride abstraction from the olefin by ozone to give a pair of caged ions that combine to form the trioxide. (Benson has proposed a similar hydride abstraction for alkanes and several other types of compounds.) The reaction may proceed through a charge-transfer complex of the olefin and ozone as an intermediate.

Ozone–olefin reactions have been the subject of intensive study for over 100 years.[1,2] The principal reaction pathway in the liquid phase is accepted to be that proposed by Criegee,[2a] a mechanism that it is generally agreed does not involve free radicals. Nevertheless, ozone is known to react with several types of molecules to produce radicals that can be detected by electron spin resonance spectroscopy (ESR).[1,3–5] Ozone reactions also have been studied in experiments that model the conditions that occur when animals breathe polluted air.[4] In these experiments there is extensive evidence that ozone reacts with pulmonary target molecules to produce radicals; for example, radical scavengers and antioxidants (including vitamin E) protect polyunsaturated fatty acids (PUFA) in vitro and whole animals in vivo against the damaging effects of ozone.[4,5]

We have previously reported that ozone reacts with methyl linoleate to give radicals that can be spin trapped (although they cannot be directly detected by ESR).[5a] In this paper we report an extension of that work to simpler monoolefins in an effort to probe the mechanism of radical formation.

Experimental Section

A Varian E-109 ESR spectrometer was used with a TE-102 cavity equipped with a quartz Dewar insert for low-temperature work. The Varian temperature controller was used to regulate the temperature in the cavity.

Ozone–oxygen mixtures were produced by flowing oxygen through a Welsbach T-23 Ozone generator; ozone–nitrogen mixtures were produced by the usual method.[3,5] The ozone concentrations in the gas streams were measured by the method of Byers and Saltzman.[6]

The spin traps used in this study, α-phenyl-*N-tert*-butylnitrone (PBN) and 2-methyl-2-nitrosopropane (MNP), were purchased from Eastman Kodak and Aldrich Chemical Co., respectively, and were used without further purification. The olefins used in this study were purified to greater than 99.9% purity by preparatory gas chromatography on a Varian Aerograph 200 gas chromatograph equipped with a 30% SE-30 column. Multiple 10-μL sample injections of each olefin were made at 25 °C; the column was held at 25 °C for 10 min and then warmed at 5°/min up to 225 °C. The purified olefins were collected in a glass U tube immersed in a dry ice–acetone bath; the purity of the combined samples was determined by capillary gas chromatography using a Varian Model 3700 gas chromatograph. The Freon-11 solvent ($CFCl_3$) used in these experiments was pretreated with ozone for 15 min at -78 °C prior to use and then any residual ozone removed by flushing with argon for 30 min.

In a typical experiment, 0.5 mL of a 0.1 M solution of the olefin in $CFCl_3$ was placed in a quartz ESR tube suspended in a dry ice–acetone bath at -78 °C. The solution was ozonated with ozone–oxygen or ozone–nitrogen to about 50% reaction based on the ozone added. The ozonated solution was then flushed with argon for 15 min while at -78 °C to remove any unreacted ozone, and 0.5 mL of a 0.1 M solution of the spin trap in $CFCl_3$ (also at -78 °C) was added. (Due to the ease with which it photolyzes,[7] all experiments using MNP as spin trap were performed in a completely darkened room.) The olefin–spin-trap solution was further flushed with argon for an additional 15 min while still at -78 °C and the ESR tube transferred to the spectrometer cavity.

In some experiments, where no attempt was made to control the rate of warming of the ozonated olefin and spin-trap solution ("fast warmup"), the ESR tube containing the solution was quickly transferred from the low-temperature bath to the spectrometer cavity and allowed to warm to room temperature while ESR spectra were obtained every 30 s. In a modification of this "fast warmup" procedure, the final argon flush was not done and the ozonated olefin–spin-trap solution was allowed to warm to room temperature with dissolved oxygen still present ("modified fast warmup"). In a third method ("slow warmup"), the temperature of the Dewar insert was pre-set at -78 °C and the ozonated olefin–spin-trap solution was rapidly transferred to the Dewar insert; the temperature of the nitrogen gas was then raised in 10° increments, and ESR spectra were obtained at each new temperature setting after attaining thermal equilibrium. The amplitudes of the spin-adduct peaks were then plotted vs. time from removal of the solution from the low-temperature bath for the fast warmup and vs. temperature for the slow warmup procedure.[8]

Concentrations of spin adducts and hyperfine splittings were determined relative to standard solutions of di-*tert*-butyl nitroxide, a photolytic product of MNP, produced by deliberately photolyzing a 0.1 M solution

(1) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. I (Olefinic Compounds), and references therein.

(2) (a) Criegee, R. *Liebigs Ann. Chem.* **1953**, *103*, 1–36. (b) Bauld, N. C.; Thompson, J. A.; Bailey, P. S. *J. Am. Chem. Soc.* **1968**, *90*, 1822–1830.

(3) Prier, D. G. Ph.D. Dissertation, Louisiana State University, 1981.

(4) (a) Pryor, W. A. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1976; Vol. I, Chapter 1. (b) Pyror, W. A. *Photochem. Photobiol.* **1978**, *326*, 787–801. (c) Pryor, W. A. In "Molecular Basis of Environmental Toxicity"; Bhatnagar, R. S., Ed.; Ann Arbor Science: Ann Arbor, MI, 1980; Chapter 1. (d) Pryor, W. A. In "Environmental Health Chemistry"; McKinney, J. D., Ed.; Ann Arbor Science: MI, 1980; pp 445–467. (e) Menzel, D. B. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1976; Vol. II, Chapter 6.

