

Initiation of Methyl Methacrylate Polymerization by the Nonvolatile Products of a Methyl Methacrylate Plasma. 4. An ESR Study of the Initiating Radicals

Charles W. Paul,[†] Alexis T. Bell,* and David S. Soong

Department of Chemical Engineering, University of California, Berkeley, California 94720.
Received September 16, 1985

ABSTRACT: The oil produced in a plasma sustained in methyl methacrylate (MMA) can serve as an initiator for free radical polymerization of MMA. In this study, ESR spectroscopy and the spin-trap method have been used to establish that the radicals produced upon thermal decomposition of the plasma-produced oil are part of bulky structures, centered on tertiary carbon atoms, and that the difference between the activation energy for generation and termination of free radicals is only 9 kcal/mol. It is postulated that this unusually low activation energy difference is due to strong repulsive forces in the oil molecules, resulting from a very congested molecular structure.

Introduction

Osada et al.¹ have reported that addition-polymerization initiators can be formed in the low-pressure plasma (or glow discharge) of certain vinyl compounds. Subsequently, other reports of this phenomenon have appeared with both vinyl²⁻⁵ and saturated^{6,7} compounds. With methyl methacrylate (MMA), it has been established that the initiator is present in a nonvolatile oily deposit formed on the walls of the plasma zone.² A recent study⁷ that used this oil to initiate MMA polymerization established that the oil generates initiating free radicals unimolecularly. The initiator is not a single compound, since size exclusion chromatography yields fractions, all of which are effective as initiators. While their effectiveness varies, the activation energy for radical generation is about the same for each fraction and close to that for the unfractionated oil. A structural characterization of the plasma-produced oil has revealed⁸ that its molecular weight is about 500 and it does not resemble PMMA oligomers. The oil contains about 6% olefinic carbon atoms and about half the oxygen of MMA—most of it is in the starting methyl ester form. In the present study, the structure of the free radicals generated by the oil and the activation energy for their generation were investigated with ESR spectroscopy and the spin-trap method. On the basis of the results obtained, it is postulated that the unusually low activation energy for free radical formation is a consequence of steric repulsions in the oil molecular structure.

Experimental Section

The system and conditions employed to produce and collect the nonvolatile oily product of a MMA plasma were those previously described.⁷ The discharge was created with two parallel-plate electrodes (10 cm × 15 cm and 1.4 cm apart) placed outside a 0.9-cm-o.d. glass tube through which MMA vapor was flowing at a pressure of ~9 torr and with a residence time of 4–9 s. The power was 40 W and the frequency 13.56 MHz. The oily deposit dripped from the plasma zone into a collection vessel. Several grams were collected in 1–3.5 days.

Electron spin resonance (ESR) spectra were recorded with a Varian 4502 system equipped with a 9-in. magnet and operating at ~9 GHz. The exact frequency was measured with a Hewlett-Packard 5255A frequency converter attached to a Hewlett-Packard 5245L electronic counter. The magnetic field was modulated at a frequency of a 100 kHz with a Varian V-4560 modulation and control unit. Sample tubes were placed in a Varian-4531 microwave cavity. For variable-temperature operation, the sample was placed in a quartz Dewar that extended through the cavity.

Wilmad 707 SQ (4.0-mm-o.d., 3.0-mm-i.d.) quartz ESR tubes were used. The tubes were cleaned by repeated rinsing with acetone and then dried in an oven. After the tubes had cooled, a rubber serum stopper was placed over the open end of each tube to prevent the entry of dust. No tube was used more than once with an oil-containing solution.

Samples of undiluted plasma-produced oil were added to the bottom of ESR tubes with a 12-in. syringe needle. This procedure ensured that there would be no oil adhering to the walls of the ampule at the point where it was to be sealed. Any such oil would be charred during sealing and possibly produce free radicals. Samples for spin-trapping experiments were prepared as follows. First, trap/benzene and plasma-produced oil/benzene solutions were prepared in 25-mL glass-stoppered Erlenmeyer flasks. These solutions were stored on dry ice until needed. On the day of an experiment, these solutions were thawed, and the desired volume of each was added to an ESR tube. The sample was then degassed on a vacuum manifold capable of 10⁻³ torr by three or more applications of the freeze-evacuate-thaw procedure. The tube was then sealed under vacuum with a torch.

Three different spin-trap molecules were used: (1) *N*-tert-butyl- α -phenylnitrone (PBN), (2) 2-methyl-2-nitrosopropane (NtB), and (3) 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO). All three were purchased from Aldrich Chemical Co. and used as received. To avoid their photodegradation, these compounds were handled with minimal exposure to light. Since DMPO is also oxygen sensitive, it was handled in a nitrogen-filled glovebag.

The magnetic field scan was calibrated and free radical *g* values were determined by reference to a spectrum, taken on the same day, of 2,2,6,6-tetramethylpiperidinoxy (TEMPO) (purchased from Aldrich Chemical Co.) dissolved in benzene. This solution was degassed and sealed as previously described. The *g* value of this stable free radical in benzene was estimated to be 2.0061 ± 0.0004, based on data in other solvents.^{9,10} Three different values for the nitrogen hyperfine splitting constant, *a*_N, of TEMPO have been reported^{9,11,12} ranging from 15.12 to 15.4 G. The most recently reported value,¹² 15.3 G, was for this study.

Solutions of TEMPO in benzene were also used for experiments in which either the absolute or relative free radical concentration was to be determined. All tubes to be used in these experiments were filled with a 1.6 × 10⁻⁶ g/mL solution of TEMPO in benzene, and ESR spectra were recorded for each under identical operating conditions. In this way, the influence of variations in sample tube diameter and wall thickness on the intensity of the TEMPO signal was evaluated. The tubes were then emptied, rinsed 5 times with toluene and twice with acetone, and oven dried. When the spectra of oil-containing samples in these tubes were recorded, they were always put in the same position in the microwave cavity that they had been in when they were filled with TEMPO. Sufficient sample was added to each tube (>5-cm liquid height) so that any difference in the amount added had no effect on relative sensitivities. Relative concentrations of the same free radical in different tubes could then be evaluated by comparing peak heights (adjusted for differences in tube sensitivity) in their ESR spectra recorded under identical conditions.

