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ELECTRON SPIN RESONANCE STUDY OF
THERMAL INSTABILITY REACTIONS IN JET FUELS

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1. SUMMARY

Free radicals have been studied by electron spin resonance (ESR) using model compounds that are representative of constituents of jet fuels. Radical formation has been initiated with peroxides and hydroperoxides by using UV photolysis at and near room temperature and thermal initiation at higher temperatures. Both oxygen free and air saturated systems have been studied. n-Dodecane has frequently been used as a solvent, and a mixture of n-dodecyl radicals has been made with a peroxide initiator in n-dodecane (free of oxygen) thermally at 212°C and photolytically at room temperature. Hydrogen abstraction from the 3,4,5 and 6-positions gives radicals that are sufficiently alike that their spectra are essentially superimposed. The radical formed by abstraction of hydrogen from the 2-position gives a different spectrum. ESR parameters for these radicals have been measured. The radical formed by abstraction of a primary hydrogen was not observed. Similar radicals are formed from n-decane.

Di-t-butyl peroxide has been used to initiate radicals photolytically and thermally at temperatures from ambient to 212°C in a variety of oxygen free systems using n-dodecane as solvent. With 20% cumene in solution there is a strong n-dodecyl spectrum and a weak cumyl spectrum at room temperature while at higher temperatures the n-dodecyl spectrum becomes weaker and the cumyl spectrum stronger. There is a temperature dependent process causing cumene to contribute more strongly to the observed radical concentrations at higher temperatures. The effect is also seen with toluene, tetralin, and indene. Indene gives the largest effect with only 1.5% in solution almost suppressing the dodecyl spectrum at 57°C and completely suppressing dodecyl and giving an indenyl spectrum at 123°C. A 20% solution of 2,2,4-trimethyl-pentane does not give an observable effect. A reasonable reaction causing the observed effect is

$$\dot{C}_{12}H_{25} + RH \rightarrow C_{12}H_{26} + \dot{R}$$
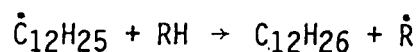
where RH in decreasing order of effectiveness is indene, tetralin, cumene,

toluene and 2,2,4-trimethylpentane (no observable effect). This order is
the same as the order of decreasing stability of $\overset{\bullet}{R}$.

The well-known reaction $\overset{\bullet}{R} + O_2 \rightarrow R\overset{\bullet}{O}_2$ has been illustrated at room
temperature by obtaining peroxy radical spectra in air saturated systems.
Photolysis of an oxygen free solution of di-t-butyl peroxide in n-dodecane
gives n-dodecyl radicals but when air saturated gives a strong spectrum of
n-dodecyl peroxy radicals. Similar systems that are discussed involve
radicals from 2,2,4-trimethylpentane and radicals from 1.5% indene in
n-dodecane which give peroxy radicals in the presence of oxygen. The
reaction of oxygen with benzyl radical has also been demonstrated, but the
resulting peroxy radical spectrum was too weak for positive verification.

Radicals have been observed with hydroperoxides in a variety of
systems. UV photolysis which was used at or near room temperature or ther-
mal initiation at higher temperatures breaks the O-O bond, and the resulting
radicals abstract hydrogen from a hydrocarbon substrate in the same manner
as that for peroxides. An important difference from peroxides, however,
which completely modifies the low temperature behavior is caused by the well
known reaction $ROOH + \overset{\bullet}{R}' \rightarrow R'H + R\overset{\bullet}{O}_2$. This reaction provides an abundant
source of peroxy radicals, and in virtually every experiment carried out
from room temperature to approximately 100°C in which a hydroperoxide was
present, only the spectrum of a peroxy radical was observed. An oxygen free
1% solution of t-butyl hydroperoxide in n-dodecane gives a spectrum of
t-butyl peroxy radical upon photolysis at room temperature. The spectrum is
much stronger when the system is air saturated, and a reaction that likely
participates is $C_{12}H_{25}\overset{\bullet}{O}_2 + (CH_3)_3COOH \rightarrow C_{12}H_{25}OOH + (CH_3)_3C\overset{\bullet}{O}_2$.
A 1% solution of cumene hydroperoxide behaves similarly at room temperature.
Peroxy radicals in the presence of cumene hydroperoxide with and without
oxygen present have also been examined in cumene solution and in a solvent
of 20% cumene in n-dodecane, and the relative signal strengths fit a
consistent mechanistic pattern. Hydroperoxides are often formed by air
oxidation of hydrocarbons. Tetralin and also n-dodecane were air oxidized,
and the corresponding peroxy radical spectra were seen upon photolysis at
room temperature. Very small amounts of hydroperoxides can produce large

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changes in hydrocarbon radical concentrations. For example, a strong spectrum of benzyl radical is obtained by photolyzing (room temperature, oxygen free) a 7% solution of di- $\underline{t}$-butyl peroxide in toluene. The addition of only 0.14% $\underline{t}$-butyl hydroperoxide decreases the concentration of benzyl to one-third and a spectrum of $(CH_3)_3C\dot{O}_2$ appears. A similar result is obtained with cumene hydroperoxide.

Peroxy radicals formed in the above manner give spectra that broaden rapidly at higher temperatures and can no longer be observed above approximately 100°C. At higher temperatures the spectrum of a hydrocarbon radical appears, a behavior like that with peroxides. For example, a 1% solution of cumene hydroperoxide in cumene gives a spectrum (photolytically) of cumene peroxy radical at room temperature, but initiation at 280°C (thermally) gives only a spectrum of cumyl radical. GC analyses of products at 280°C have shown that initiation of cumyl has taken place in the same manner expected with a peroxide initiator, and there is no apparent participation of peroxy radicals. Other systems containing $\underline{t}$-butyl hydroperoxide and cumene hydroperoxide have been examined from room temperature to 280°C and in each case there is a transition from observing only a peroxy radical at room temperature to only a hydrocarbon radical at the higher temperatures.

A variety of exploratory experiments have been carried out with systems that give free radical spectra to which has been added small amounts of 2,5-dimethylpyrrole. The pyrrole frequently lowers the steady state concentration of free radicals, and in some systems there is an accompanying formation of paramagnetic solid. Photolytic systems seem especially susceptible to solid formation, and there is some indication that the presence of hydroperoxides enhances the effectiveness of the pyrrole.

Jet A was examined with a variety of conditions. Neither photolysis at room temperature nor heating to 480°C with the short contact time of less than 5s normally used gave spectra. Heating to 480°C with a much longer contact time (and even to somewhat lower temperatures but in excess of 400°C) resulted in sufficient pyrolysis of the fuel to give the spectra of

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very stable radicals. The predominant radical was phenalenyl (perinaphthenyl). A sample of Jet A air oxidized at 75°C for 22 hours gave neither a spectrum upon photolysis at room temperature nor upon heating to 280°C. Initiation of radicals at 212°C after adding di-t-butyl peroxide gave a spectrum of radicals of the type $RCH_2\overset{\bullet}{C}HCH_2R'$ arising from long chain aliphatic hydrocarbons.

2. INTRODUCTION

This basic research effort in electron spin resonance (ESR) is related to thermal stability of jet fuels. Free radicals are formed and studied in model compounds that are representative of constituents of fuels. The program is new, and the experiments are largely exploratory in nature covering a broad range of systems and experimental conditions in order to search out and identify significant free radical reaction pathways. Emphasis has been given to alkyl aromatics, to peroxides and hydroperoxides, and to the frequent use of n-dodecane as a solvent. Also reported are a few experiments with 2,5-dimethylpyrrole and with Jet A.

Two ESR spectrometers were used which had been developed[1,2] for observing short lived free radicals in fluids at high pressures and high temperatures (up to 700°C). In the present work most experiments were done at temperatures below 300°C. Generally, peroxides and hydroperoxides rapidly initiate free radical formation in the intermediate temperature regime broadly covering 200° to 300°C, and ESR spectra may often be observed. These substances also initiate free radical signals that may be seen at lower temperatures by using UV light. One of the spectrometers was equipped with a UV lamp. Photolysis could be used at room temperature and up to temperatures where thermal production of radicals became fast enough to see signals. Typical steady-state concentrations of radicals <u>from</u> <u>hydrocarbons</u> were in the micromolar region with mean lifetimes ranging downwards from typical room temperature values near 1 ms.

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3. EXPERIMENTAL METHODS

Each ESR spectrometer uses a flow system like that shown in Figure 1. The sample, a liquid at room temperature, is contained in a reservoir and, unless otherwise noted, is always purged with helium to remove dissolved oxygen. In some cases the effects of dissolved oxygen are studied by replacing the helium purge with an air or oxygen purge. The liquid flows to a positive displacement high pressure pump, and in the results described here pressures from 8.3 to 17.2 MPa (1,200 to 2,500 psi) were used with a flow rate of 1 ml/min unless otherwise noted. The provision for injecting a high pressure gas such as hydrogen (Figure 1) was not used. The liquid flows through a silica capillary that traverses the microwave cavity of the ESR spectrometer and then to a back pressure regulator where the system pressure is set. The liquid exiting the regulator is at atmospheric pressure and may be recirculated as shown in Figure 1 or collected without recirculation.

The method of heating the silica capillary, not shown in Figure 1, is detailed in Figure 2. The capillary is surrounded by a vacuum jacketed tube (fused silica), and electrically heated air is forced through the annular space. Temperatures are monitored with a thermocouple in the annular space. Temperature calibrations to give highly accurate values for the fluid inside the capillary were not made for each set of experimental conditions because of the large number and survey nature of the experiments. However, corrections from earlier work have been made to give approximate fluid temperature inside the capillary. These corrections range from zero at room temperature to the subtraction of 45° when the thermocouple (Figure 2) reads 550°C. The contact time of the sample in the high temperature region was ordinarily less than 5s.
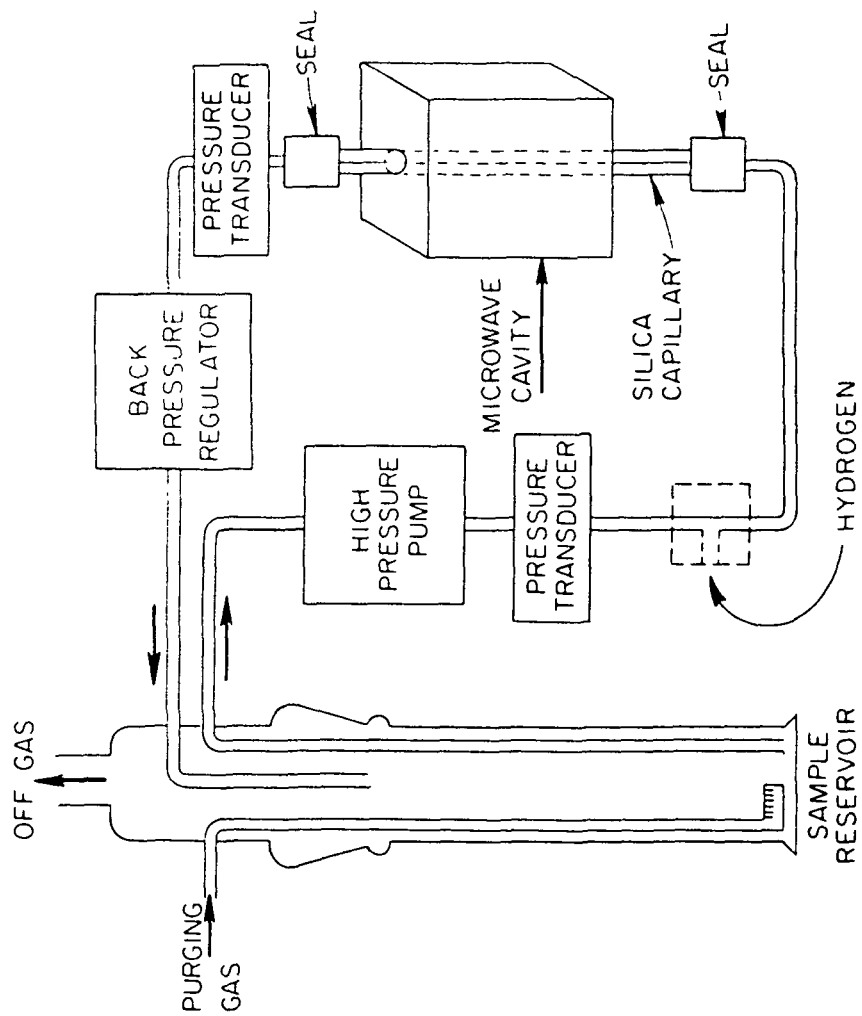
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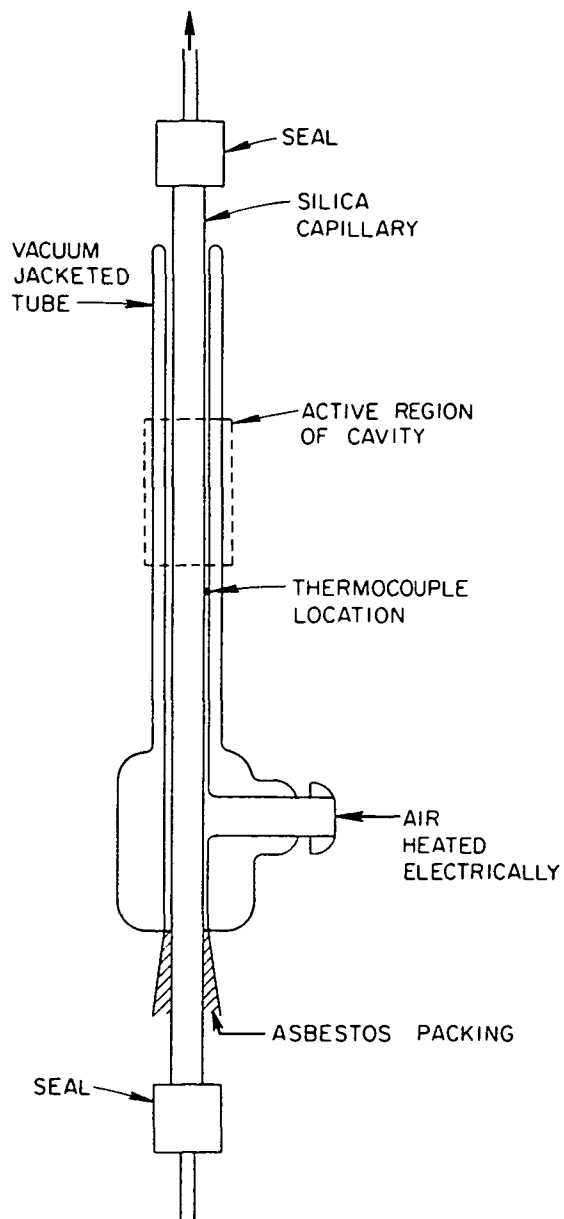Figure 1. Flow System for Pyrolytic and Photolytic Studies