(5) (a) Pryor, W. A.; Prier, D. G.; Church, D. F. *Environ. Res.* **1981**, *24*, 42–52. (b) Pryor, W. A.; Dooley, M. M.; Church, D. F. In "Advances in Modern Toxicology"; Mustafa, M. G., Mehlman, M. A., Eds.; Ann Arbor Press: Ann Arbor, MI, in press. (c) Pryor, W. A.; Stanley, J. P.; Blair, E.; Cullen, G. B. *Arch. Environ. Health* **1976**, *31*, 201–210.

(6) Byers, D. H.; Saltzman, B. E. *Adv. Chem. Ser.* **1959**, *21*, 93–101.

(7) (a) Janzen, E. G. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1980; Vol. IV, Chapter 4. (b) Broekhoven, F. J. G.; Bolsman, Th. A. B. M.; de Boer, T. J. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 12–16.

Table I. Relative Yields of Spin-Trapped Radicals

olefin	yields,[a] %	relative yield
cis-$CH_3CH_2CH=CHCH_2CH_3$	5.5×10^{-4}	(1)
trans-$CH_3CH=CHC(CH_3)_3$	6.0×10^{-4}	1.1
trans-$CH_3CH_2CH=CHCH_2CH_3$	1.1×10^{-3}	2.0
$CH_2=CHCH(CH_3)CH_2CH_2CH_3$	1.0×10^{-3}	5.7
$CH_2=CHC(CH_3)_3$	3.6×10^{-3}	6.6
$CH_2=C(CH_3)CH_2C(CH_3)_3$	1.0×10^{-2}	18.2
$CH_3C(CH_3)=C(CH_3)CH_3$	1.4×10^{-2}	25.0
$CH_3C(CH_3)=CHCH_2CH_3$	3.2×10^{-2}	58.0

[a] (Moles of spin adduct)/(mole of ozone added) × 100%.

of MNP in $CFCl_3$ and determining the concentration of the nitroxide spectrophotometrically.[7,9]

Results

Survey of Olefins. The yield of spin adducts was measured for the series of olefins listed in Table I. This survey was made by using the modified fast warmup procedure in which oxygen is present during warmup. In this method, carbon-centered radicals react with oxygen and unstable peroxyl spin adducts decay (see below) so the only ESR signal observed is due to the stable alkoxyl spin adducts. Two olefins, tetramethylethylene (TME) and 2-methyl-2-pentene (2-MP), gave the highest yields of spin adducts, as shown in Table I, and these two were subjected to more thorough study.

The spin-adduct yields shown in Table I range from 0.03 to 0.0006%, based on the amount of ozone added. This calculation assumes that all radicals are trapped with 100% efficiency. However, it is known that spin trapping can be extremely inefficient, as low as 1% or lower.[10-12] Thus, the yields reported in Table I must be taken merely as lower limits for the yields of radicals from these ozone–olefin reactions. Nevertheless, it is clear that the principal ozone–olefin reaction is the Criegee process. Radical production from ozone–olefin reactions either is a slower independent process or a very small yield of radicals "leaks" out of the Criegee process.

Ozonation of Tetramethylethylene (TME). When an ozonated solution of TME is mixed with PBN at -78 °C, a very weak ESR spectrum is obtained that cannot be assigned (Figure 1A). As the temperature is raised in 10° intervals, the absorption begins to increase slowly. When the temperature approaches -35 °C, as shown in Figure 2, the signal intensity begins to increase very rapidly. The spectrum obtained at -30 °C, shown in Figure 1B, consists of two superimposed signals: a triplet of doublets with $a(N) = 1.31$ and $a(H) = 0.14$ mT and a triplet of doublets that has $a(N) = 1.35$ and $a(H) = 0.18$ mT. The former splittings are consistent with either a acyloxyl radical spin adduct of PBN (**1a**)

1a   1b   2
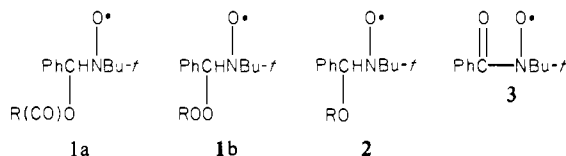
(8) Peak shapes did not appear to depend on temperature, and peak heights were used as an approximate measure of relative concentration of spin adducts. The work done here was performed on a Varian ESR spectrometer without computer attachement. Using our newer IBM ESR spectrometer with Aspect computer, we have compared peak height with peak area for nitroxide signals; the two appear to give comparable results within the overall accuracy of the spin-trap method.

(9) Knauer, B. R.; Napier, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 4395–4400.

(10) Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1979**, *101*, 4975–4981.

(11) Schmid, P.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 2493–2500.

(12) (a) For example, Merritt and Johnson[12b] report that alkoxyl radicals are spin trapped by PBN with only about 0.2% efficiency at 0.1 M PBN; their system is complex and involves the production of radicals from the reactions of potassium superoxide with an alkyl bromide at room temperature in benzene or Me_2SO in the presence of a crown ether. (b) Merritt, M. V.; Johnson, R. A., *J. Am. Chem. Soc.* **1977**, *99*, 3713–3719. (c) Since M is an even-electron species, it must give a pair of free radicals.
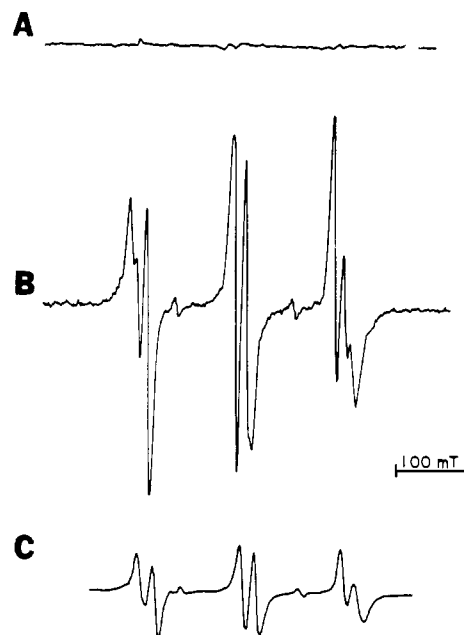