[†] Present address: Allied Corporation, Morristown, NJ 07960.

Power = 60 mw
Mod. = 6 G
Amp. = 8000

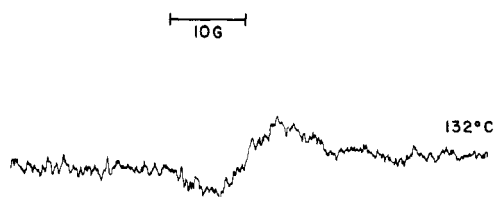


Figure 1. ESR spectrum of plasma-produced oil taken at 132 °C.

The accuracy with which a change in the free radical concentration in a tube could be measured depended on the time scale over which the change occurred. This accuracy was gauged by measurements on a TEMPO sample (in which the free radical concentration is constant). It was found that ESR spectrum from this sample was reproducible to within a few percent if spectra were recorded within an hour or so of one another. However, day to day, the standard deviation in peak height was 20% of the mean.

For one spin-trapping sample, the absolute number of free radicals was determined. To do this, the sample and a tube containing a TEMPO solution were run one after the other under identical operating conditions. The operating conditions were chosen to ensure that neither sample would be saturated or overmodulated. Thus, the modulation was reduced to $\sim 1/10$ of the line width (peak to peak distance, ΔH_{pp}), and the power was reduced until the peak height was proportional to the square root of the power.¹³ The spectrometer resolution and scan time were also adjusted so that no distortion of the spectra occurred. The first-derivative spectra were converted to absorption spectra by graphical integration. The total absorption area in each spectrum was, under these spectrometer conditions, a relative measure of the radical concentration in each tube. Since the concentration of free radicals in the TEMPO-containing tube was known, the concentration in the spin-trapping sample could be determined.

Results

Direct Detection of Free Radicals. An ESR spectrum of a degassed and sealed sample of plasma-produced oil, taken at room temperature, showed no absorption, indicating that the free radical concentration in the oil was below the detectable limit (2×10^{-7} M) at this temperature. Since previous investigations^{2,7} had shown that the generation of free radicals from plasma-produced oil is a thermally activated process, the ESR experiments were repeated at elevated temperatures. Figure 1 shows a spectrum taken at 132 °C. The g value of the absorption is 2.0057 ± 0.0008 based on TEMPO as a reference material ($g = 2.0061 \pm 0.0004$). This value of g is higher than that of most hydrocarbon radicals ($g = 2.0023$ to 2.003^{14}) but well within the range for substituted hydrocarbon radicals. The assignment of the observed radical to peroxy radicals can be excluded since the g value for such species is usually greater than 2.01.

The spectrum in Figure 1 exhibits only a single peak with no hyperfine splitting. This is typical of ESR spectra of plasma-produced organic compounds¹⁵⁻¹⁹ and is probably due to the overlap of many signals with different numbers of peaks and hyperfine splitting constants, but only slightly different g values. The line width (ΔH_{pp} , peak-to-peak separation) of the ESR signal from the plasma-produced oil is 10 G at 75 and 132 °C. This is the true line width; it is neither modulation nor saturation broadened. Similar line widths (2.63–18 G) have been reported in other studies of plasma-produced organic radicals.¹⁶⁻¹⁸

When ESR measurements were carried out at various temperatures, it was observed that the signal intensity at each temperature was reproducible and independent of time. This indicates that an equilibrium free radical

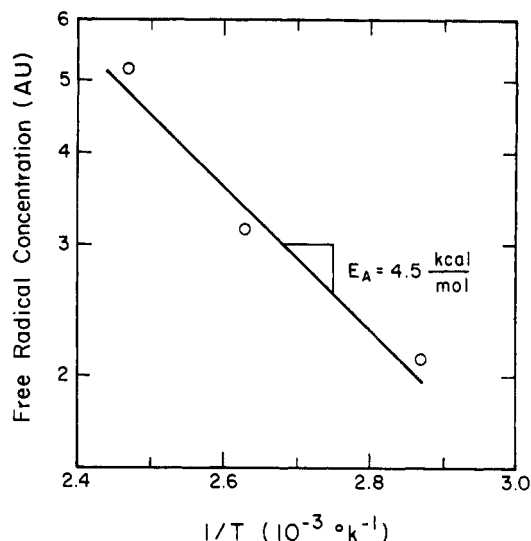


Figure 2. Free radical concentration (in arbitrary units, AU) in the plasma-produced oil vs. $1/T$.

concentration is achieved at each temperature. A plot of the relative free radical concentration vs. $1/T$ is shown in Figure 2. The overall activation energy for the free radical concentration, E_A , determined from the slope of the line in this figure is 4.5 kcal/mol. The value of E_A is related to the activation energies for radical generation, E_i , and radical consumption, E_t , as follows. On the basis of a study⁷ of the kinetics of polymerization of MMA initiated by the plasma-produced oil, it is known that the processes of free radical generation and consumption can be represented by



where I is the initiator (plasma-produced oil) and P is a nonradical termination product. The free radicals, $R\cdot$, may be situated on a single molecule. At steady state

$$\frac{d[R\cdot]}{dt} = 0 = 2k_i[I] - 2k_t[R\cdot]^2 \quad (3)$$

Solving eq 3 for $[R\cdot]$ gives

$$[R\cdot] = \{(k_i/k_t)[I]\}^{1/2} \quad (4)$$

The overall activation energy is therefore related to E_i and E_t by

$$-\frac{d \ln [R\cdot]}{d(1/T)} = E_A/R = (E_i - E_t)/2R \quad (5)$$

or

$$E_A = (E_i - E_t)/2 \quad (6)$$

Since $E_A = 4.5$ kcal/mol, $(E_i - E_t) = 9$ kcal/mol. This value of $(E_i - E_t)$ is close to that determined from the kinetics of MMA polymerization, 12.4 kcal/mol.⁷