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Fig. 2   Heating System for Pyrolytic Studies

The spectrometer used for photolytic production of radicals was provided with a 500W high pressure mercury arc and fused silica lenses. One face of the microwave cavity (Figure 1) has a window, and the UV irradiation was focused through the window upon the silica capillary within the cavity. The silica of the capillary contains trace impurities which give rise to spurious ESR signals upon UV irradiation. These spurious signals appear in the central region of the spectrum and may be seen between the vertical lines drawn on the relevant figures.

The ESR spectrometers operated at a nominal frequency of 9.2 GHz and employed 100 kHz magnetic field modulation. The illustrated spectra are the customary derivative of absorption as a function of magnetic field, and in each case the field scale in gauss and the direction of increasing field is indicated. Short lived free radicals frequently exhibit spin polarization phenomena, and this is manifested in the ESR spectra by the corresponding hyperfine lines symmetrically disposed about the center having unequal intensity. The lines at higher field are stronger. This effect is present in many of the spectra illustrated here at temperatures up through 212°C.

In some experiments GC analyses were made on the liquid exiting the back pressure regulator (Figure 1). In these cases the sample in the reservoir was not recirculated, and the GC sample was collected while the ESR spectrum was being recorded. The analyses were carried out with a 12-m methyl silicone (SP-2100) fused silica capillary column and a flame ionization detector.

Some experiments were carried out with air oxidized hydrocarbons (cumene, tetralin, indene, etc.), and a simple apparatus was built and its use standardized for this oxidation. (Depending upon the hydrocarbon, oxidations carried out in this manner may be hazardous!) The aeration is carried out at 75°C. The apparatus consists of a 500 ml 3-neck flask heated with an electric mantle. The central neck has a dip tube with a frit and air at 100 ml/min (rotometer) is introduced. One side neck contains a well into which a platinum resistance thermometer is inserted. This gives a
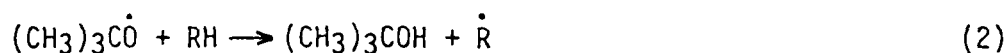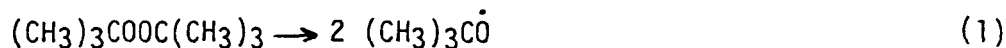
reading of the temperature and provides for automatic temperature control (±0.5°C). The third neck contains a reflux condenser and serves as an exit for air passed through the system. Teflon cones are used on the standard taper joints. The hydrocarbon charge is 250 ml. Cumene hydroperoxide is often synthesized by passing air through cumene. Cumene was chosen as a test substance. After a 19 hours aeration at 75°C a very clean preparation of cumene hydroperoxide was obtained. The amount formed was 1.3% (added to the small amount initially present as an impurity). ESR experiments using this source of cumene hydroperoxide gave the same results as those obtained with purchased cumene hydroperoxide.

In some experiments peroxides and hydroperoxides present in hydrocarbons as impurities were removed by vigorous stirring in contact with an aqueous solution of ferrous ammonium sulfate followed by washing with water and drying over anhydrous magnesium sulfate.

4. RESULTS AND DISCUSSION

4.1 Peroxides in Oxygen Free Systems

Peroxides have been widely used photolytically and thermally for the initiation of free radical reactions. Di-$\underline{t}$-butyl peroxide (DTBP) and dicumyl peroxide have been especially useful because of their stability and ready availability. DTBP was used for the results illustrated here, but some of the experiments were also done with dicumyl peroxide with the same results. With DTBP and a substrate RH the reactions proceed as follows:

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2 \; (CH_3)_3C\dot{O} \tag{1}$$

$$(CH_3)_3C\dot{O} + RH \longrightarrow (CH_3)_3COH + \dot{R} \tag{2}$$

$$(CH_3)_3C\dot{O} \longrightarrow (CH_3)_2CO + \dot{C}H_3 \tag{3}$$

$$\dot{C}H_3 + RH \longrightarrow CH_4 + \dot{R} \tag{4}$$

Reaction (1) may be initiated photolytically with UV or thermally, and the main reaction pathway for forming $\dot{R}$ proceeds through reaction (2). A side reaction (3) takes place in which acetone and $\dot{C}H_3$ are formed, and usually additional $\dot{R}$ is formed through reaction (4). This scheme has been widely used for the ESR observation of radicals formed photolytically at lower temperatures. With the advent of the ESR equipment described here thermal initiation has also been used. In some cases weak ESR signals from $\dot{C}H_3$ have been seen but not in the work described here. Initiation with dicumyl peroxide proceeds in parallel fashion.

n-Dodecane is representative of the straight chain, saturated, hydro-carbons in jet fuel and a mixture of n-dodecyl radicals has been made with thermal initiation using DTBP at 212°C as shown in Figure 3a. Five
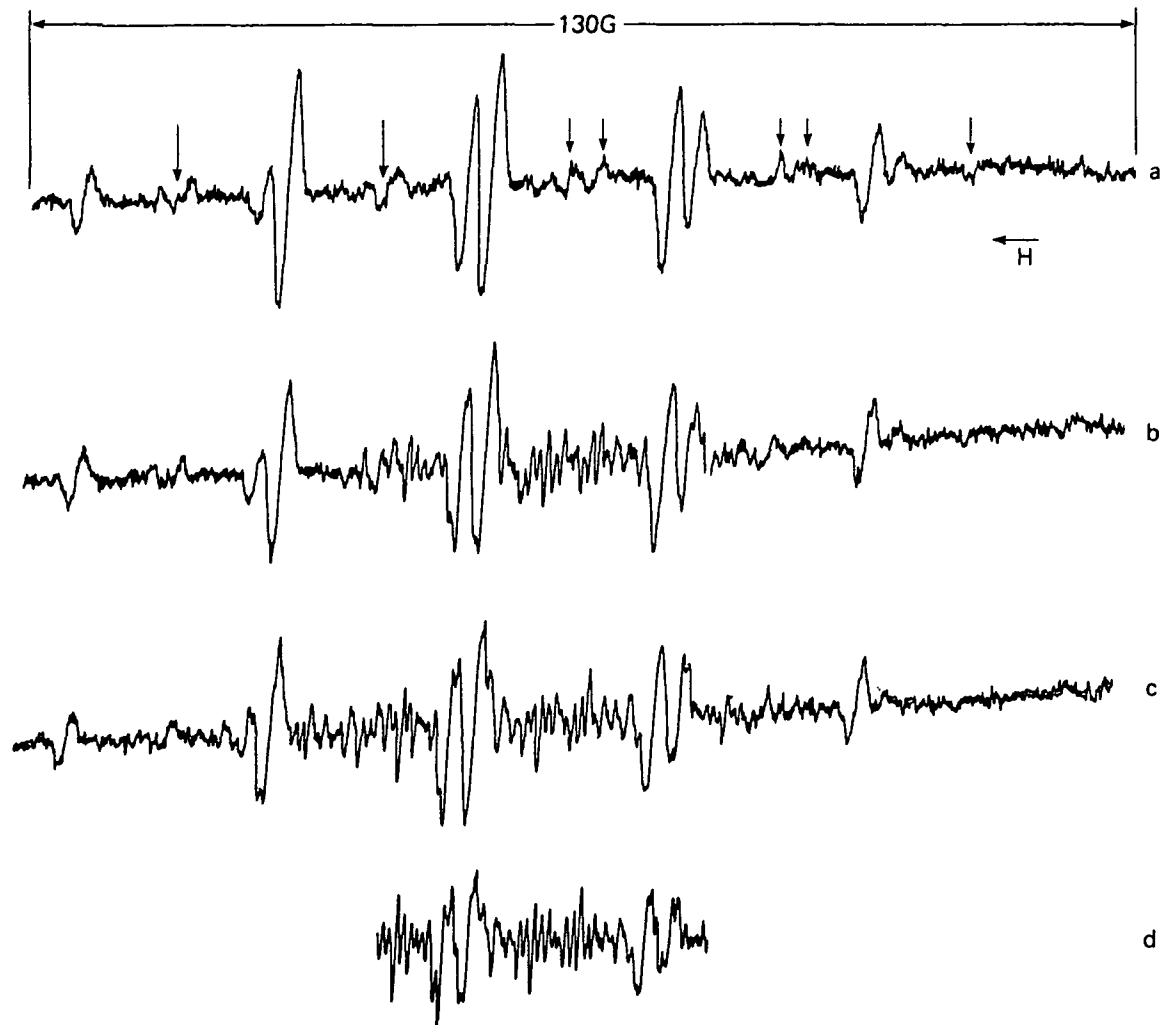
a. n-Dodecyl radicals from 7% DTBP in n-dodecane at 212°C, 13.8 MPa. Arrows indicate some of the lines from $CH_3(CH_2)_9\dot{C}HCH_3$.

b. Same as a but 10% toluene is present and benzyl appears.

c. Same as a but 10% cumene is present and cumyl appears.

d. A portion of the spectrum of c at higher resolution.
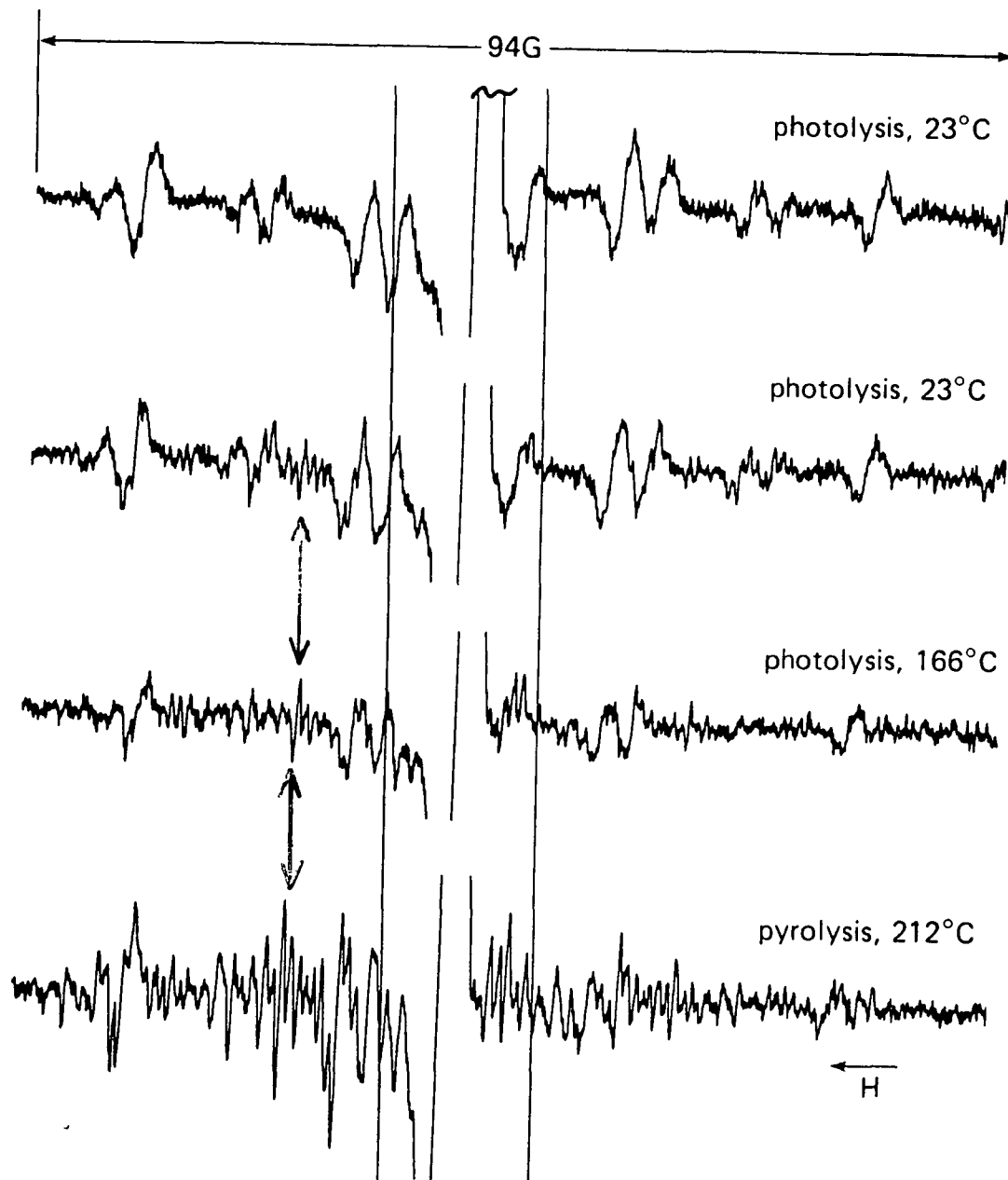
Figure 3