Figure 1. Spectra resulting from the ozonation of tetramethylethylene at -78 °C followed by flushing, addition of PBN, and slow warmup. (A) At -78 °C, showing only a weak, unassigned signal. (B) At -30 °C, showing a spectrum attributable to both **1** and the alkoxyl adduct of PBN; in addition, a weak signal due to PBNOx can also be seen. (C) At room temperature, showing a spectrum attributable primarily to the alkoxyl adduct of PBN with an additional weak signal due to PBNOx. The relative gains for A:B:C are 4:6:1.
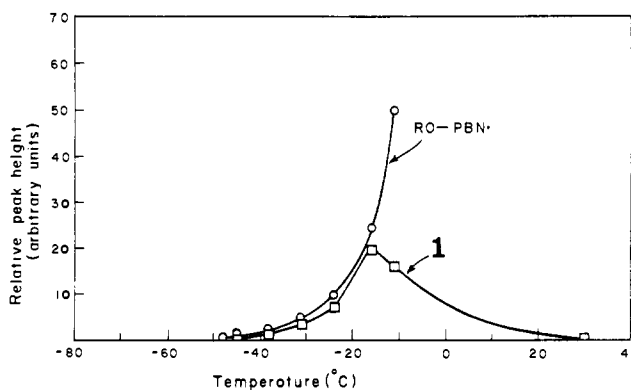

Figure 2. Relative peak heights of **1** and the alkoxyl radical spin adduct of PBN from a solution of tetramethylethylene that was ozonated at -78 °C and then slowly warmed to room temperature in the presence of PBN.

or a peroxyl radical adduct (**1b**); the latter are consistent with an alkoxyl radical spin adduct (**2**).[12b] The weaker triplet signal that is visible in Figures 1B and 1C with $a(N) = 0.77$ mT is due to benzoyl-*tert*-butyl nitroxide, (PBNOx, **3**) an oxidation product of PBN.[13] Spin adduct **1** continues to grow in intensity until the temperature of the solution reaches about -15 °C where it starts to decay (Figure 2); the alkoxyl radical spin adduct continues to grow until the temperature of the solution reaches room temperature (Figure 1C). Identical results are obtained when the ozonation is performed with ozone–nitrogen.

When the ozonated solution of TME and PBN is allowed to warm to room temperature without the low-temperature controller (fast warmup), both **1** and the alkoxyl spin adducts are once more observed (Figure 3A). The two signals are superimposed and appear simultaneously within the first minute after removal of the solution from the low-temperature bath. After 2–4 min, adduct **1** begins to decrease in intensity and is no longer observed after 5 min out of the low-temperature bath; the alkoxyl spin adduct

(13) Janzen, E. G. In "Creation and Detection of the Excited State"; Ware, W. R., Ed.; Marcel Dekker: New York, 1976; Chapter 3.
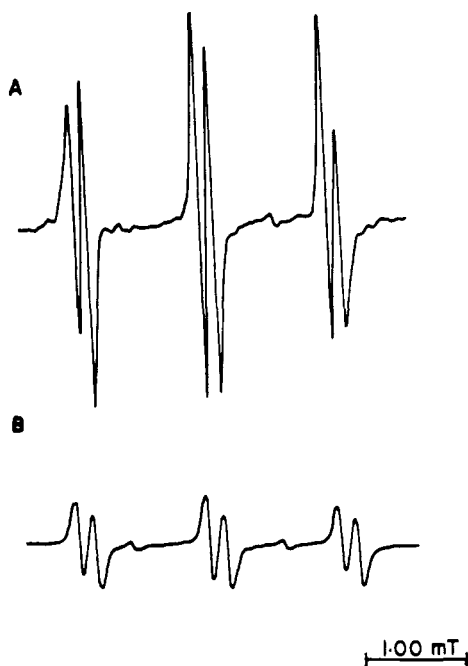
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Figure 3. Spectra resulting from the ozonation of tetramethylethylene at −78 °C followed by flushing, addition of PBN, and fast warmup. (A) Spectrum obtained about 1 min after removing sample from the −78 °C bath. The strong signal is due to adduct **1**; a weaker signal due to the alkoxyl adduct is observable as a shoulder. (B) Spectrum after 5 min, by which time the solution has reached room temperature. The signal is due to an alkoxyl adduct of PBN; a much weaker PBNOx signal is again observed. Relative gains for A:B are 5:1.

persists for over an hour after the solution has reached room temperature (Figure 3B). The signal due to PBNOx is again observed and persists at room temperature for over an hour. Again, identical results are obtained when the ozonation is performed with ozone–nitrogen.

The above results suggest that the radicals we spin trap may arise from a common nonradical intermediate, M, which decays to give a pair of radicals, Q·, as shown in eq 1.[12c] If eq 1 is slow relative to the spin-trapping reaction, (eq 2), then the rate of

$$M \xrightarrow{k_m} 2Q\cdot \tag{1}$$

$$Q\cdot + \text{spin trap} \xrightarrow{\text{fast}} \text{spin adduct} \tag{2}$$
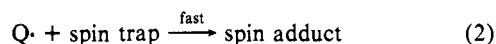
appearance of the spin adduct, SA, is equal to the rate of radical formation, corrected for f, the efficiency of radical production from M, and e, the efficiency of spin trapping (eq 3). For a large excess

$$\frac{d[SA]}{dt} = -2ef\frac{d[M]}{dt} \tag{3}$$

of spin trap, ST, in solution relative to the Q· radicals or M, the final yield of spin adduct, $[SA]_f$, is equal to $2ef[M]_0$, where $[M]_0$ is the initial concentration of M.