Detection of Trapped Free Radicals. ESR spectra of the plasma-produced oil yielded little information about the molecular structure of the free radicals generated. To investigate the structure of these radicals and also the kinetics of their generation, a technique known as spin-trapping was used. In this method, short-lived radicals ($R\cdot$) are converted to long-lived or stable radicals by reaction with molecules (T) containing nitroso or nitron functional groups (referred to as spin traps). The stable radicals

Table I
Samples for Spin-Trapping ESR Experiments

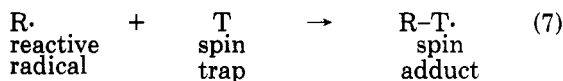
sample ^a	plasma-produced oil concn, 10 ⁻³ g/mL	spin trap concn, 10 ⁻³ M	spin trap
4A	37.9	587	NtB
15A	37.9	66.1	
3A	37.9	6.01	
17B	0	66.1	PBN
9A	44	7.3	
10A	44	0.67	
14A	0	14.7	
L	~50	136	
J	0	571	DMPO
G	~30	~440	
K	0	~440	

^a Benzene was the solvent in each case.

Table II
Hyperfine Splitting Constants of Spin Adducts Formed by Reaction with NtB of Free Radicals Generated by the Plasma-Produced Oil

spin adduct	a_N , G	a_H , G	no. of peaks
1	14.7 ± 0.2	9.7 ± 0.2	9
2	14.8 ± 0.3		3
3	13.5 ± 0.4		3

produced are nitroxides ($R_1N(\dot{O})R_2$) and are termed spin adducts.



Experiments were conducted with three different spin traps: (i) 2-methyl-2-nitrosopropane (NtB), (ii) *N*-tert-butyl- α -phenylnitron (PBN), and (iii) 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO).

(i) **2-Methyl-2-nitrosopropane (NtB).** To study the kinetics of free radical generation from the plasma-produced oil, it is necessary that the trapping reaction (reaction 7) be very fast relative to any other radical destruction reactions. Only when this is the case will the increase in the spin-adduct signal with time be an accurate measure of the radical generation rate. The trapping reaction is sufficiently fast if the rate of spin adduct production is independent of the spin-trap concentration.²⁰

To see if the spin-trapping reaction is sufficiently fast, three samples were prepared, all with 0.0379 g/mL of plasma-produced oil but with different concentrations of NtB, ranging from 5.87×10^{-1} to 6.01×10^{-3} M (see Table I). A control sample containing only NtB (6.61×10^{-2} M) was also prepared. Benzene was the solvent in each case. All samples gave ESR signals when kept in the dark at room temperature, although in the control the signal was very weak. The signals recorded after about 3 days and then after about 11 days are shown for the three oil-containing samples in Figure 3, parts a and b, respectively. The settings used to record these spectra are listed on the figure. The power and modulation amplitude were chosen so as to obtain unsaturated, undistorted spectra. Three separate signals (1, 2, and 3) are present in the spectra of samples 4A and 15A. Sample 3A shows only two signals, presumably the third (signal 1) is too weak to be detectable above the noise. The spectra have been shifted to avoid peak overlap, but all three spin adduct signals appear at the same magnetic field in each sample. The spectra in Figure 3b are 180° out of phase with those in Figure 3a. Spin adduct signals 2 and 3 are triplets, while signal 1 is probably a triplet of triplets (for reasons to be discussed later) with the central peak of each triplet lying beneath

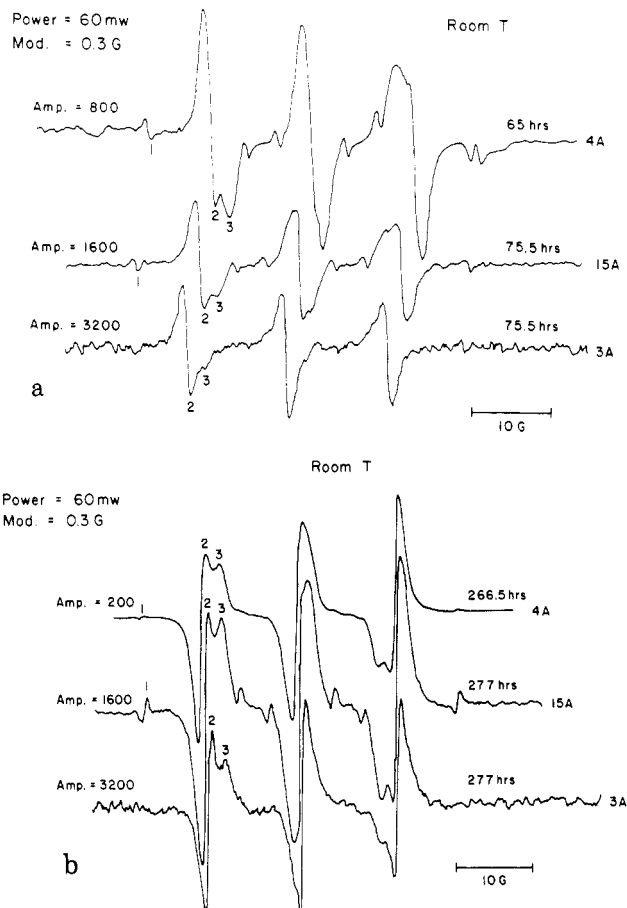


Figure 3. ESR spectra from samples 4A, 15A, and 3A taken after ~3 days (a), and after ~11 days (b). (Spectra are shifted to avoid peak overlap.)