n-dodecyl radicals are formed by abstraction of secondary hydrogens. The spectra of four of these radicals formed by abstraction of hydrogen from the 3,4,5, or 6-position are sufficiently alike that they are superimposed (the stronger lines of Figure 3a). The lines of the spectrum are broad, and with conditions of higher resolution some structure is present in each line but not sufficiently well resolved for detailed analysis. This structure almost certainly arises from a lack of perfect superposition of the spectra of the four radicals, a very small hyperfine coupling to γ-hydrogens, and/or unresolved second order effects.[3] The ESR parameters for these radicals are a_α = 20.9G, a_β = 23.9G, and g = 2.00263. A fifth radical with a weak spectrum (arrows in Figure 3a) is formed by the abstraction of hydrogen from the 2-position. The ESR parameters are a_α = 21.0G, a_β = 24.3G, and g = 2.0026. The spectral components also are broad. A contributing factor is likely due to a small difference in coupling values for the two groups of β-hydrogens for which an average value is given above. There is no evidence for the radical formed by abstracting a primary hydrogen. A similar experiment was done with n-decane, and the ESR parameters were the same for the n-decyl and the corresponding n-dodecyl radicals. We would expect a mixture of n-decane and n-dodecane to give a spectrum virtually indistinguishable from Figure 3a. Fessender and Schuler[4] have studied radicals of the type $RCH_2\overset{\bullet}{C}HCH_2R'$ from other hydrocarbons at much lower temperatures. The radicals from n-octadecane had coupling values of a_α = 21.0G and a_β = 24.8G. Essentially the same values were found for radicals from n-tridecane and n-tetradecane. It is concluded that a mixture of the longer, saturated, straight chain hydrocarbons would give families of radicals of the type $RCH_2\overset{\bullet}{C}HCH_2R'$ with their ESR spectra approximately superimposed. Reference will be made to this in later discussion of Jet A.

The effect of 10% additions of toluene and cumene is shown in Figures 3b and 3c respectively. In each case the n-dodecyl lines become somewhat weaker, and spectra of benzyl and cumyl appear. The spectra of these

radicals have been previously characterized in detail,[1] and there is great confidence in their identification. Identification is usually made with much higher resolution so that the sharp hyperfine lines making up the spectrum are more clearly separated. Slightly higher resolution is shown in Figure 3d, and examples with much higher resolution will be illustrated in later figures. The spectra of Figure 3 show the effect of spin polarization. The positions of lines from a given radical are symmetrically disposed about the midpoint of the spectrum but the intensities are not. Those at higher field are stronger.

The temperature chosen for Figure 3 provides optimum signal strength for thermal initiation with DTBP. At lower temperatures the rate of decomposition of DTBP, reaction (1), becomes slower leading to lower steady state concentration of radicals. At higher temperatures most of the DTBP is consumed before the fluid arrives in the active region of the microwave cavity. GC analyses of typical systems have shown that over 50% of the DTBP is consumed at the optimum temperature of 212°C. At lower temperatures, including room temperature, photolytic initiation may be used. With the available UV source only a few percent of the DTBP is consumed, and the spectra are much weaker than with optimum thermal initiation. The solutions used for Figure 3 were also examined photolytically at room temperature. The spectrum of dodecyl was readily observed, but the spectra of benzyl and cumyl were too weak to be seen. This suggested the presence of a temperature activated process which causes radical formation from the alkyl aromatics to be relatively more important at higher temperatures. More detailed experiments were carried out which are illustrated in Figures 4-7.

In Figure 4 results with dodecane (top) and a 20% solution of cumene in dodecane are shown. The hydrocarbons were freed of oxidizing impurities by treatment with ferrous ammonium sulfate prior to adding DTBP. A higher concentration of cumene was chosen to give a more readily observable effect.
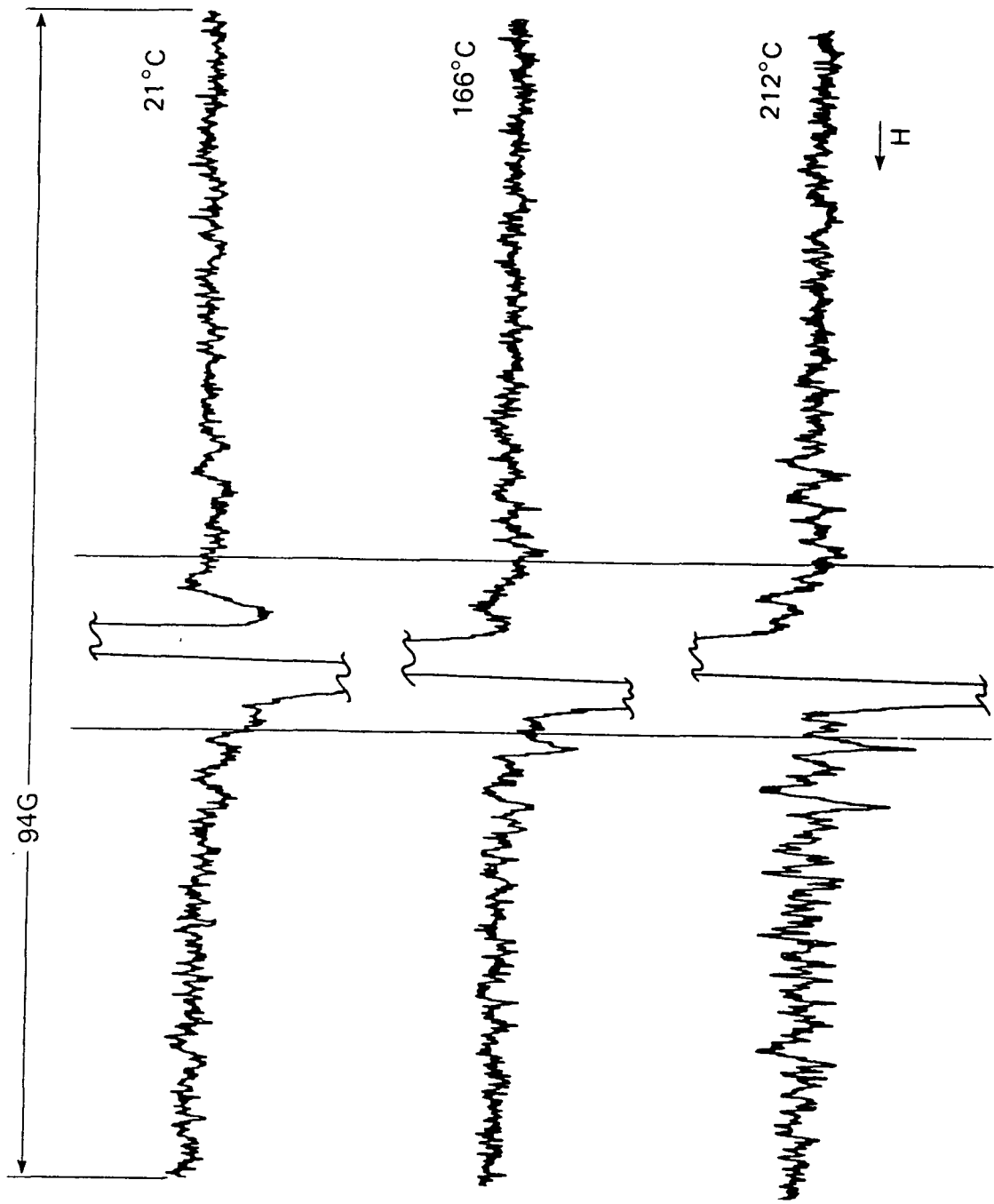
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Top: 5% DTBP in n-dodecane at 10.3 MPa.
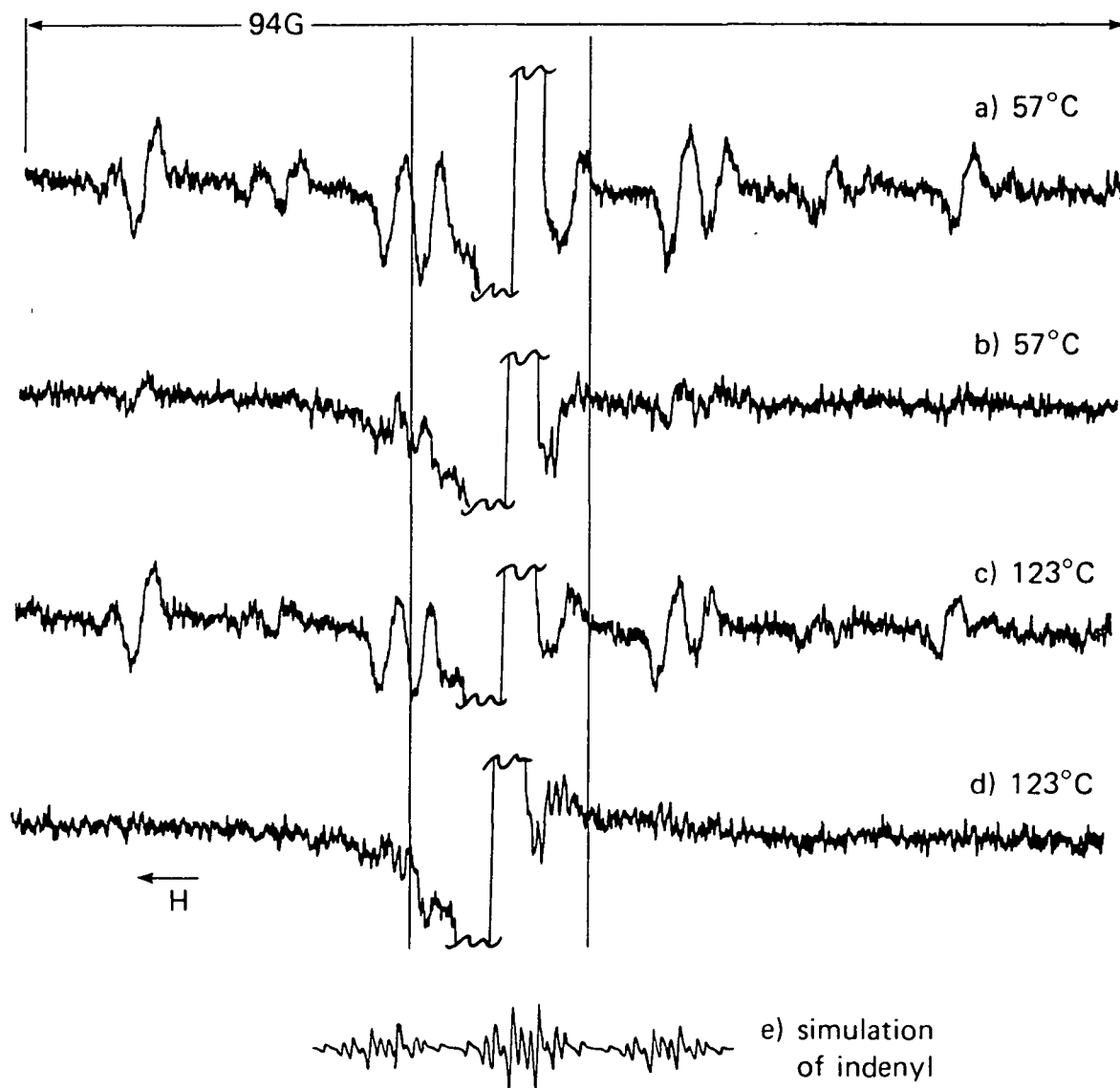All Others: 5% DTBP + 20% cumene in n-dodecane.