Thus, at a given temperature, the concentration of M remaining at time t can be expressed as in eq 4.[14] Equations 3 and 4 lead to eq 5 and 6.

$$2ef[M] = [SA]_f - [SA]_t \tag{4}$$

$$\frac{d[SA]}{dt} = k_m ([SA]_f - [SA]_t) \tag{5}$$

$$-\log\left|\frac{[SA]_f - [SA]_t}{[SA]_f}\right| = 2.303 k_m t \tag{6}$$

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(14) In the nonpolar solvent, CFCl₃ (fp = −111 °C), very little change is observed in a given ESR spin-adduct spectrum in going from −78 °C to room temperature.

Table II. Rate Constants for Appearance of Spin Adducts in the TME–PBN–Ozone System

| T, °C	k_m,[a] s⁻¹
−61	8.8×10^{-6}
−51	3.6×10^{-5}
−40	1.6×10^{-4}

[a] Defined in eq 6.

Thus, a plot of log ($[SA]_f - [SA]_t$) vs. t should give a straight line, the slope of which is $-2.303 k_m$. The rate constants k_m resulting from such plots[3] at three temperatures are listed in Table II.[15] These data give activation parameters of log A = 9 and E = 14 kcal/mol (see Discussion below).

Ozonation of 2-Methyl-2-pentene (2MP). When 2-MP was ozonized at −78 °C and then slowly warmed to room temperature, similar results were obtained as those with the TME; spin adduct **1** appears, only to decay as the temperature is raised further. At room temperature, the only spin adduct left, other than PBNOx, is that due to an alkoxyl radical.

The ozonation of 2-MP also was studied by using the fast warmup procedure. Three spin-adduct signals are obtained: spin adduct **1**, PBNOx, and a triplet of doublets with $a(\text{N})$ = 1.40 and $a(\text{H})$ = 0.30 mT, values consistent with an acyl radical spin adduct of PBN.[16] The peak heights, adjusted for attenuation, of the three radicals observed are plotted in Figure 4 vs. t, the time from removal of the ozonated solution from the low-temperature bath to the start of the ESR scan. Spin adduct **1** is observed as a rapidly growing triplet of doublets that appears, reaches a maximum, and vanishes within the first 3 min after removal of the solution from the low-temperature bath; the acyl adduct and PBNOx are more persistent.

Figure 5 shows the ESR spectrum that is obtained when an ozonated solution of 2-MP is warmed from −78 °C in the presence of MNP in the fast warmup procedure. The spectrum consists of a triplet of triplets with $a(\text{N})$ = 2.92 and $a(\text{H})$ = 0.11 mT, consistent with a primary alkoxyl radical spin adduct of MNP (**4**),
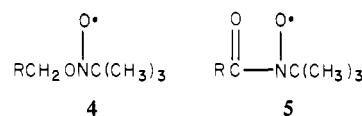
and a triplet with $a(\text{N})$ = 0.77 mT, consistent with a spin-trapped acyl radical (**5**).[17] The alkoxyl spin adduct rapidly decays as the temperature of the solution reaches room temperature.[18]

Discussion

Our spin-trapping results for the ozone–TME and ozone–2-MP systems are summarized in Table III. Using the slow warmup protocol (see Experimental Section), we find the same results for both olefins; the differences observed when using the fast warmup procedure appear to reflect the presence of aldehyde produced during the ozonation of 2-MP (but not TME) and will be discussed presently.

Production of a Trioxidic Species in the Ozonation of Olefins. We wish to suggest that the radicals that are spin trapped on ozonation of both TME and 2-MP result from the decomposition of a trioxidic species.[19,20] Figure 6 compares the temperature

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(15) In this experiment $(SA)_f$, the maximum spin-adduct concentration, was measured at −30 °C where both spin adduct **1** and the alkoxy spin adduct are stable; above this temperature and adduct **1** is not stable.

(16) Janzen, E. G.; Lopp, I.; Hongany, T. V *J. Phys. Chem.* **1973**, *77*, 139–141.

(17) Mackor, A.; Wajer, Th. A. J. W.; de Boer, T. J. *Tetrahedron* **1968**, *24*, 1623–1631.

(18) Alkoxyl radical spin adducts of MNP are known to be unstable at room temperature: (a) Sargent, F. P.; Gardy, E. M. *Can. J. Chem.* **1974**, *52*, 3645–3650. (b) Sargent, F. P. *J. Phys. Chem.* **1977**, *81*, 89–90.