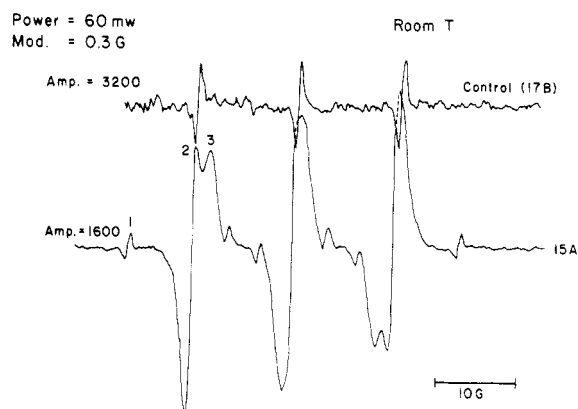


Figure 4. ESR spectra from samples 17B and 15A after ~11 days. Spectra are not shifted so that peak positions can be compared.

signals 2 and 3. A summary of the nitrogen and hydrogen splitting constants (a_N and a_H) for these spin adducts is given in Table II. None of the spin adducts is a direct decomposition product of the trap, since the weak signal in the control sample (17B) has peaks at different positions than signals 1, 2, or 3 (see Figure 4).

From Figure 3, it is apparent that while the total signal strength builds with time in each sample, samples with higher trap concentrations have higher concentrations of spin adducts. The rate of spin-adduct production is not zero order in a trap. Attempts to achieve a zero-order dependence by raising the sample temperature to 55 °C were unsuccessful, due apparently to the instability of the spin adducts at this temperature.

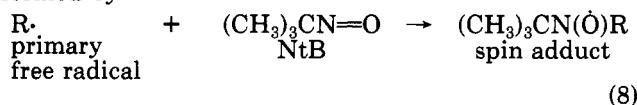
Table III
Reported Hyperfine Splitting Constants for Spin Adducts of NtB^a

free radical trapped	a_N , G	a_H , G	ref
CH ₃ ·	15.2	11.3	25
CH ₃ CH ₂ ·	15.2	10.4	25
CH ₃ (CH ₂) ₇ CH ₂ ·	15.0	9.9	25
(CH ₃) ₃ C·	15.2		25
C ₆ H ₅ ·	12.3	$a_o = a_p = 2$ $a_m = 0.9$	25
(CH ₃) ₃ CO·	26.6		25
	28.1 ^b		27
CH ₃ C=O	8.0		28
RCOO·	<i>c</i>		23
-CH ₂ CC ₆ H ₅	14.9	3.2	26
polystyrene			
-CH ₂ C(CH ₃)(COOCH ₃)	15.1		26
poly(methyl methacrylate)			
-CH ₂ CHCOOCH ₃	13.9	2.8	26 ^d
poly(methyl acrylate)			
-CH ₂ CHOCOCH ₃	12.6	1.8	26 ^d
poly(vinyl acetate)			
-CH ₂ CHOCH=CH ₂	13.1	2.1	26 ^d
poly(divinyl ether)			
-CH ₂ CHOCH ₂ CH(CH ₃) ₂	13.2	1.6	26 ^d
poly(isobutyl vinyl ether)			
-CH ₂ CHC≡N	14.9	2.6	26 ^d
polyacrylonitrile			
-CH ₂ CH=CHCH ₂ ·	15.3	8.4	26 ^d
polybutadiene			

^a All spectra were recorded at room temperature in benzene except where otherwise noted. ^b Ethylbenzene was the solvent. ^c Not trapped by NtB. ^d In these samples, the solvent was ~50% (by volume) benzene and the rest was polymer and monomer. Polar solvents raise a_N but only significantly if they are strongly polar. For example, the (CH₃)₃C· spin adduct gives a_N values in the following solvents²⁴ of: 15.5 G (benzene), 15.8 G (Me₂SO), 16.2 G (diethylene glycol), 16.5 G (formamide), and 17.3 G (water).

Because the trapping rate was not zero order in the NtB concentration, spin trapping with NtB could not be used to measure the radical generation kinetics. Still, it is of interest to determine how many of the free radicals being generated by the plasma-produced oil were being trapped. The concentration of spin-adduct radicals after 266 h, in the sample with the highest NtB concentration (sample 4A), was 8×10^{-5} M as determined by the procedures described previously. The concentration of spin adducts expected, if all free radicals generated by the oil were trapped, can be computed with the results of a polymerization study⁷ in which the plasma-produced oil was used as the free radical initiator. From these results the free radical production rate in sample 4A should have been 1.5×10^{-10} mol/L·s.²¹ If all radicals produced were trapped, after 266 h the spin-adduct concentration would have been 1.4×10^{-4} M, roughly twice that observed in sample 4A. Thus, it appears that not all of the radicals generated were observed even in the sample containing the highest concentration of NtB. The proposed explanation for this is the decomposition of the spin adducts rather than the failure of NtB to trap the radicals generated, since it is known that NtB is a very reactive spin trap.^{22,23}

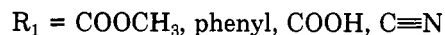
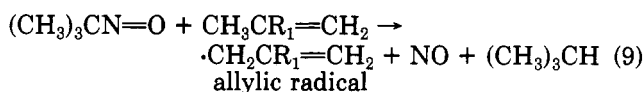
By comparing the splitting constants listed in Table II with reported values for various spin adducts (see Table III) structural information about the radicals generated by the plasma-produced oil is gained. Spin adducts are formed by



Nitrogen has a spin of 1 and therefore splits the ESR signal from the spin adduct into three equal peaks. If the pri-

mary radical center that bonds to the nitrogen atom has n hydrogens attached to it, these will split the signal into a total of $3(n+1)$ peaks. This primary radical center can also alter the ESR signal through its electronegativity, which affects the unpaired electron density on the nitrogen and therefore the nitrogen splitting constant.