Figure 4

ORNL DWG 83-15605

photolysis, 20°C

photolysis, 166°C

212°C

94G

H
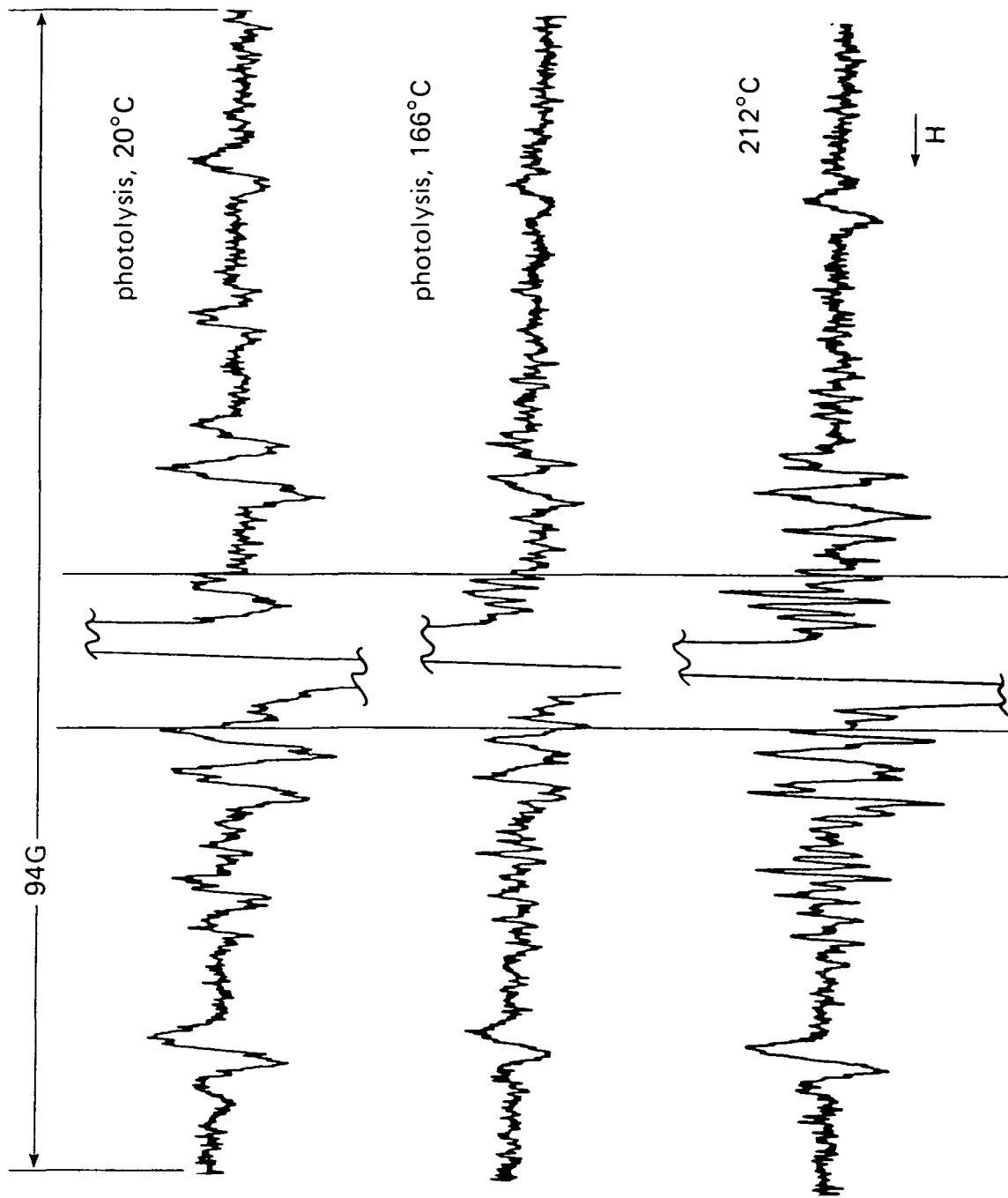
5% DTBP + 20% toluene in n-dodecane at 10.3 MPa.

Figure 5

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ORNL DWG 83-15606

21°C

166°C

212°C

94G

H

5% DTBP + 20% tetralin in n-dodecane during photolysis at 10.3 MPa.

Figure 6

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Photolysis of 3% DTBP in n-dodecane at 10.3 MPa.
b) and d) contain 1.5% indene.

Figure 7

The top spectrum is for DTBP in dodecane and shows lines from dodecyl radicals at 23°C. At 23°C the presence of 20% cumene gives weak lines of cumyl which become progressively stronger at higher temperatures. Arrows at the high field side of center indicate one of the strongest cumyl hyperfine lines, and the pronounced increase in cumyl concentration is apparent. The corresponding intensity for dodecyl, however, becomes much weaker. The increase in the relative importance of cumene as a source of radicals at higher temperatures is apparent. Figure 5 is a similar sequence for toluene with benzyl appearing in addition to dodecyl. There is a relative enhancement of benzyl at higher temperatures, but the effect is less pronounced than that for cumyl in Figure 4.

Figure 6 shows results with 20% tetralin in n-dodecane and with DTBP as an initiator. The tetralin was distilled and with the dodecane was freed of oxidizing impurities before adding the DTBP. The spectrum of tetralin-1-yl formed from tetralin with an initiator has been reported in detail.[5] Because of the large number of inequivalent hydrogens in this radical the spectrum is split into a very large number of component lines with an attendant loss in intensity of individual lines. Lines that are almost surely from tetralin-1-yl appear at 212°C (Figure 6) at the high field side of center. A detailed analysis of these lines at higher resolution was not made. Especially noteworthy is the spectrum at 21°C where the presence of tetralin has all but eliminated n-dodecyl radicals. Without tetralin being present the n-dodecyl radicals appear with the same signal-to-noise ratio as in the top of Figure 4. Tetralin shows a temperature dependent effect with the formation of tetralin-1-yl being more important at higher temperatures. Judging from the manner in which dodecyl concentration is suppressed tetralin appears to have a larger effect than cumene.

Indene appears to have the largest effect of any of the substances tested as illustrated in Figure 7. At 57°C and without indene present a good spectrum of n-dodecyl is obtained. The addition of only 1.5% indene

(Figure 7b) almost completely eliminates the dodecyl, and the first traces of lines from indenyl appear. At 123°C dodecyl is completely eliminated by 1.5% indene, and stronger indenyl lines are present. The simulation of indenyl is from previously measured[1] ESR parameters and shows the expected location of experimental lines. It is striking that such a small amount of indene will produce such a large effect. Note also that the amount of initiator (3%) is less than the other cases (5%) and the maximum temperature (123°C) is much less than the other cases considered (212°C). The use of small amounts of indene at lower temperatures was suggested by the study of Mayo and coworkers[6] on the effect of indene on oxygen consumption by n-dodecane at 130°C which they attributed to the high activity of indene.

Finally, experiments were done with 20% 2,2,4-trimethylpentane (iso-octane) and 5% DTBP in n-dodecane at 24°C and 212°C. Whereas neat iso-octane with an initiator will give spectra from a mixture of radicals, in the above case with predominantly n-dodecane present only spectra of n-dodecyl radicals were seen at both temperatures. Iso-octane is at the opposite extreme (no observable effect) from indene (maximum effect).

A reasonable mechanism for the observed effect is

$$\overset{\bullet}{C}_{12}H_{25} + RH \rightarrow C_{12}H_{26} + \overset{\bullet}{R} \qquad (5)$$

where RH is indene, tetralin, cumeme, etc. At higher temperatures reaction (5) is sufficiently rapid as to occur within the bimolecular disappearance lifetime for the observed radicals. The decrease in effectiveness of the reaction for the various RH's is in the order indene, tetralin, cumene, toluene and iso-octane (no observed effect) which is in the order of decreasing reactivity of these hydrocarbons as hydrogen atom donors. Indenyl is the most stable being both a benzylic radical and having an allylic moiety. This provides for great resonance stabilization. The

remaining radicals are also benzylic except those from iso-octane. Mayo and coworkers[6] considered the cooxidation of n-dodecane and ethylbenzene and found it necessary to include the above reaction where RH is ethylbenzene and $\dot{R}$ is $C_6H_5\dot{C}HCH_3$. If we had studied this case we would have expected ethylbenzene to be between cumene (Figure 4) and toluene (Figure 5) in behavior.

4.2 Peroxides in Systems Containing Oxygen

Experiments have been done in which air and oxygen have been used as purging gases (Figure 1) which equilibrates the sample with these gases at atmospheric pressure and room temperature. The solubility of oxygen is quite low. In air saturated fuels, for example, the dissolved oxygen content is typically 50 to 75 ppm. It would be 5-fold greater if saturated with pure oxygen.

Two major effects may occur from dissolved oxygen: physical and/or chemical. The physical effect is a consequence of the paramagnetism of the oxygen molecule which is a ground state triplet. The oxygen produces a great increase in linewidth and is the reason why, for example, stable free radicals showing sharp, closely spaced hyperfine lines must be studied under oxygen free conditions. A typical line of less than 0.1 G in width may be broadened to a few gauss in width upon air saturating the solution. The position of the line remains essentially unchanged.

Many free radicals chemically react with oxygen to form peroxy radicals:

$$\dot{R} + O_2 \longrightarrow R\dot{O}_2 \qquad\qquad (6)$$

The spectra of peroxy radicals are shifted to higher g values; they appear at noticeably lower field than spectra from hydrocarbon radicals. The

spectra are very broad with the linewidth changing greatly with temperature, and hyperfine structure is rarely observed. Usually only a single broad line shifted to low field is seen. The chemical lifetime of $R\dot{O}_2$ is usually much longer than that of $\dot{R}$, and rather large steady state concentrations may be formed.

The consequences of reaction (6) are illustrated in Figure 8. The top spectrum shows a mixture of n-dodecyl radicals formed photolytically at 23°C with 5% DTBP in n-dodecane. (This is the same spectrum already shown at the top of Figure 4.) Upon replacing the helium purge with an air purge the spectrum at the bottom of Figure 8 is obtained. A strong signal from mixed n-dodecyl peroxy radicals appears as a single broad line of 6.6G width shifted to low field. The amount of oxygen initially in solution is very limited, and if substantial quantities of radicals are formed this oxygen may be depleted. This is apparently what has happened in Figure 8. Weak signals from n-dodecyl are present in the air-purged case; the oxygen has been depleted before all of the n-dodecyl has been converted to peroxy radicals. The concentration of free radicals is proportional to the area under the absorption spectrum the evaluation of which would require a double integration of the signals in Figure 8. This area would be proportional to the height of the signal and to the square of the width. With these considerations the steady state concentration of peroxy radicals in Figure 8 is very large compared to that of n-dodecyl. This is a consequence of the much longer lifetime of $R\dot{O}_2$.

Another example of reaction (6) is shown in Figure 9. Radicals have been made photolytically at 23°C using 5% DTBP in 2,2,4-trimethylpentane. Abstraction of the tertiary hydrogen gives the spectrum labeled a in the top part of the figure. Sharp clusters of lines more centrally located arise from the abstraction of a secondary hydrogen. These radicals are converted to a mixture of peroxy radicals when air is present as shown by the very