(19) (a) Nangia, G. A.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105–3115. (b) Bartlett, P. D.; Lehav, M. *Isr. J. Chem.* **1972**, *10*, 101–109. (c) Pryor, W. A.; Kurz, M. E. *J. Am. Chem. Soc.* **1978**, *100*, 7653–7959. (d) Bartlett, P. D.; Gunther, P. *Ibid.* **1966**, *88*, 3288–3294. (e) Bartlett, P. D.; Guaraldi, G. *Ibid.* **1967**, *89*, 4799–4801. (f) Benson, S. W. In "Thermochemical Kinetics"; 2nd ed.; Wiley: New York, 1976; pp 97.
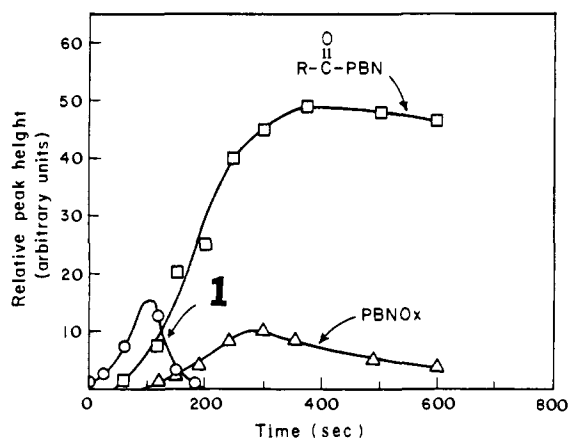
Figure 4. Relative peak heights of **1** and the acyl radical spin adduct of PBN and of PBNOx from 2-methyl-2-pentene that was ozonated at −78 °C and then allowed to rapidly warm to room temperature, plotted vs. the time out of the −78 °C bath.
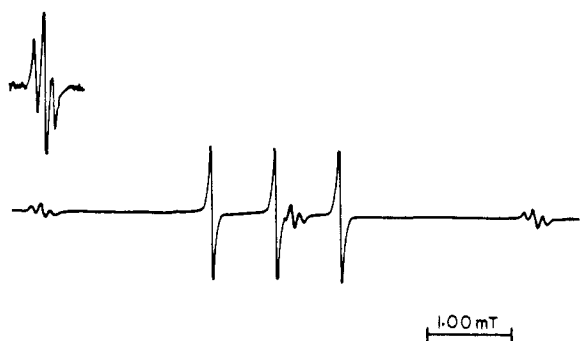

Figure 5. Spectrum resulting from the ozonation of 2-methyl-2-pentene at −78 °C followed by flushing, addition of MNP, and fast warmup to room temperature. The signals can be assigned to a spin adduct of a primary alkoxyl radical, $RCH_2ON(O\cdot)C_4H_9\text{-}t$, and an acyl adduct of MNP, $RC(=O)N(O\cdot)C_4H_9\text{-}t$. The insert shows the downfield triplet at a gain 20 times greater.

profile for appearance of the alkoxyl spin adduct from the TME–PBN–ozone system with that for the thermal decomposition of di-*tert*-butyl trioxide, determined from the rate of oxygen evolution by Bartlett and Gunther.[19d] If allowance is made for the much greater sensitivity of the ESR method relative to oxygen evolution, it appears that the radical precursor in the TME–PBN–ozone system has a temperature profile for decomposition that is much like that of di-*tert*-butyl trioxide.[21]

Table IV gives the calculated activation energies and rate constants for decomposition of a homologous series of oxygenated compounds.[19f] The data show that the radical precursor in our system could *not* be either a peroxide or a tetroxide but that all four of the trioxide species that are listed must be considered.[22] Therefore, we hypothesize that a trioxygen species is the radical precursor, M.

(20) (a) Deslongchamps, P.; Moreau, C., Frehel, D., Atlani, P. *Can. J. Chem.* **1972**, *50*, 3402–3404. (b) Deslongchamps, P.; Atlani, P.; Frehel, D.; Malaval, A.; Moreau, C. *Ibid.* **1974**, *52*, 3651–3664. (c) Kovac, F.; Plesnicar, B. *J. Chem. Soc., Chem. Commun.* **1978**, 122–124. (d) Kovac, F.; Plesnicar, B. *J. Am. Chem. Soc.* **1979**, *101*, 2677–2681.
(21) These data have been scaled in a way that affects the comparison but appears to be reasonable in view of the differences in the two systems.
(22) (a) The measured activation energy for appearance of the spin adduct in the TME system is 14 kcal/mol, far lower than the value of 20–23 kcal/mol expected for decomposition of a trioxide, and the experimental log *A* value is 9, a value that is lower than the expected log A of 16 ± 1 for a unimolecular homolysis.[19f,22b] If the activation energy is assumed to be 23 kcal/mol, the expected value, a value of log *A* of 19 is obtained, close to the expected value; this parallel in errors in *E* and log *A* values for real data is quite common and may explain our low values. In addition, it is possible that there is a chain component to the decomposition, even in the presence of the spin trap, a factor making both log *A* and *E* too small. The Arrhenius parameters for decomposition of trioxidic species are discussed in ref 22b. (b) Pryor, W. A.; Ohto, N.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5813.
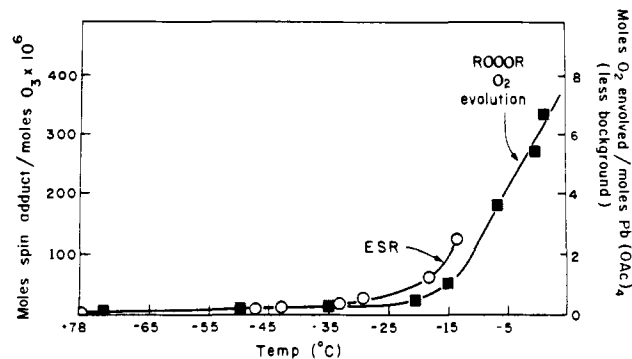

Figure 6. Comparison of the temperature profile for oxygen evolution from di-*tert*-butyl trioxide and the appearance of ESR signal in the tetramethylethylene–PBN–ozone system. The data have been scaled so as to make them comparable, although the amounts of reaction differ substantially in the two cases. The oxygen evolution data are taken from ref 19d.