Spin adduct signal 1 appears, in Figure 3, to be a triplet of doublets. However, if this were the case, then a_H would be 19.6 G, which, by comparison with Table III is far greater than any a_H value previously observed for any type of radical. In all probability, signal 1 is rather a triplet of triplets with a very reasonable value of $a_H = 9.7$ G, where the central peak of each triplet is obscured by signals 2 and 3. Thus, two hydrogens are attached to the radical center. The value of a_N (14.7 G) is typical of a carbon-centered radical, and therefore signal 1 is due to the spin adduct of a RCH₂· radical. Attached to this radical center are probably nonelectronegative groups, since electronegative groups tend to reduce a_N to 14 G or below (see Table III).²³ Signal 1 is believed to be a byproduct of NtB decomposition. NtB decomposes in the presence of vinyl monomers containing α -methyl groups to produce allylic radicals ($a_N \approx 15$ G, $a_H \approx 10$ G) as follows.²⁶



These allylic radicals are then trapped by NtB. Reaction 9 is particularly facile with MMA monomer. However, no hydrogen abstraction from PMMA in the presence of NtB occurs.²⁶ The weak triplet of triplets (signal 1) is probably due to the decomposition reaction above, occurring either with the small amount of MMA present in the plasma-produced oil or with the various CH₃CR₁=CR₂R₃ groups that are part of the plasma-produced oil structures.⁸

Spin adduct 2 in Table II is probably also the spin adduct of an alkyl-like (nonelectronegative) radical, judging from its a_N value (14.8 G); however, this radical center has no hydrogens attached. Spin adduct 3 also is due to a radical center with no attached hydrogens, but this spin adduct has a lower a_N value (13.5 G). This value of a_N is characteristic of carbon-centered radicals with an electronegative group attached, perhaps an ester or ether. (One surprising exception to this generalization is the growing-chain PMMA radical, which has $a_N = 15.1$ G for its spin adduct.) The a_N values of the observed spin adducts rule out any possibility that the radicals being trapped are any of the following types: R-O· ($a_N \approx 27$ G), R-C=O ($a_N \approx 8.0$ G), or phenyl radicals ($a_N \approx 12.3$ G). The trapped radicals also are not R-COO· or ROO·, as neither radical is trapped by NtB at room temperature.^{23,29}

(ii) *N-tert-Butyl- α -phenylnitrone (PBN)*. A set of experiments were conducted with the spin trap PBN to see if it would be more suitable for studying the kinetics of free radical generation by the plasma-produced oil. The samples used in this experiment are described in Table I: samples 9A, 10A, and 14A. After about 5 days at room temperature, sample 9A gave only a weak spin-adduct ESR signal, sample 10A gave a barely detectable signal (of about $1/8$ the intensity of sample 9A), and the control sample, 14A, gave no signal. Apparently, the trapping reaction was not zero order in PBN or both 9A and 10A should have given signals of equal intensity. Therefore, PBN also was not suitable for kinetic studies of free radical generation by the oil.

As with NtB, the ESR signal of the spin adducts of PBN can yield structural information about the free radicals

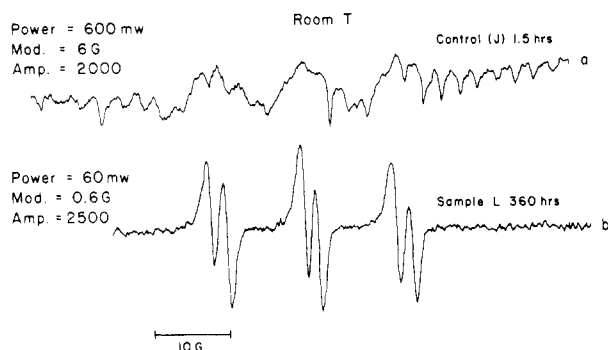
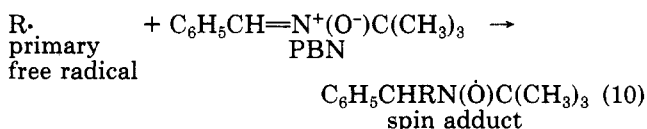


Figure 5. ESR spectra of (a) sample J after 1.5 h; (b) sample L after 360 h.

trapped. The samples discussed above, however, gave signals that were so weak that they could only be observed under signal-distorting conditions. Another sample, L (see Table I), was prepared with a higher concentration of PBN, and it gave a stronger signal. This signal is shown in Figure 5b. A control sample, J, was prepared at the same time as sample L. Sample J, gave a weak, broad triplet signal when analyzed 1.5 h after it was prepared (see Figure 5a). This signal disappeared slowly and was gone after 8 days. The signal from sample L increased with time until 5 days had elapsed, after which it remained unchanged. Even placing sample L in a 76 °C oil bath for 3 days did not alter its signal strength. This limiting signal was about 3 times weaker than that obtained over the same time interval with a sample containing less than half as much NtB and slightly less plasma-produced oil (sample 15A of Table I). Perhaps PBN can trap only certain types of free radicals generated from the plasma-produced oil. The supply of this type of radical may be depleted after 5 days. NtB may be capable of trapping a greater variety of radicals and therefore continue to trap radicals for a longer period. Alternatively, the spin-adduct concentration may have reached steady state. This situation has been observed by Schmidt and Ingold,³⁰ who continuously generated primary alkyl radicals in the presence of PBN and observed a constant ESR signal. The strength of the signal increased with the concentration of PBN. The weaker ESR signal obtained with PBN to trap oil-generated free radicals, relative to that observed using NtB, may be due to the fact that the spin-trapping rate constant is substantially lower for PBN.²² PBN spin adducts, however, once formed, are more than 100 times more stable than NtB spin adducts toward decomposition with one another but no more stable than NtB spin adducts toward decomposition with primary radicals, R.³⁰ Thus, the decomposition of PBN spin adducts may be somewhat slower than NtB spin adducts, but this may be more than offset by the slower trapping reaction for PBN, resulting overall in a lower spin-adduct concentration in the PBN-containing sample compared to that containing NtB.