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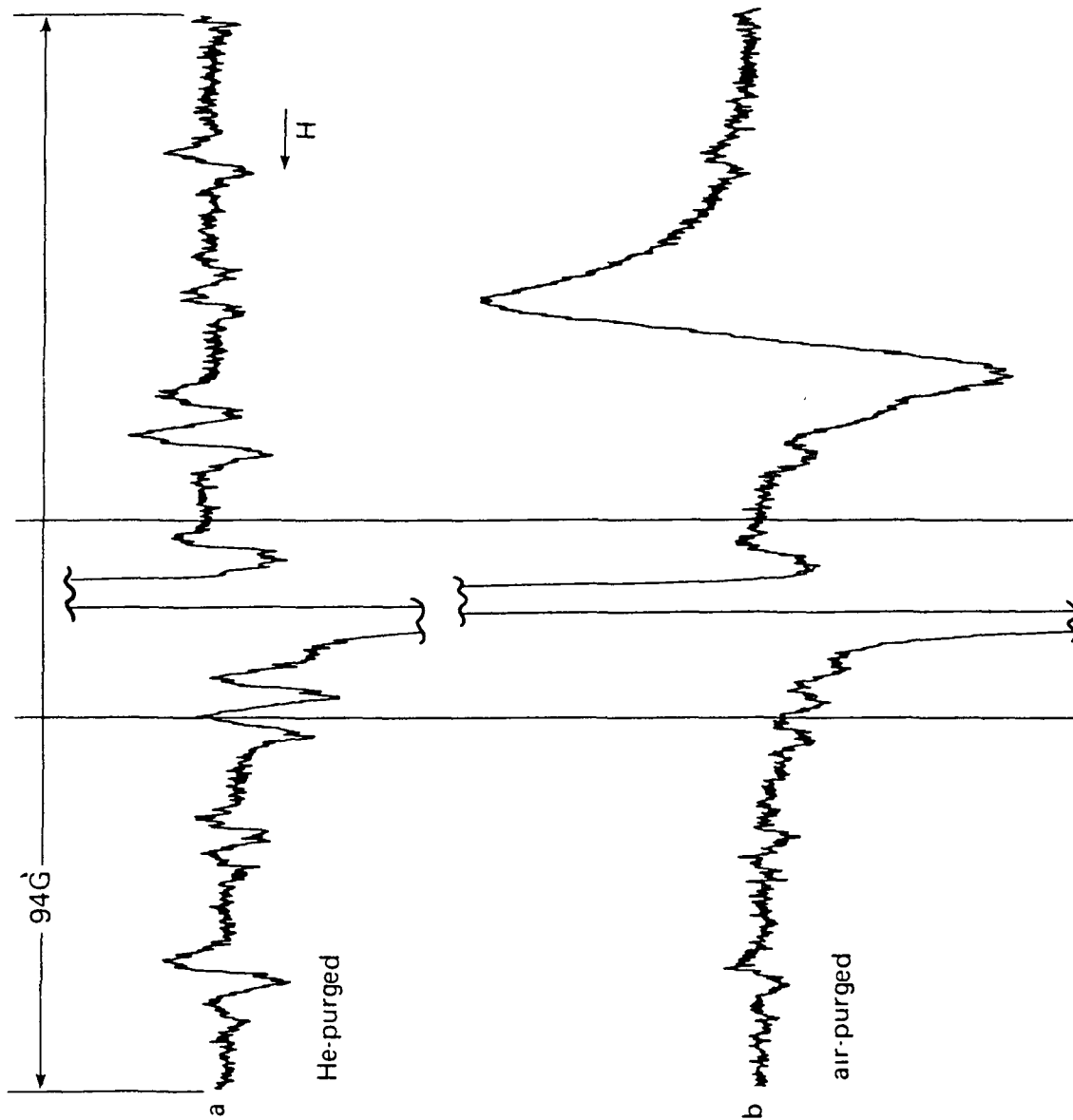
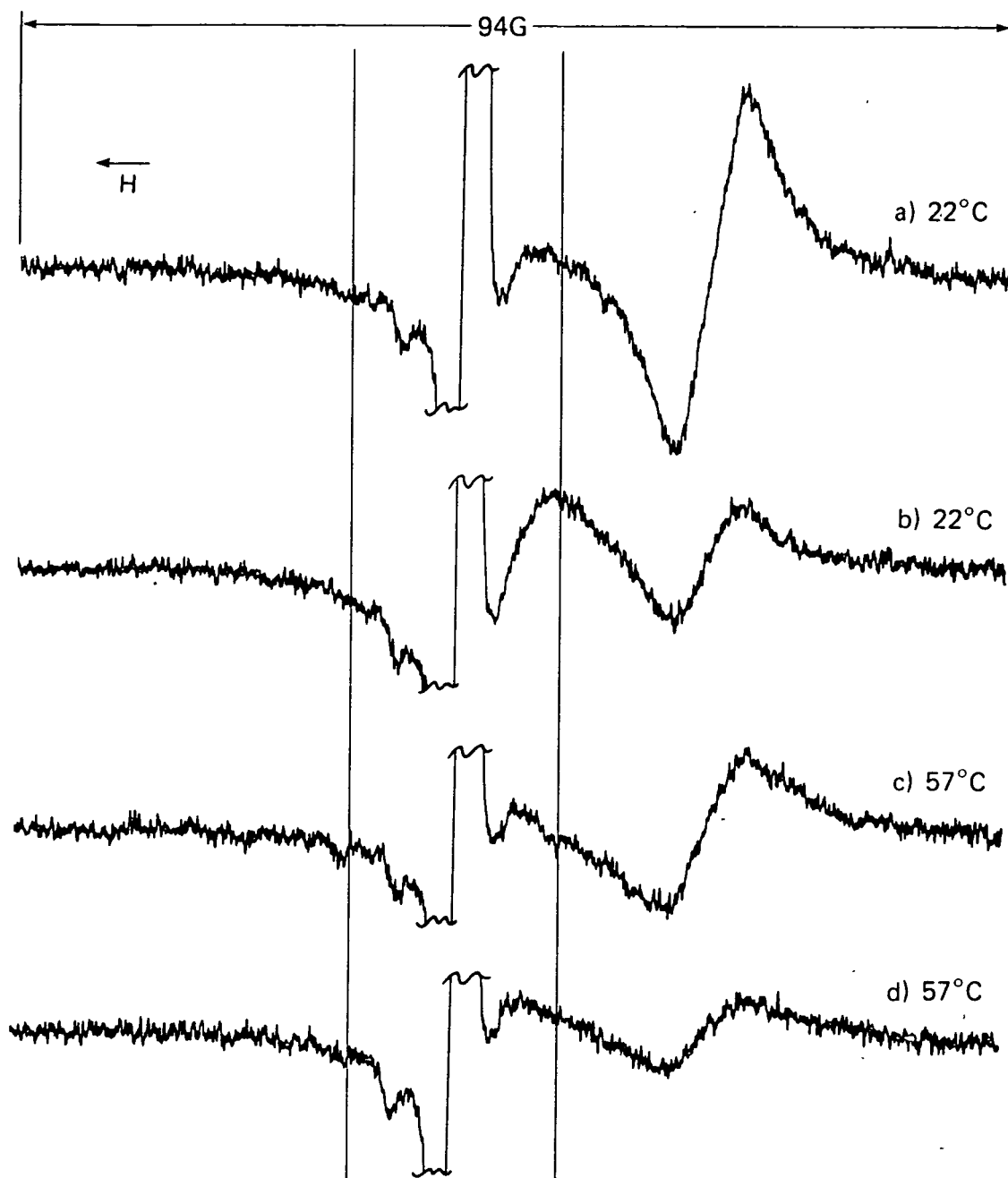Photolysis at 23°C, 10.3 MPa of 5% DTBP in n-dodecane.

Figure 8
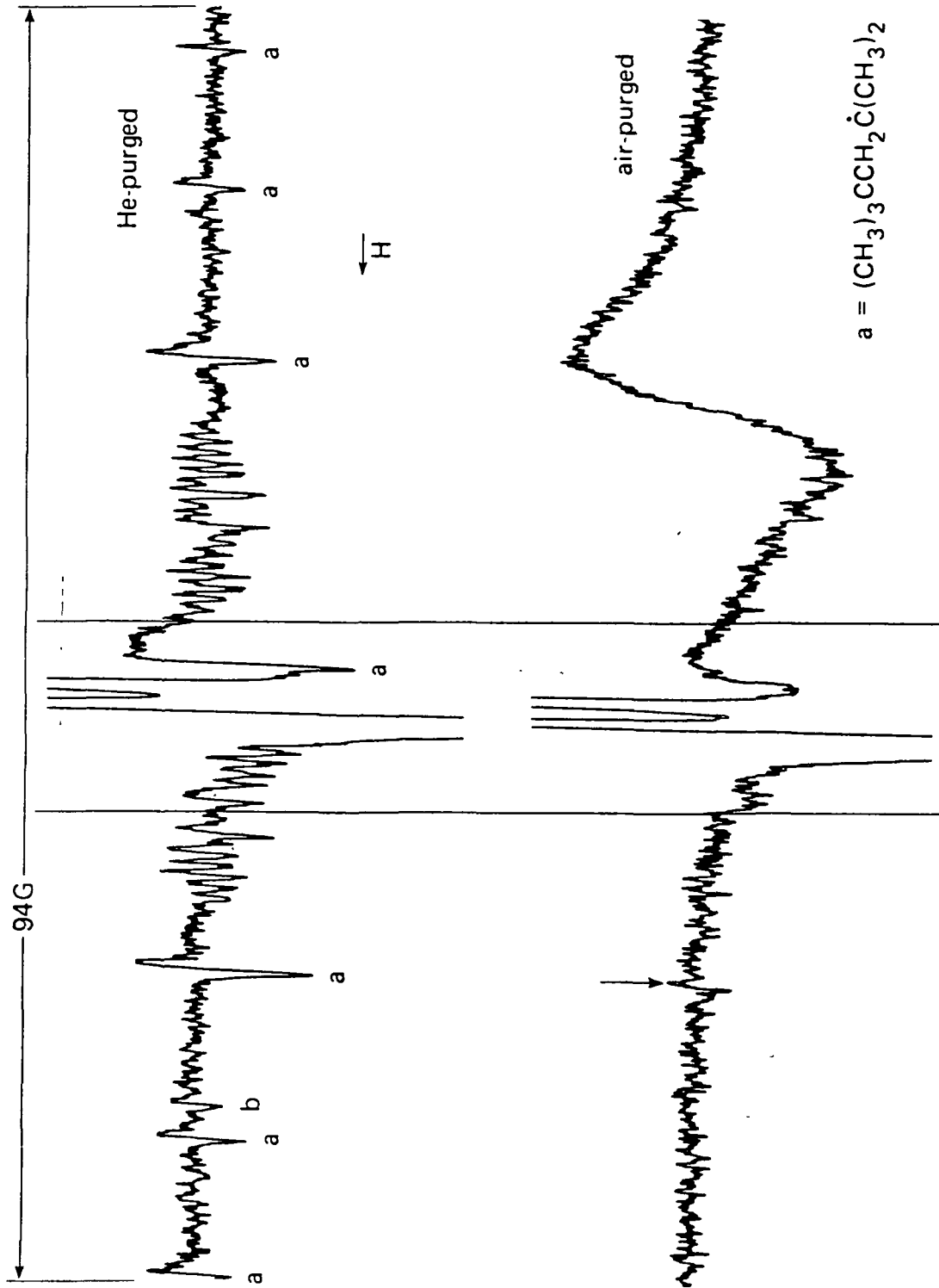
Photolysis at 23°C, 10.3 MPa of 5% DTBP in 2,2,4-trimethylpentane.

Figure 9

broad line in the bottom part of Figure 9. Only a weak line from radical $\underline{a}$ persists (arrow) when oxygen is present. This weak line remains quite sharp which indicates that little or no physically dissolved oxygen remains in solution. The tertiary peroxy radical formed from radical $\underline{a}$ is probably the major contributor to the peroxy spectrum of Figure 8 because tertiary peroxy radicals typically have much smaller termination rate constants.

An attempt was made to detect the benzyl peroxy radical, $C_6H_5CH_2\overset{.}{O}_2$ by photolyzing an air-purged solution of 6% DTBP in toluene at 21°C. A good, sharp spectrum of benzyl radical was present indicating that the dissolved oxygen had been consumed, and a very weak signal was present that might have been the peroxy radical. Upon replacing the air purge by a helium purge the benzyl lines doubled in height, and there was no apparent change in linewidth indicating a doubling of the benzyl concentration. These observations indicate that oxygen had reacted with benzyl, but the resulting spectrum of benzyl peroxy radical was too weak for positive verification.

Air purged solutions of 3% DTBP in n-dodecane with and without 1.5% indene have been examined during photolysis at 22 and 57°C. As shown in Figure 10 the only radicals observed are peroxy radicals. The spectra are broader at 57°C than at 22°C which is the general behavior found for spectra of peroxy radicals with increasing temperature. At each temperature the presence of indene markedly reduces the peroxy radical concentration without perceptibly changing the linewidth. Before adding indene the signals are from n-dodecyl peroxy radicals, and it is likely that the weaker signals remaining after indene addition are still those from n-dodecyl peroxy radicals. (In various experiments, we have not yet observed a spectrum that we can attribute to indenyl peroxy radical.) The conversion of n-dodecyl radicals to n-dodecyl peroxy radicals is an important step in the oxidation of n-dodecane. The suppression of peroxy radical concentration by indene

Photolysis of 3% DTBP in n-dodecane at 10.3 MPa
and air-purged. b) and d) contain 1.5% indene.

Figure 10

relates closely to the work of Mayo and coworkers[6] where indene markedly suppressed the oxidation of dodecane. Note that the spectra at 57°C in Figure 10 involve the identical conditions used in Figure 7 except for an air purge being used instead of a helium purge.

4.3 Systems with Hydroperoxides at Low Temperatures

The O-O bond of hydroperoxides may be broken by UV irradiation and by heat to give $R\dot{O}$ and $\dot{O}H$ and both of these radicals are very effective in abstracting hydrogen. This gives rise to radical initiation similar to that for peroxides. Thermal initiation with a hydroperoxide requires somewhat higher temperature than for the corresponding peroxide. An important difference that often completely modifies the chemistry for hydroperoxides is the abstraction of hydrogen from hydroperoxides through the well known reaction

$$ROOH + \dot{R}' \rightarrow R'H + R\dot{O}_2 \tag{7}$$

This provides an abundant source of peroxy radicals, and in virtually every experiment that we have done from room temperature to approximately 100°C in which a hydroperoxide was present, only the spectrum of a peroxy radical was observed. As described later at much higher temperatures the situation changes and the observed radicals are those seen with peroxides.