Table III. Summary of Spin Adducts Observed from the Ozonation of Tetramethylethylene (TME) and 2-Methyl-2-pentene (2-MP)

	spin adduct(s)	
protocol and spin trap	TME	2-MP
slow warmup; PBN	$R(CO)O\text{-}/ROO\text{-}$[a] RO– PBNOx	$R(CO)O\text{-}/ROO\text{-}$[a] RO– PBNOx
fast warmup; PBN	$R(CO)O\text{-}/ROO\text{-}$[a] RO– PBNOx	$R(CO)O\text{-}/ROO\text{-}$[a] R(CO)– PBNOx
fast warmup; MNP		$RCH_2O\text{-}$ R(CO)–

[a] Identified as "spin adduct **1**" in the text; see discussion in text.

Table IV. Calculated Bond Dissociation Energies and Rate Constants for Decomposition of Oxygenated Species

		log k^c	
compound[a]	BDE[b]	−78 °C	−35 °C
dioxide species			
ROOH	43	−32	−24
ROOR	38	−27	−19
trioxide species			
ROOOR	23	−9.8	−5.1
ROOOH	23	−9.8	−5.1
$CH_3(CO)OOOH$	20	−6.4	−2.4
$CH_3(CO)OOO(CO)CH_3$	20	−6.4	−2.4
tetroxide species			
ROOOOR	7.4	7.7	9.2

[a] R is taken as *tert*-butyl, but BDE is constant for all alkyl groups. [b] The BDE is for the weakest O–O bond. [c] Assuming $\Delta H = E_a$, log $A = 16$, and with k in s^{-1}.

We wish to suggest that the intermediate is a hydrotrioxide, ROOOH. However, before considering possible routes to a hydrotrioxide from the reaction of olefins with ozone, it would be useful to eliminate some unlikely possibilities. First, the primary ozonide (the 1,2,3-trioxolane) is itself a trioxide, but it is generally agreed that it decomposes by a synchronous path that does not involve homolysis to a diradical intermediate;[1,19a] in addition, it would decompose below −78 °C whereas our radical precursor is stable at −78 °C.

A second unlikely mechanism is the homolysis of ozone itself (eq 7). Since the BDE for the ozone molecule is 26 kcal/mol,

$$O_3 \rightarrow O_2 + O \tag{7}$$

it is clear that reaction 7 cannot contribute to radical production at the reduced temperatures we have studied. In any case, the experimental design used here involves blowing out all unreacted ozone before spin traps are added. Furthermore, there is no mechanism to produce trioxide species starting from eq 7.
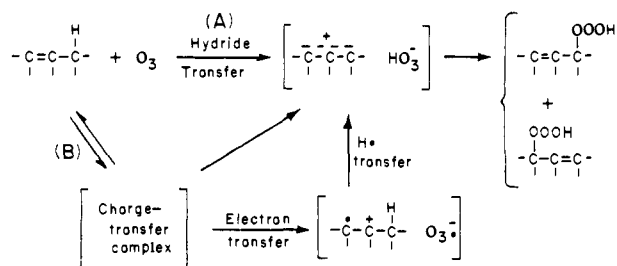
Free Radicals from Ozone–Olefin Reactions

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Scheme I

Table V. Calculated Rate Constants for Hydrogen Abstraction by Ozone

$$RH + O_3 \xrightarrow{k} R\cdot + HO_3\cdot$$

| substrate RH	R–H BDE	ΔH^a	log k^b −78 °C	37 °C
RH	98	29	−25	−12
allylic H	87	18	−12	−3
1,4-pentadiene H	84	15	−9	−2

^{a} Calculated from BDE. ^{b} In units of L/mol·s. Calculated assuming log $A = 8.5$ and $\Delta H = E$.

Another unlikely possibility is that hydroperoxides react with ozone to form radicals (eq 8). This reaction can occur at reduced

$$ROOH + O_3 \rightarrow ROO\cdot + HO\cdot + O_2 \qquad (8)$$
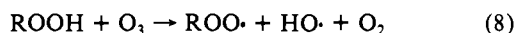
temperatures, but it is too slow for an appreciable fraction of the ozone to react with hydroperoxides in competition with olefin when both are present.[19c] Furthermore, this would not rationalize the production of the initial hydroperoxide.

One might suggest that ozone directly abstracts an allylic hydrogen atom in composition with addition to the double bond.[22] This process is shown in eq 9.[22] Benson has calculated[19a] the

$$RH + O_3 \rightarrow (R\cdot \, \cdot O_3H) \rightarrow ROOOH \qquad (9)$$
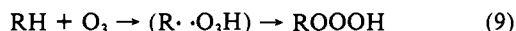
H–OOO· bond dissociation energy (BDE) to be 69 kcal/mol, making the abstraction of an allylic hydrogen by ozone endothermic by 18 kcal/mol. Table V shows calculated rate constants for reaction 9 for various hydrogen donors at both −78 and 37 °C. The value of log k of −12 at −78 °C for hydrogen abstraction from an olefin indicates this reaction cannot be important at the temperature where the radical precursor is formed in our experiments.[23]

Thus, to explain trioxide production in our system, one is left with an ion-pair process such as that recently suggested by Benson[19a] to rationalize the low-temperature reactions of ozone with alkanes, alcohols, and hydrotrioxides. This process involves hydride abstraction to produce an ion pair that collapses to form a hydrotrioxide (eq 10). Benson calculates that in favorable cases,