The spin adducts of PBN, or other nitron traps, exhibit an ESR signal that is a triplet of doublets like that shown in Figure 5b. Spin adducts are formed by



The nitrogen atom splits the spin-adduct ESR signal into a triplet, and the β -hydrogen splits each of these signals into doublets. The nitrogen splitting constant (a_N) in Figure 5b is 14.6 ± 0.1 G while that of the β -hydrogen (a_H) is 2.4 ± 0.1 G. Literature values of a_N and a_H are given

Table IV
Reported Hyperfine Splitting Constants for Spin Adducts of PBN^a

free radical trapped	a_N , G	a_H , G	ref
H \cdot	15.4	8.1	33
	15.06	7.54	32
CH $_3\cdot$	14.82	3.47	34
	14.63	3.58	34
	14.94	3.30	32
CH $_3$ CH $_2\cdot$	14.34	3.26	34
<i>n</i> -C $_4$ H $_9\cdot$	14.64	3.21	35
C $_6$ H $_5\cdot$	14.41	2.21	36
	14.5	2.2	37
C $_6$ H $_{11}\cdot$	14.5	2.2	38
C $_6$ H $_5$ (CH $_2$) $_2\cdot$	14.25	2.19	36
decahydronaphthalen-2-yl	14.3	2.26	36
(C $_6$ H $_5$) $_3\cdot$	13.86 ^b	2.00	31
CH $_3$ COO \cdot	12.93 ^b	1.82	31
C $_6$ H $_5$ COO \cdot	12.73 ^b	1.39	31
(CH $_3$) $_3$ COO \cdot	13.42 ^c	0.95	29
(CH $_3$) $_3$ CO \cdot	13.62	1.72	29
	13.79	2.01	35
CH $_3$ O \cdot	13.76	2.00	35
CH $_3$ CH $_2$ O \cdot	14.01	2.01	35
CF $_3\cdot$	13.3	1.54	39
Cl \cdot	12.1	0.75	33
Cl $_3\cdot$	13.6	1.6	40

^a All spectra were recorded at room temperature in benzene except where otherwise noted. ^b The a_N values reported in ref 31 are consistently lower than other literature values by 0.6–0.7 G. The principal investigator later corrected⁴¹ several of his previously determined a_N values by this amount. ^c The solvent was toluene and the temperature was –20 °C. Above 0 °C this spin adduct was not stable. Upon decomposition, alkoxy spin adducts appeared.

in Table IV. As with NtB, a_N is affected by the electronegativity of the primary radical center. The effect is smaller, however, with PBN (and other nitron traps) since the primary radical attaches to a carbon adjacent to the nitrogen atom rather than to the nitrogen itself as with nitroso spin traps. Consequently, it is difficult to learn much about the structure of the primary radical from a_N —since most spin adducts have similar a_N values. However, it is clear that the radicals trapped are not very electronegative. Electronegative radicals lower a_N to below 14 G. For example, alkoxy (RO \cdot) spin adducts have $a_N \sim 13.8$ G, acyloxy (RCOO \cdot) spin adducts exhibit $a_N \sim 12.8$ G, spin adducts from peroxides (ROO \cdot) which are only stable below 0 °C have $a_N \sim 13.4$ G, chlorine atoms reduce a_N to 12.1 G, and CF $_3\cdot$ produces a spin adduct with $a_N \sim 13.3$ G. The observed value of a_N (14.6 G) is typical of a relatively nonelectronegative primary radical. For non-electronegative radicals, a_H depends predominantly on the bulkiness of the radical being trapped (see the first nine entries in Table IV). Bulky radicals push the β -hydrogen further from the radical site on the spin adduct and therefore lower a_H .⁴² As the radicals become very bulky, a_H is a less sensitive function of radical size. The observed value of a_H (2.4 G) is characteristic of a bulky radical, but it is difficult to say exactly how bulky.

The bulkiness of a free radical reduces its trapping reaction rate with PBN. In fact, very bulky radicals like trityl radical [(phenyl) $_3\cdot$] are not trapped by PBN, and if the spin adduct is synthesized, it is not stable at room temperature.²³ It is possible that even bulkier radicals were generated by the plasma-produced oil but were not trapped by PBN. The low steady-state concentration of spin adducts was possibly due to the slow trapping rate of PBN toward those radicals that it could trap.

(iii.) **5,5-Dimethyl-1-pyrroline-N-oxide (DMPO).** Attempts to use DMPO as a spin trap were not successful. Only weak signals were observed, which gradually decayed

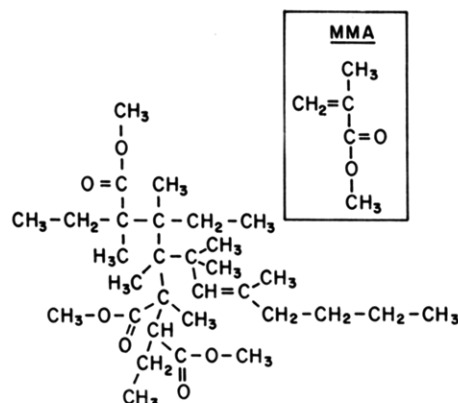


Figure 6. Prototypical structure of a plasma-produced oil molecule.⁸

in strength over a period of several days. DMPO, while not as reactive as NtB towards primary free radicals, is more reactive than PBN.³⁰ However, the spin adducts of DMPO are much less stable than those of PBN.⁴² Quite possibly DMPO trapped radicals from the plasma-produced oil, but the spin adducts were too short-lived to build up to an observable steady-state concentration.

Discussion

The ESR results reported here strongly support the conclusion drawn previously⁷ that the plasma-produced oil generates free radicals. From the overall activation energy for the free radical concentration in the pure oil, the value of 9.0 kcal/mol was obtained for the difference, $E_i - E_t$, between the activation energies for radical formation and termination. This agrees fairly well with the value of 12.4 kcal/mol obtained from polymerization experiments⁷ using the plasma-produced oil to initiate MMA. The latter value may be slightly higher due to a lower value of E_t for termination of growing PMMA chains compared to that for termination of primary radicals from the plasma-produced oil. From the spin-trapping experiment using PBN it was determined that the primary radicals are fairly bulky; thus there may be some steric hindrance to their termination with one another, and this would raise E_t .