Peroxy radical spectra are characteristically shifted to low field (high g value), but there is too little variation in g value to differentiate between two or more different peroxy radicals. Hyperfine structure which is most helpful in identifying radicals is rarely present in the spectra of peroxy radicals. We have found, however, that in certain simple systems the linewidth can sometimes be used to differentiate between two different peroxy radicals. For example, t-butyl peroxy radical has a width of approximately 17 G while, as indicated earlier, that of n-dodecyl peroxy radicals is 6.6 G, and cumyl peroxy is also a little over 6 G. In Figures 11 and 12 peroxy radical spectra have been formed by UV irradiation of

94G

H

He-purged
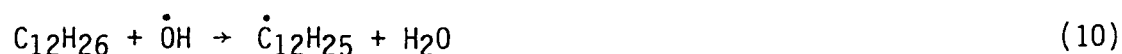
air-purged
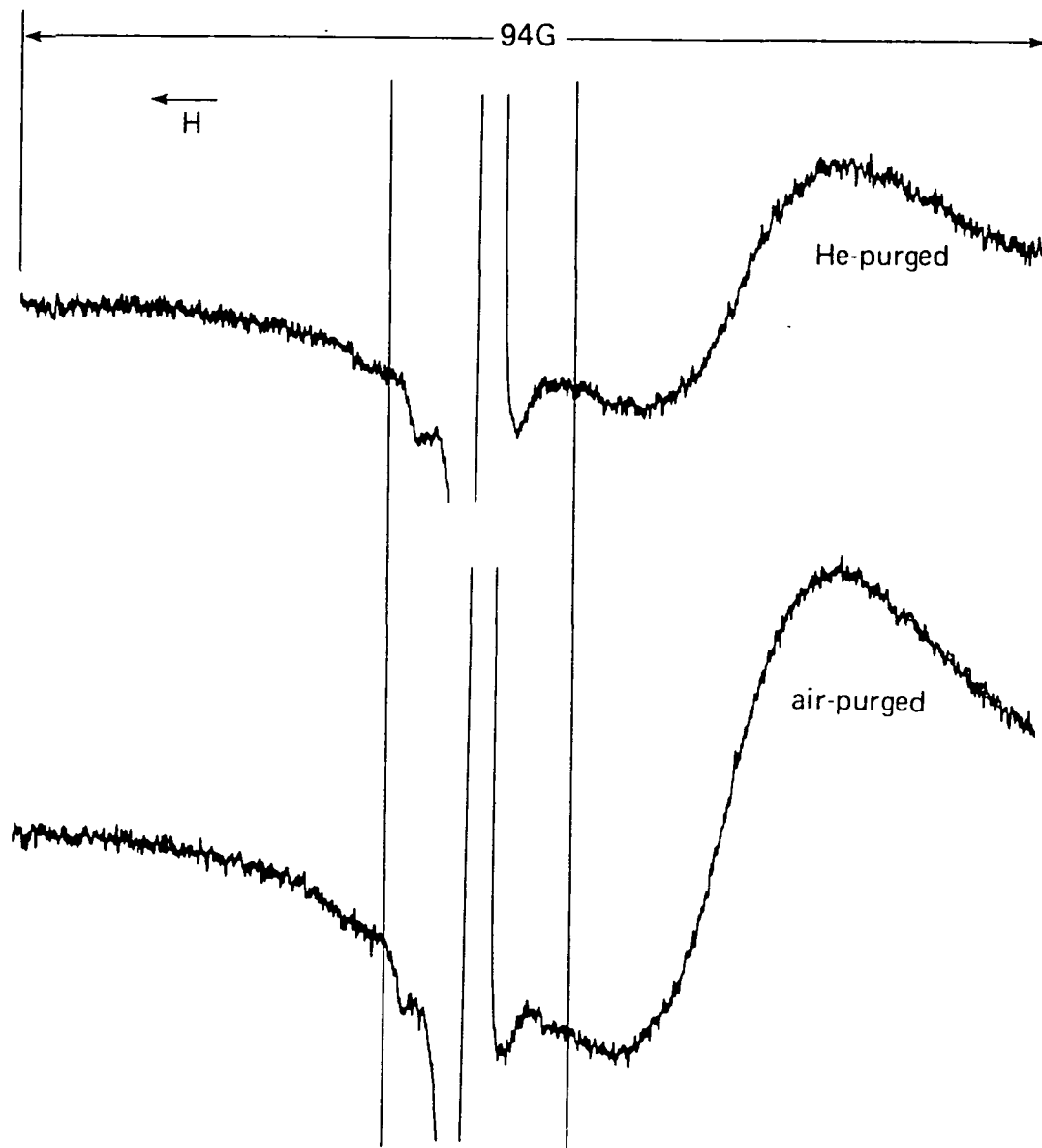
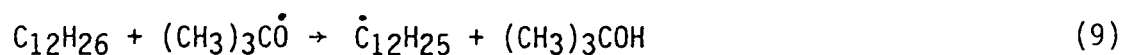Photolysis at 23°C of 1% TBHP in n-dodecane at 10.3 MPa.

Figure 11
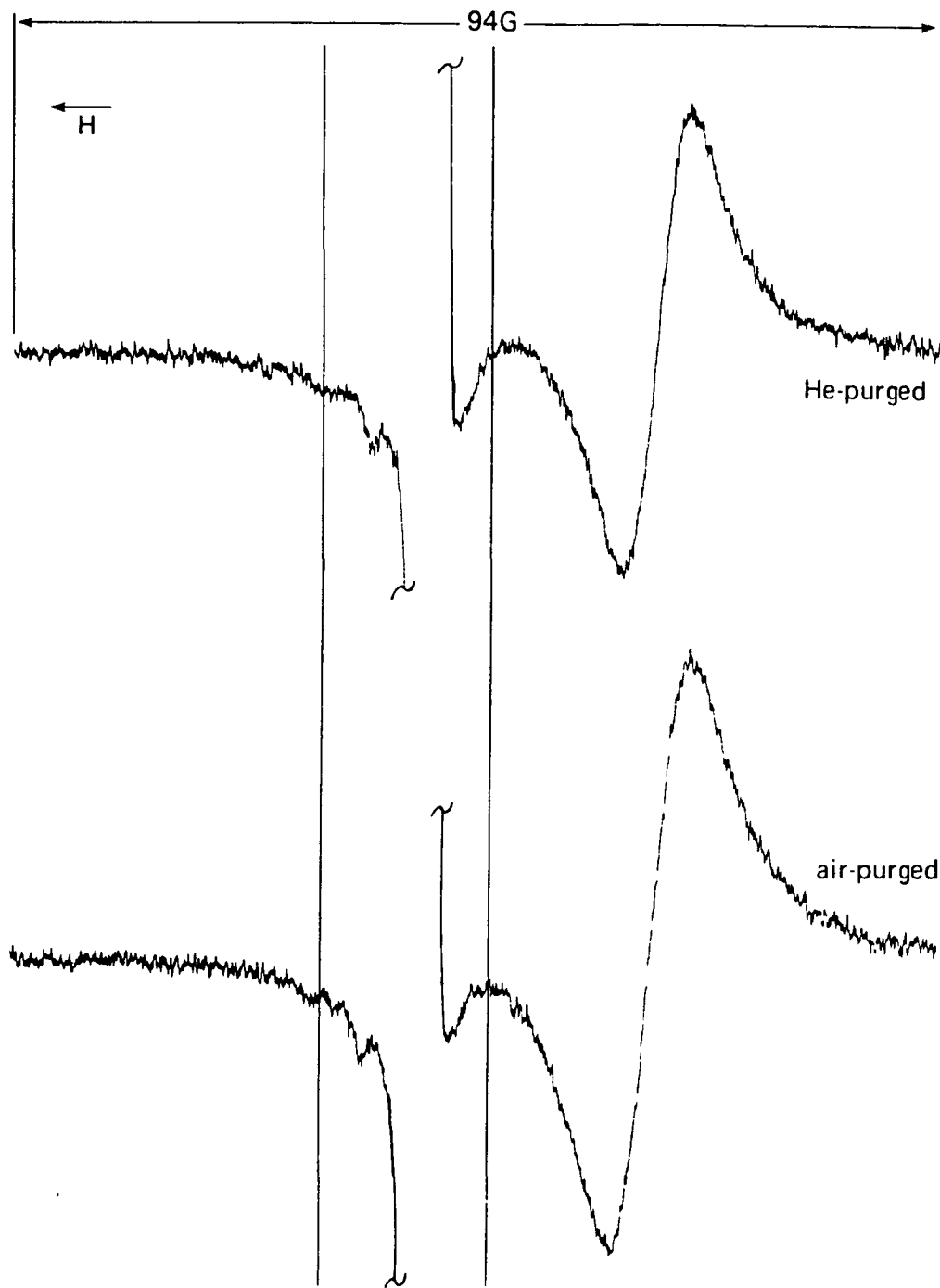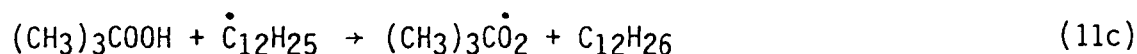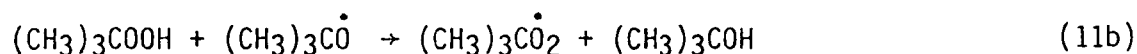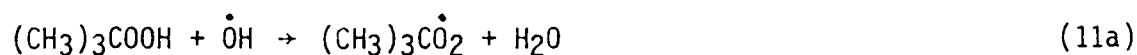
Photolysis at 22°C of 1% CHP in n-dodecane at 10.3 MPa.

Figure 12

1% t-butylhydroperoxide (TBHP) and 1% cumylhydroperoxide (CHP) respectively in n-dodecane at room temperature. The widths of the peroxy radical spectra are greatly different in the two figures; different peroxy radicals have formed. In Figure 11 the width, within experimental error, is that of t-butyl peroxy radical and not n-dodecyl peroxy which was reported upon earlier in n-dodecane solution. It is clear that the major radical at steady state is t-butyl peroxy, and the major reaction pathway seems reasonably straightforward:

$$(CH_3)_3COOH \xrightarrow{h\nu} (CH_3)_3C\dot{O} + \dot{O}H \tag{8}$$

$$C_{12}H_{26} + (CH_3)_3C\dot{O} \rightarrow \dot{C}_{12}H_{25} + (CH_3)_3COH \tag{9}$$

$$C_{12}H_{26} + \dot{O}H \rightarrow \dot{C}_{12}H_{25} + H_2O \tag{10}$$

Reactions (8), (9), and (10) give rise to n-dodecyl radicals and are similar to that taking place with peroxide initiation (reactions (1) and (2)). Reaction (7) has a major role which for this case becomes

$$(CH_3)_3COOH + \dot{O}H \rightarrow (CH_3)_3C\dot{O}_2 + H_2O \tag{11a}$$

$$(CH_3)_3COOH + (CH_3)_3C\dot{O} \rightarrow (CH_3)_3C\dot{O}_2 + (CH_3)_3COH \tag{11b}$$

$$(CH_3)_3COOH + \dot{C}_{12}H_{25} \rightarrow (CH_3)_3C\dot{O}_2 + C_{12}H_{26} \tag{11c}$$

Reactions (11a) and (11b) are well known. They compete for the primary radicals formed in reaction (8) and thereby reduce the amount of dodecyl radical that would otherwise be formed. Reaction (11c) is proposed as a possible way to account for differences in behavior between the use of cumene as a solvent instead of n-dodecane as described later. Upon going

from a helium to an air purge (Figure 11) the concentration of $(CH_3)_3C\dot{O}_2$ approximately doubles. The presence of oxygen introduces a new pathway in which oxygen rapidly reacts with n-dodecyl radicals to give n-dodecyl peroxy radicals, and a likely subsequent step is

$$C_{12}H_{25}\dot{O}_2 + (CH_3)_3COOH \longrightarrow C_{12}H_{25}OOH + (CH_3)_3C\dot{O}_2. \qquad (12)$$
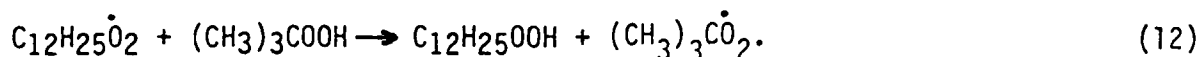
It should be pointed out that the UV lamp that was used decomposed only a few percent of the hydroperoxide. Much of the initial $(CH_3)_3COOH$ remains and is available for reactions (11) and (12). Also note that tertiary peroxy radicals have long lifetimes which means that a very large steady state concentration can form from small steady state concentrations of other radicals present which have very short lifetimes. In Figure 12 the peroxy radical signal should be that of cumyl peroxy radicals, $C_6H_5C(CH_3)_2\dot{O}_2$. There is some enhancement of signal strength when oxygen is present. The overall mechanism should be similar to that with t-butyl hydroperoxide.