$$RH + O_3 \rightarrow [R^+ + HOOO^-] \rightarrow ROOOH \rightarrow RO\cdot + HOO\cdot \qquad (10)$$
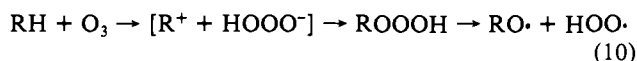
such as where R^+ is a *tert*-butyl carbocation, about 5 eV from electrostatic interaction and 1 eV of solvation energy are released even in a hydrocarbon solvent; this is sufficient to make the overall reaction approximately thermoneutral. Clearly, an allylic cation also would be such a favorable case;[22] however, it is unprecedented to suggest that ozone can react with allylic hydrogen atoms in competition with addition to the double bond, an extremely exothermic process. Our results show that radical production is a small fraction of the total reaction. A radical production pathway that is from 10^2 to 10^6 slower than the Criegee dipolar addition process could be consistent with our data.
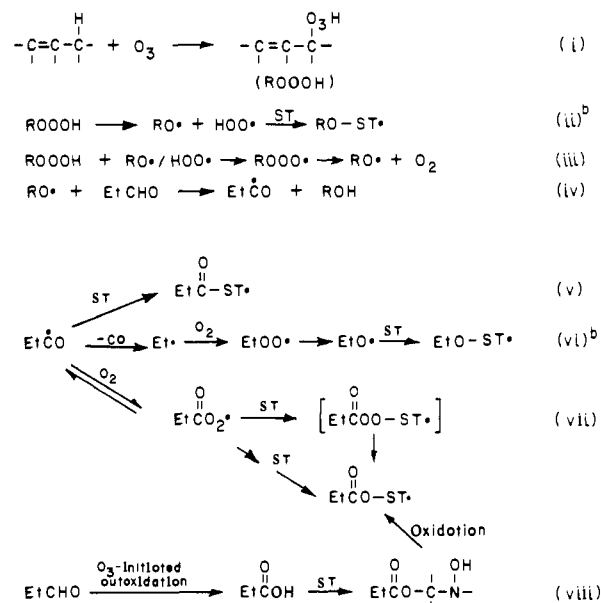
Scheme II[a]

^{a} ST is a spin trap. ^{b} Both HOO-ST· and ROO-ST· are too unstable to be detected with PBN.

The ion-pair intermediate shown in eq 10 could also be formed via a charge-transfer (CT) complex,[24] as shown in Scheme I, path B. CT complexes between ozone and a number of organic substrates,[24] including olefins, have been proposed on the basis of spectroscopic studies at low temperatures. We have presented evidence[24b] that cumene reacts with ozone via a CT complex; however it is not clear that the CT complex of olefins and ozone would be sufficiently stable for the CT pathway to be important.

Mechanism for the Production of Radicals from the Ozonation of TME and 2-MP. Thus, we suggest that the radical precursor for olefins that possess allylic hydrogens is a hydrotrioxide that results from hydride abstraction, possibly via a charge-transfer complex[22b,24,25] (Scheme I). Hydrotrioxides would thermally decompose to the alkoxyl radicals that we spin trap (Scheme II, eq ii). The hydroperoxyl radicals that are also produced when hydrotrioxides decompose are not trapped as efficiently as the alkoxyl radicals;[12b] thus one would not expect to observe the hydroperoxyl radical adduct at the same time as the alkoxyl adduct.
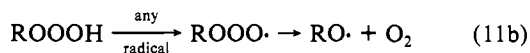
We cannot at this time unambiguously identify the spin adduct **1**. The observed splitting constants are intermediate between those observed for peroxyl[12b] and acyloxy[26b] adducts of PBN. (The literature suggests[26a] that the hydroperoxyl adduct of PBN has a somewhat larger hydrogen hfsc than we observe for spin adduct **1**.) From a mechanistic point of view, however, it is difficult to imagine a process in which acyloxyl radicals would be formed in the ozonation of TME; for this olefin, therefore, it seems most

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(23) Reaction 9 does become fast (with log $k = -2$) at 37 °C when the donor is a diene; thus, reaction 9 could contribute to radical production when mammals breathe polluted air and expose pulmonary polyunsaturated fatty acids to ozone.[5b]

(24) (a) Bailey, P. S.; et al. *J. Am. Chem. Soc.* **1974**, *96*, 6136. (b) Cumene reacts with ozone in to give a charge-transfer (CT) complex at −78 °C. Cumyl hydrotrioxide can be produced by photolyzing the CT complex at −78 °C. Cumyl hydrotrioxide can be produced by photolyzing the CT complex at −78 °C or heating it to −40 °C. On warming to −35 °C, the trioxide decomposes to produce cumyl alcohol, among other products, and peroxyl radicals can be detected directly by ESR. See ref 22b.
(25) (a) Our evidence for the intermediacy of a charge-transfer intermediate in the production of a hydrotrioxide was obtained in a study of cumene as a substrate.[24b] Olefins are far more reactive in the Criegee process than is an aromatic compound, and olefins may not react with ozone via a CT complex for this or other reasons. (b) A π-complex was suggested as an intermediate in the reaction of trimesitylvinyl alcohol with ozone. Bailey, P. S.; Ward, J. W.; Potts, F. E.; Change, Y.; Hornish, R. E. *J. Am. Chem. Soc.* **1974**, *96*, 7228. (c) Hull, L. A.; Hisatune, I. C.; Heicklen, J. *Ibid.* **1972**, *94*, 4856. (d) However, for a paper that discounts the idea of ozone–olefin complexes, see: Nelander, B.; Nord, L. *Ibid.* **1979**, *101*, 3769.
(26) (a) Janzen, E. G.; Nutter, D. E. Davis, E. R.; Blackburn, B. J.; Poyer, J. L.; McCay, P. B. *Can J. Chem.* **1978**, *56*, 2237. (b) Janzen, E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1969**, *91*, 4481.