With the 12.4 kcal/mol value of $E_i - E_t$ and a value of 2.3 kcal/mol⁴³ for the activation energy for termination of growing PMMA chains, E_i is calculated to be 14.7 kcal/mol. While this value is much lower than that expected for the rupture of a C-C bond (~85 kcal/mol), or even a peroxide linkage (~35 kcal/mol), activation energies in the range 5–16 kcal/mol have been reported for the thermal decomposition of plasma-produced films.^{19,44}

An explanation for the unusually low value of E_i can be developed from a consideration of the structure of the plasma-produced oil. Using ¹H and ¹³C NMR spectroscopy, Paul et al.⁸ have concluded that the typical oil molecule may have a structure such as that shown in Figure 6. A characteristic feature of this structure is the crowding that occurs around each of the quaternary carbon atoms. The close contact of functional groups in such a structure will give rise to steric repulsion. The amount of repulsive energy at a given site can be calculated from a knowledge of the atomic positions and the nonbonded interatomic potential functions.^{45,46}

For example, in the configuration shown in Figure 7, 26 atom pairs overlap to such an extent that their repulsion is ≥10 kcal/mol. Six of these strongly repelling pairs are members of the CH₂ and CH₃ groups labeled in Figure 7 as 1 and 2, respectively. The hydrogen atom of the CH₃ group, which protrudes into the CH₂ group, repels each

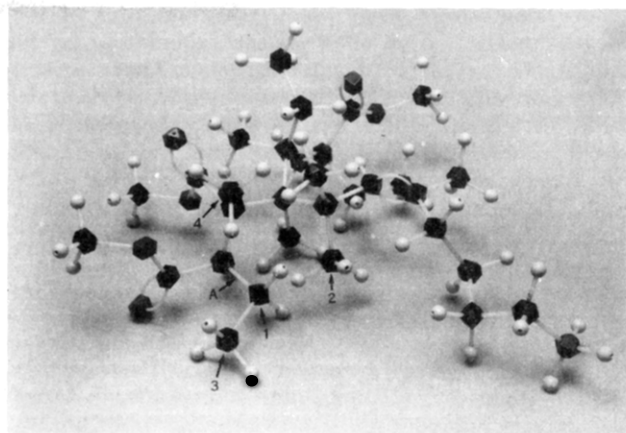


Figure 7. Ball and stick model of the molecule shown in Figure 6.

of the CH₂ hydrogen atoms by 33 kcal/mol and the CH₂ carbon by 315 kcal/mol. The CH₂ hydrogens repel the CH₃ carbon by 50 kcal/mol each. The CH₂ and CH₃ carbon atoms repel one another by 34 kcal/mol. A rotation about bond A can reduce this repulsion. However, even in the minimum energy rotational position, the repulsive energy among the atoms in groups labeled 1–4 is still ~65 kcal/mol. The oil molecule in Figures 6 and 7 was put together in such a manner that steric repulsion was ubiquitous. It serves to illustrate, however, that using the composition of the oil in terms of the various carbon environments,⁸ it is possible to generate structures containing sufficient repulsion that they can decompose with an average activation energy of only 15 kcal/mol. The decomposition of such structures should occur at a strained site and therefore generate bulky radicals. The spin-trapping experiments support this interpretation since the trapped radicals were in fact found to be bulky. Additional support may be drawn from the work of Yasuda et al.,⁴⁷ who observed the presence of expansive stresses in plasma-deposited hydrocarbon films. Such stresses can be attributed to steric repulsion in the film.

How might steric repulsion be produced in the structure of organic plasma deposits? The dominant structure-forming processes in high-frequency glow discharges of organic vapors are believed to be free radical reactions.^{48,49} Of the various free radical reactions, initiation and termination are usually far more important than propagation.⁴⁸ Of the possible free radical initiation reactions, one of the most frequent is C-H fragmentation, often by hydrogen abstraction by hydrogen atoms.^{50,51} Thus the organic deposit is envisioned to be formed by repeat initiation and termination. The initiation steps reduce the mass of the deposit by a lesser amount on average (usually by loss of a hydrogen atom) than the termination steps augment its mass. The structure is built up sequentially in a somewhat random manner. As various organic groups are added to the structure by combining with radical sites on it, they may introduce steric repulsion into the structure due to overlap with other groups. Eventually the total repulsive energy in the deposited molecule may approach a bond strength. It may be possible to release much of this repulsive strain by breaking only one or two bonds in the molecule. Thus the observed activation energy for decomposition of such a molecule may be far less than a bond strength due to the simultaneous release of this strain as the bond ruptures. The random structure-forming process may also lock in strained molecular conformations, making it impossible to release this strain simply by adopting a lower energy conformation even if one is available.

Steric repulsion in the molecular structures of the plasma-produced oil is one possible explanation for its ability to generate free radicals with such a low activation energy (15 kcal/mol). There may be other possible explanations not discussed here. However, any postulated radical production mechanism that involves specific types of chemical reactions is unlikely to be applicable to the variety of compounds, containing various functional groups, which have been shown to produce polymerization initiators in a plasma.¹⁻⁷ The steric-repulsion-induced initiation mechanism gains plausibility from the fact that it can apply to any type of compound.

Conclusions

ESR spectroscopy has been used successfully to detect free radicals produced by the decomposition of a plasma-produced oil, derived from MMA, which can serve as an initiator for the free radical polymerization of MMA. The difference between the activation energy for generation and termination of free radicals ($E_i - E_t$) is only 9 kcal/mol. This value is in good agreement with the value deduced previously⁷ from a study of the kinetics of MMA polymerization initiated by the oil. Spin-trapping experiments reveal that upon decomposition the plasma-derived oil produces free radicals that are part of bulky structures and centered on tertiary carbon atoms. The unusually low activation energy for free radical formation is ascribed to strong steric repulsion occurring in the plasma-produced oil. Such an interpretation is consistent with a recently reported⁸ study of the oil structure.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. PMMA, 9011-14-7; NtB, 917-95-3; PBN, 3376-24-7; DMPO, 3317-61-1.