Figures 13 and 14 further illustrate the formation of cumyl peroxy radical at room temperature from 1% cumene hydroperoxide using a solvent of 20% cumene in n-dodecane and a solvent of neat cumene respectively. The yield of peroxy radicals (helium purged) is far less in cumene (Figure 14) than in a solvent containing large amounts of n-dodecane (Figures 12 and 13). The primary radicals from the hydroperoxide are $\dot{O}H$ and $C_6H_5C(CH_3)_2\dot{O}$ and these can form hydrocarbon radicals from the solvent in similar manner to reactions (9) and (10). These primary radicals can also readily abstract hydrogen from the excess cumene hydroperoxide present in similar manner to reactions (11a) and (11b) giving peroxy radical that is observed by ESR. In a solvent rich in dodecane, dodecyl radicals form and possibly they can contribute to peroxy radical formation by abstracting hydrogen from the hydroperoxide (like reaction (11c). This pathway for peroxy radical formation is much less likely to be available
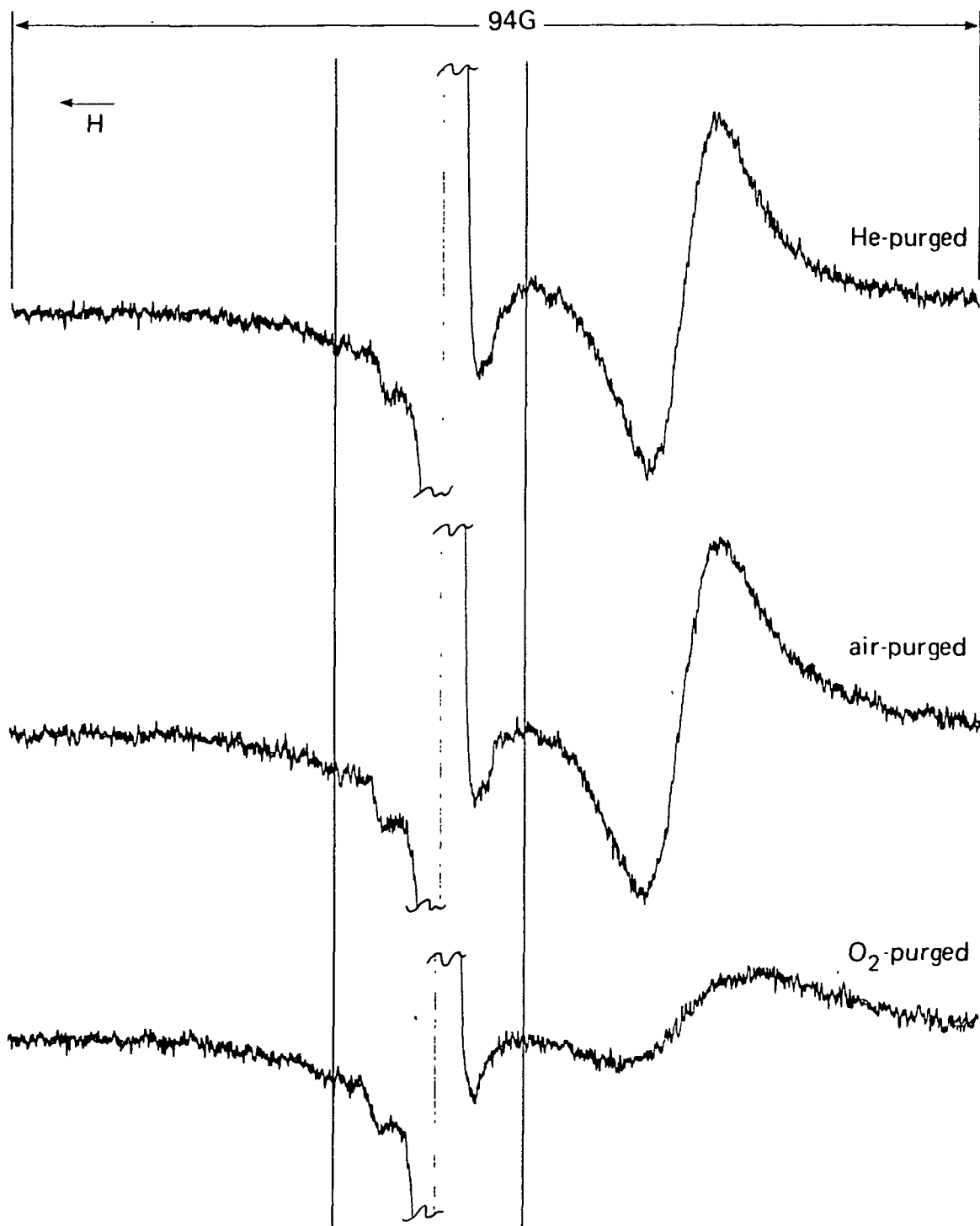
Photolysis at 23°C of 1% CHP and 20% cumene in n-dodecane at 10.3 MPa.

Figure 13
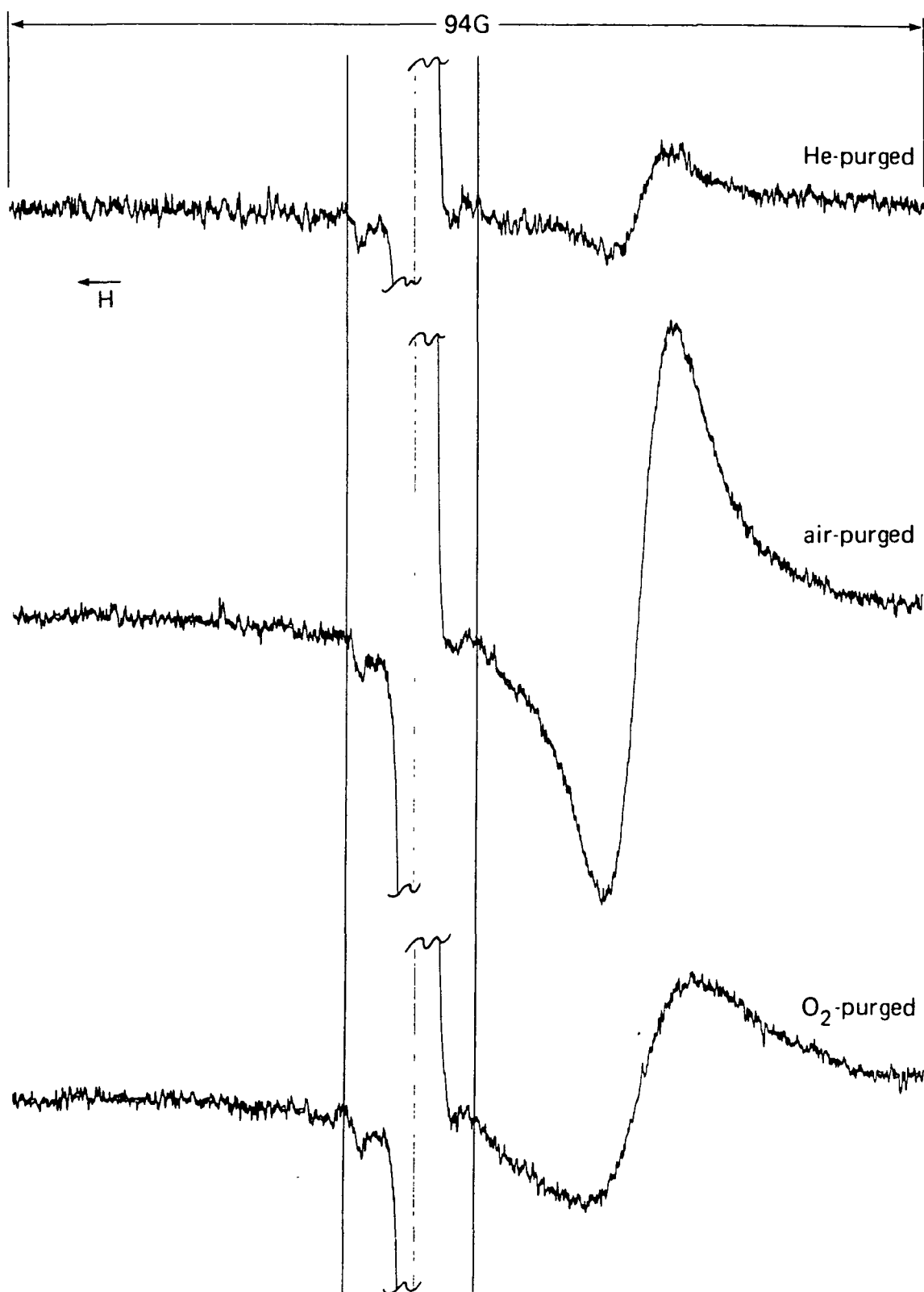
Photolysis at 23°C, 10.3 MPa of 1% CHP in cumene.

Figure 14

with cumene as a solvent since cumyl radicals would be formed which are much less reactive than dodecyl radicals. More detailed study is needed. In Figure 14 the increase in concentration of peroxy radical in going from a helium purge to an air purge is especially large, approximately a 9-fold increase. This large effect is attributed to the reaction of oxygen with cumyl, a fast reaction which directly enhances the concentration of cumyl peroxy radical. This is a more direct pathway than that in a solvent of dodecane. In Figures 13 and 14 the peroxy radical spectrum with an oxygen purge is substantially broadened with an accompanying decrease in intensity compared to an air purge. When account is taken of width and intensity it is found that the peroxy radical concentration is essentially unchanged. As indicated earlier, the width increase results from the physical presence of triplet state (magnetic) oxygen molecules.

Other variations in reagents that further illustrate the formation of $(CH_3)_3C\dot{O}_2$ and $C_6H_5C(CH_3)_2\dot{O}_2$ through the reaction pathways already discussed have been tried. For example, photolysis at room temperature of a 7% solution of di-$\underline{t}$-butyl peroxide in toluene gives a strong, well resolved spectrum of benzyl. The addition of 0.14% $\underline{t}$-butyl hydroperoxide decreases the concentration of benzyl to one-third its former value, and a spectrum of $(CH_3)_3C\dot{O}_2$ appears as a consequence of Reaction (7). It's interesting that such a small amount of hydroperoxide has such a large effect. Measurements of the spectrum of $(CH_3)_3C\dot{O}_2$ at 23.2°C gave a width of 17.0 G and g = 2.01518 ± 0.00010. This g value falls within the range reported[4,7] for a variety of peroxy radicals. If more hydroperoxide is added to the above reaction mixture the spectrum of benzyl can no longer be seen, but that of $(CH_3)_3C\dot{O}_2$ remains. Results similar to the above were obtained with a solution of 6.5% dicumyl peroxide in toluene. A spectrum of benzyl was obtained. This spectrum became much weaker with the addition of 1% cumene hydroperoxide, and a spectrum of $C_6H_5C(CH_3)_2\dot{O}_2$ appeared. Measurements were made at 21.4°C giving a linewidth of 6.4 G and g = 2.01497 ± 0.00015. With an additional 2% cumene hydroperoxide the benzyl spectrum almost disappeared and the spectrum of $C_6H_5C(CH_3)_2\dot{O}_2$ became 2.7 times stronger.

Hydroperoxides are often formed by air oxidation of hydrocarbons. As explained in the section entitled **Experimental Methods** an aeration device was built and tested with cumene. Tetralin is known to form a hydroperoxide upon air oxidation, and an experiment was carried out with tetralin purified by vacuum distillation over $LiAlH_4$. Aeration was carried out for 18 hours at 75°C which yielded a pale amber colored solution containing a small amount of tetralin hydroperoxide. Photolysis at room temperature gave a weak spectrum of the peroxy radical of tetralin-1-yl, and the mechanism for its formation from the hydroperoxide should parallel that already described. The spectrum was interesting because it showed a partially resolved doublet resulting from a hyperfine interaction with the single hydrogen located alpha to the peroxy group. This material was also photolyzed at room temperature as a 10% solution in n-dodecane. A very weak spectrum, also a doublet, of the same peroxy radical was obtained. n-Dodecane as purchased (Phillips Chem. Co., pure grade, 99%) was examined by ESR to see if there was any indication of hydroperoxides. No spectrum was obtained upon photolysis at room temperature. After aeration at 75°C for 27 hours a very weak peroxy spectrum was seen. Other experiments with aerated hydrocarbons will be described later.

GC analyses of a few of the systems containing hydroperoxides were made after photolysis at or near room temperature. The amount of conversion of the hydroperoxide to products was too small to give highly useful analytical data. In particular, solutions containing 5% t-butyl hydroperoxide in toluene and also in benzene with helium purge and also with air purge were analyzed after photolysis at room temperature. In all cases a small amount of t-butyl alcohol was found corresponding to conversion of a few percent of the hydroperoxide to products. Also present were a large number of unidentified products in trace amounts. More meaningful assays would require experimental conditions in which a larger amount of hydroperoxide is converted to products.

4.4 Systems with Hydroperoxides at Elevated Temperatures

As shown earlier, photolysis of solutions of hydroperoxides in hydrocarbons at room temperature gives peroxy radicals. In general, upon raising the temperature the spectrum of the peroxy radical broadens rapidly, loses amplitude, and becomes undetectable at approximately 100°C. It has not been possible to ascertain if the loss in signal is entirely due to the increase in width or if there is also a decrease in concentration of the peroxy radical. In general, with further increases in temperature there is a moderate range over which no spectra are observed. At still higher temperatures the spectrum of a hydrocarbon radical emerges. At high enough temperatures thermal initiation takes over. Some of these steps are illustrated in Figure 15 for a solution of 1% cumene hydroperoxide and 20% cumene in n-dodecane. The spectrum at 25°C is that of cumyl peroxy radical. This spectrum can no longer be seen at 100°C. At higher temperatures a spectrum of cumyl emerges and is easily observed at 212°C with photolysis as shown in the figure. This temperature is not quite high enough to give a spectrum by thermal initiation, and, as shown in the figure, when the UV lamp is turned off the spectrum almost completely disappears. A few of the strongest lines are just detectable in the noise background. With further heating thermal initiation gives a stronger spectrum of cumyl which reaches optimum intensity at 280°C (in our spectrometer at 1 ml/min flow) as shown in Figure 15. Initiation by hydroperoxides at elevated temperatures resembles that observed with peroxides. In the example given, n-dodecyl radicals must have also been formed, but they cannot be seen; they generate more cumyl by Reaction (5).
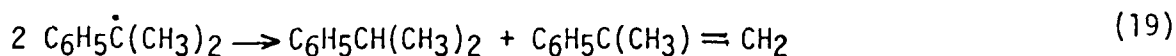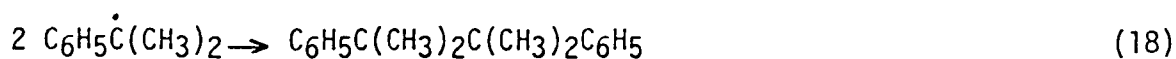
A more detailed study was made at 280°C in a system similar to the above. A solution of 1% cumene hydroperoxide in cumene was used, and the spectrum of cumyl was much more intense than that shown in Figure 15 at 280°C. The system was observed with helium, air, and oxygen purges, and there was no detectable variation in the spectrum. The fact that there was no line broadening means that all of the oxygen was consumed by the time the