reasonable to assign spin adduct **1** as a peroxyl radical adduct. The route to peroxyl radicals from a hydrotrioxide requires discussion. The decomposition of a hydrotrioxide would be expected to lead to alkoxyl radicals, both from the initial homolysis (eq 11a)[29a] and from an induced decomposition (eq 11b). However,

$$ROOOH \rightarrow RO\cdot + HOO\cdot \tag{11a}$$

$$ROOOH \xrightarrow[\text{radical}]{\text{any}} ROOO\cdot \rightarrow RO\cdot + O_2 \tag{11b}$$

eq 11b produces oxygen in situ in these experiments; furthermore, oxygen is present even at time zero, since it is not possible to completely deoxygenate solutions in thin ESR tubes by flushing with an inert gas.[26] (Oxygen also could be produced from the combination reactions of ROO· and HOO· radicals that are present.[27]) Thus, carbon-centered radicals would be expected to react with oxygen and be converted to peroxyl radicals, eq 11c,

$$R\cdot + O_2 \rightarrow ROO\cdot \tag{11c}$$

in competition with being spin trapped. Carbon-centered radicals are expected to arise in these experiments from abstraction of allylic hydrogen atoms by any radical present in the system (eq 11d). Therefore, peroxy radicals can be produced by the sequence of reactions 11d, 11c (with O_2 arising in eq 11b); this rationale

$$\text{olefin} \xrightarrow[\text{radical}]{\text{any}} R\cdot \tag{11d}$$

is consistent with the observation that both alkoxyl radical spin adducts and spin adduct **1**, the peroxyl radical adduct, are observed at about the same temperature when TME is the substrate (see Figure 2).

When 2-MP is the substrate, both spin adduct **1** and alkoxyl spin adducts are observed, as in the case with TME. However, for 2-MP, with both PBN and MNP as the spin trap, acyl adducts are observed during the first warmup procedure. Propanal is produced from the ozonolysis of 2-MP, and we believe the acyl adducts arise from acyl radicals produced from this aldehyde product. Aldehydes are known to react with ozone to give radicals; in fact, the ozone-initiated autoxidation of acetaldehyde to peracetic acid is a commercial process.[28] However, in the presence of high concentrations of olefins, which are more reactive toward ozone than is an aldehyde, it is likely that radical production from the direct reaction of ozone with the aldehyde is relatively unimportant.[29b] Perhaps a more likely mechanism for the formation of acyl radicals, therefore, is the hydrotrioxide-initiated autoxidation of aldehydes. (See Scheme II, eq i–v.)

When 2-MP is the olefin we again see spin adduct **1**. In the discussion on TME above, spin adduct **1** was identified as a peroxyl adduct; however, in the case of 2-MP, a reasonable mechanism can be written to rationalize the production of an acyloxyl spin adduct, Scheme II, eq vi–viii. We have previously discussed the trapping of acyloxyl radicals,[31a] which generally are thought[31b] to decarboxylate faster than they could be spin trapped. We believe acyloxyl spin adducts often arise[31a] from pathways that do not involve acyloxyl free radicals. In the 2-MP system studied here, the production of both propanoic peroxyacid and carboxylic acid is likely, and both these species are known to react with spin traps (either by radical or nonradical pathways) to give products that can be oxidized to acyloxyl spin adducts (Scheme II, eq vii and viii). Further evidence for acyloxyl radicals from 2-MP is that with MNP as the spin trap, we also identify a spin adduct that arises from a *primary* alkoxyl radical. This $RCH_2O\cdot$ radical could arise from decarbonylation of the propanoyl radical to give an ethyl radical that might react with oxygen to form the ethylperoxyl radical (see Scheme II, eq vi). Peroxyl radicals are not readily trapped by nitroso spin traps[30] and would be expected to be converted to the corresponding alkoxyl radicals that are then spin trapped.

Conclusions

The temperature profile for appearance of spin adducts from both tetramethylethylene and 2-methyl-2-pentene is consistent with some type of trioxidic species being the immediate radical precursor. Neither a peroxide (which is far too stable) nor a tetroxide (which would decompose at a much lower temperature than we observe spin-adduct formation) can be the radical precursor. The nature of the trioxide is less certain; as shown in Table IV, virtually any type of trioxidic compound can rationalize the temperature profile for spin-adduct appearance that we observe. At present, we postulate that the trioxide is a hydrotrioxide, since a reasonable mechanism can be suggested for hydrotrioxide formation.[22b] It must be stressed, however, that the evidence presented here indicates that the radical precursor is a trioxide but does not indicate the nature of the trioxidic species. Further, it has not yet been demonstrated that olefins react with ozone to form allylic hydrotrioxides.

(27) The appearance of oxygen in these solutions from the decomposition of an unstable species can be observed by the slow broadening of the ESR signal that occurs as an initially deoxygenated solution becomes oxygenated.

(28) (a) Bailey, P. S. In "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. I, Chapter V. (b) Wei, Y. K.; Cvetanovic, R. J. *Can. J. Chem.* **1963**, *41*, 913.

(29) (a) Homolysis of ROOOH to give RO· and HOO· is favored over the split to give ROO· and HO· by kcal/mol. Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976. (b) When a 1:1 mixture of propanal and TME is ozonized at −78 °C and then warmed to −40 °C, a peroxyl radical can be detected by ESR. (Pryor, W. A.; Ohto, N., unpublished; also see ref 22b). Since peroxyl radicals cannot be directly observed by ESR from the ozonation of TME, it is clear that some interaction of these two substrates leads to the peroxyl radicals that are detected. One possibility is that radicals produced by the reaction of ozone and TME initiate the autoxidation of the aldehydes, leading to peroxyl radicals.

(30) (a) Howard, J. A.; Tait, J. C. *Can. J. Chem.* **1978**, *56*, 176. (b) Pfab, J. *Tetrahedron Lett.* **1978**, 843.

(31) (a) Pryor, W. A.; Govindan, C. K.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 7563–7566. (b) Forrester, A. R.; Hepburn, S. P. *J. Chem. soc. C* **1971**, 701.