References and Notes

- Osada, Y.; Bell, A. T.; Shen, M. In *Plasma Polymerization*, Shen, M., Bell, A. T., Eds.; American Chemical Society: Washington, DC, 1979; ACS Symp. Ser. No. 108.
- Johnson, D. R.; Osada, Y.; Bell, A. T.; Shen, M. *Macromolecules* **1981**, *14*, 118.
- Simionescu, B. C.; Leanca, M.; Ananiescu, G.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1980**, *3*, 437.
- Simionescu, B. C.; Leanca, M.; Ioan, S.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1981**, *4*, 415.
- Simionescu, C. I.; Simionescu, B.; Leanca, M.; Ananiescu, C. *Polym. Bull. (Berlin)* **1981**, *5*, 61.
- Kuzuya, M.; Kawaguchi, T.; Daikyo, T.; Okuda, T. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 515.
- Paul, C. W.; Bell, A. T.; Soong, D. S. *Macromolecules* **1985**, *18*, 2312.
- Paul, C. W.; Bell, A. T.; Soong, D. S. *Macromolecules*, preceding paper in this issue.
- Briere, R.; Lemaire, H.; Rassat, A. *Bull. Soc. Chim. Fr.* **1965**, *12*, 3273.
- Hoffman, B. F.; Eames, T. B. *J. Am. Chem. Soc.* **1969**, *91*, 2169.
- Kriellick, R. W. *J. Chem. Phys.* **1967**, *46*, 4260.
- Whistnant, C. C.; Ferguson, S.; Chesnut, D. B. *J. Phys. Chem.* **1974**, *78*, 1410.
- Poole, C. P., Jr. *Electron Spin Resonance*; Wiley: New York, 1967.
- Forrester, A. R.; Hay, J. M.; Thomson, R. H. *Organic Chemistry of Stable Free Radicals*; Academic: New York, 1968.
- Morosoff, N.; Crist, B.; Bumgarner, M.; Hus, T.; Yasuda, H. *J. Macromol. Sci., Chem.* **1976**, *A10*, 451.
- Yasuda, H.; Hsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 81.
- Kobayashi, H.; Shen, M.; Bell, A. T. *J. Macromol. Sci., Chem.* **1974**, *A8*, 373.
- Morita, S.; Sawa, G.; Ieda, M. *J. Macromol. Sci., Chem.* **1976**, *A10*, 501.
- Oberbeck, W. F., Jr.; Mayhan, K. G.; James, W. J. *J. Appl. Polym. Sci.* **1978**, *22*, 2805.
- Janzen, E. G.; Anderson, C. A.; Nishi, Y. *J. Am. Chem. Soc.* **1972**, *94*, 8236.
- Paul, C. W.; Ph.D. Thesis, University of California, Berkeley, CA, 1984.
- Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1979**, *101*, 4975.
- Janzen, E. G.; *Acc. Chem. Res.* **1971**, *4*, 31.
- Lemaire, H.; Rassat, A. *J. Chim. Phys.* **1964**, *61*, 1580.
- Perkins, M. J.; Ward, P.; Horsfield, A. *J. Chem. Soc. B* **1970**, 401.
- Kunitake, T.; Murakami, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 67.
- Mackor, A.; Wajer, Th. A. J. W.; de Boer, Th. J.; van Voorst, J. D. W. *Tetrahedron Lett.* **1967**, 385.
- Mackor, A.; Wajer, Th. A. J.; de Boer, Th. J. *Tetrahedron* **1968**, *24*, 1623.
- Howard, J. A.; Tait, J. C. *Can. J. Chem.* **1978**, *56*, 176.
- Schmidt, P.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 2439.
- Janzen, E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1969**, *91*, 4481.
- Janzen, E. G.; Kasai, T.; Kuwata, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2061.
- Janzen, E. G.; Knauer, B. R.; Williams, L. T.; Harrison, W. B. *J. Phys. Chem.* **1970**, *74*, 3025.
- Janzen, E. G.; Lopp, I. G. *J. Phys. Chem.* **1972**, *76*, 2056.
- Bersohn, M.; Thomas, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 959.
- Ohto, N.; Niki, E.; Kamiya, Y. *J. Chem. Soc., Perkins Trans. 2* **1977**, 1770.
- Sargent, F. P.; Gardy, E. M. *J. Chem. Phys.* **1977**, *67*, 1793.
- Iwahashi, H.; Ishikawa, Y.; Sato, S.; Koyano, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1278.
- Janzen, E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1968**, *90*, 5909.
- Kamimori, M.; Sakuragi, H.; Suehiro, T.; Tokumara, K.; Yoshida, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1195.
- Janzen, E. G.; Kasai, T.; Kuwata, K. *Bull. Chem. Soc. Jpn.* **1969**, *91*, 4481.
- Evans, C. A. *Aldrichimica Acta* **1979**, *12*, 23.
- Ross, R. T.; Lawrence, R. L. *AIChE Symp. Ser.* **1976**, *160*(72), 74.
- Thompson, L. F.; Mayhan, K. G. *J. Appl. Polym. Sci.* **1972**, *16*, 2317.
- Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
- Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1965**, *42*, 2209.
- Yasuda, H.; Hirotsu, T.; Olf, H. G. *J. Appl. Polym. Sci.* **1977**, *21*, 3179.
- Yasuda, H. *Macromol. Rev.* **1981**, *16*, 199.
- Bell, A. T. *Top. Curr. Chem.* **1980**, *94*, 43.
- Cappezzuto, P.; Cramarossa, F.; D'Agostino, R.; Molinari, E. *Beitr. Plasmaphys.* **1977**, *17*, 205.
- Jensen, R. J.; Ph.D. Thesis, University of California, Berkeley, CA, 1981.