36
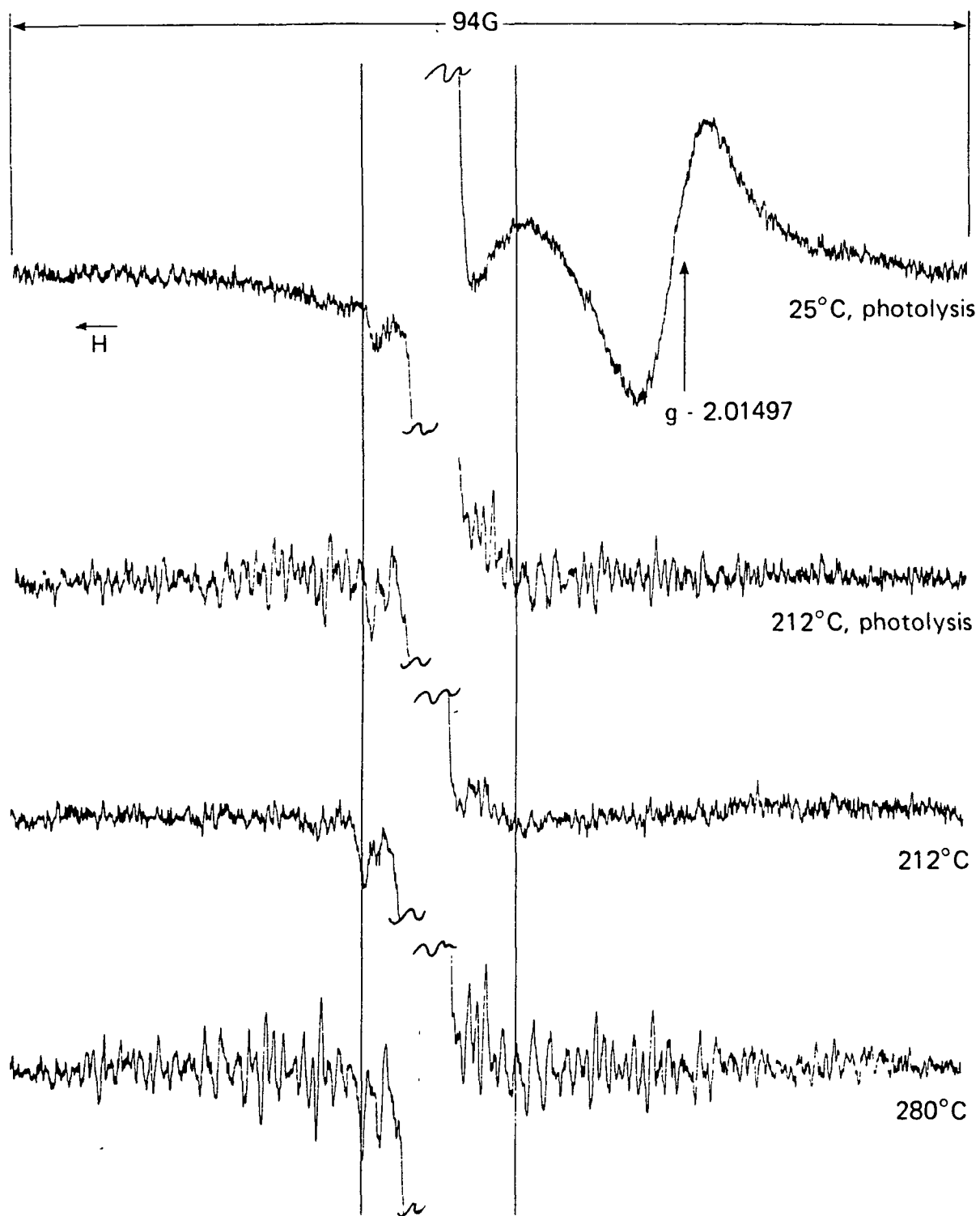
Radicals from 20% cumene and 1% CHP in n-dodecane at 10.3 MPa.

Figure 15

sample arrived in the active region of the spectrometer. Subsequent GC
analyses showed no changes in products with the nature of the purge. In the
several seconds the sample was at 280°C approximately 73% of the cumene
hydroperoxide was consumed, and the amount of oxygen present in the samples
(saturated at atmospheric pressure) was trivial compared to the total
chemical change taking place. The fate of the dissolved oxygen is not
known, but it is likely that it ended up in forming cumene hydroperoxide
making a very tiny addition to that already present. Major products found
were α-methylstyrene, acetophenone, 2-phenyl-2-propanol (cumyl alcohol), and
2,3-dimethyl-2,3-diphenylbutane (dicumyl). One product found in small
amount in solution was tentatively assigned to methane. Considerable
gaseous product was formed, and this probably was largely methane. A
mechanism accounting for these products is virtually the same as that for
initiation by peroxides with essentially all steps being well documented in
the literature.

$$C_6H_5C(CH_3)_2OOH \longrightarrow C_6H_5C(CH_3)_2\overset{\bullet}{O} + \overset{\bullet}{O}H \tag{13}$$

$$C_6H_5C(CH_3)_2\overset{\bullet}{O} + C_6H_5CH(CH_3)_2 \longrightarrow C_6H_5\overset{\bullet}{C}(CH_3)_2 + C_6H_5C(CH_3)_2OH \tag{14}$$

$$\overset{\bullet}{O}H + C_6H_5CH(CH_3)_2 \longrightarrow H_2O + C_6H_5\overset{\bullet}{C}(CH_3)_2 \tag{15}$$

$$C_6H_5C(CH_3)_2\overset{\bullet}{O} \longrightarrow \overset{\bullet}{C}H_3 + C_6H_5COCH_3 \tag{16}$$

$$\overset{\bullet}{C}H_3 + C_6H_5CH(CH_3)_2 \longrightarrow C_6H_5\overset{\bullet}{C}(CH_3)_2 + CH_4 \tag{17}$$

$$2\ C_6H_5\overset{\bullet}{C}(CH_3)_2 \longrightarrow C_6H_5C(CH_3)_2C(CH_3)_2C_6H_5 \tag{18}$$

$$2\ C_6H_5\overset{\bullet}{C}(CH_3)_2 \longrightarrow C_6H_5CH(CH_3)_2 + C_6H_5C(CH_3)=CH_2 \tag{19}$$
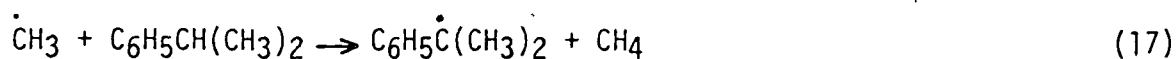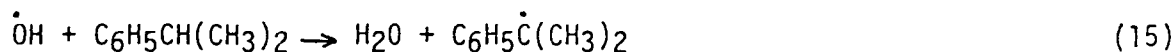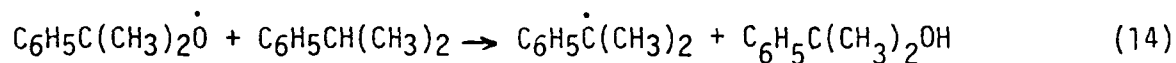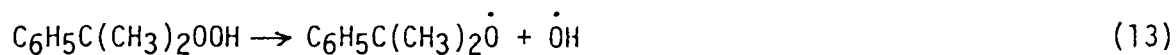
Reaction (13) may be initiated photolytically or thermally. Reaction (14)
gives rise to a portion of the observed cumyl radical and the observed

product cumyl alcohol. Similarly (15) gives a portion of the observed cumyl. Reaction (16) is a branch pathway, a well known reaction, giving rise to the observed product acetophenone and $\overset{\bullet}{C}H_3$. The $\overset{\bullet}{C}H_3$ is largely consumed in (17) to give more cumyl radical and CH_4 which accounts for the large amount of gas formed. The branching through reactions (16) and (17) is a relatively minor pathway at low temperatures, but appears to be much more important in this work at high temperature. Reactions (18) and (19) are the major pathways for the disappearance of cumyl radical. Near room temperature cumyl disappears exclusively through (18) while at much higher temperatures,[1] it goes through reaction (19). At 280°C both reactions are important and account for the products dicumyl and α-methylstyrene. A moderate amount of n-propylbenzene is also formed, and we do not know the mechanism. In earlier work[1] we obtained a cumyl radical spectrum during the pyrolysis of cumene (without initiator) at considerably higher temperatures, and here too n-propylbenzene was found as one of the products. The above mechanism has the appropriate stoichiometry to account for observed products, but it very likely is an over simplification since it does not include peroxy radicals which very likely are present even though not observed by ESR. One possibility is that peroxy radical quickly decomposes to the hydrocarbon radical and O_2 with the O_2 subsequently being consumed. Another possibility is that peroxy radical may rapidly abstract hydrogen from the hydrocarbon at high temperature: $RH + R'\overset{\bullet}{O}_2 \rightarrow \overset{\bullet}{R} + R'OOH$. More research is intended in this area.

A number of other experiments were done which further illustrate the change in character of systems with hydroperoxides in going from room to elevated temperatures. Solutions of t-butyl hydroperoxide and of cumene hydroperoxide in toluene have been examined over a comparable temperature range to that illustrated in Figure 15, and the general behavior was the same. Benzyl radical was observed at the higher temperatures. GC analyses were made at many temperatures. Bibenzyl is a combination product of benzyl radicals. At low temperatures bibenzyl was not found. At higher

temperatures where the spectrum of benzyl radical first appeared the GC's showed bibenzyl appearing in small amounts as a product. At higher temperatures the benzyl radical spectrum became more intense and the amount of bibenzyl as a product increased.

Other initiators made by aeration of hydrocarbons have been examined at elevated temperatures. As described earlier, a dilute solution of tetralin hydroperoxide was made by aerating tetralin. This material gave a peroxy radical spectrum upon photolysis at room temperature. The peroxy radical was not observed at high temperatures. At 270°C a weak spectrum of many sharp lines was present which very likely came from the tetralin-1-yl radical. Air oxidation of indene (redistilled) at 75°C for 20 hours gave a clear, deep yellow liquid. A spectrum was not obtained by photolysis at room temperature, but at elevated temperatures a spectrum of indenyl radical was observed.

4.5 Experiments with 2,5-Dimethylpyrrole

Exploratory experiments were carried out with 2,5-dimethylpyrrole to see if its presence would affect the concentration of free radicals present in a system and to see if formation of solids would be initiated. The first experiments were in systems initiated photolytically. A very strong spectrum of cumyl peroxy radical was obtained at room temperature upon photolyzing 5% cumene hydroperoxide in toluene. The addition of 0.1% 2,5-dimethylpyrrole reduced the peroxy signal to 25% of its original strength. Upon adding an additional 0.2% of the pyrrole the signal strength dropped to 15% of its original value. Clearly the pyrrole had a large affect on the peroxy radical chemistry. In this experiment the sample was recirculated, and after the addition of the pyrrole the system was examined at progressively higher temperatures. By the time 120°C was reached a spectrum had developed that was characteristic of a paramagnetic solid deposit, and this spectrum became very strong at higher temperatures. Upon cooling the system to room temperature and flushing with toluene the spectrum persisted which confirmed that it was a solid deposit formed in the silica capillary.

A spectrum of n-dodecyl radicals was formed thermally at 212°C from 7% DTBP in n-dodecane (Figure 3a). The addition of 1% 2,5-dimethylpyrrole weakened the n-dodecyl spectrum but did not produce a paramagnetic deposit. On the other hand, a solution of the same composition containing the pyrrole (and recirculated) gave a signal from a solid deposit upon photolysis at room temperature. Subsequent heating to 217°C gave copious production of solid throughout the entire liquid handling system. These preliminary experiments show what we regard as a large effect on free radical chemistry by the presence of small amounts of 2,5-dimethylpyrrole, and the systems appear particularly sensitive to solid formation when initiated photolytically.

Subsequent experiments were done exclusively with thermal initiation. An intense, well resolved spectrum of benzyl was obtained from toluene containing 3% di-t-butyl peroxide at 212°C as shown at the top of Figure 16. This solution was modified by adding 0.1% and 1% 2,5-dimethylpyrrole with and without the addition of 1% t-butyl hydroperoxide. Some of the spectra are shown in Figure 16. The center shows that the addition of 1% of the pyrrole produces only a small decrease in signal intensity. Similarly (not shown in the figure) the addition of 1% t-butyl hydroperoxide produces only a small decrease. However, as shown in the bottom of Figure 16 when both are present there is a very noticeable decrease in benzyl concentration. Smaller effects were observed with 0.1% pyrrole. The liquid samples from this sequence of experiments were collected and stored in the dark. All were colored ranging from light yellow to dark brown and the depth of color correlated with the decrease in benzyl signal strength. The darker samples gave solid deposits that coated the bottoms of the glass bottles as tenacious films after storage from one to several days. No solid paramagnetic deposit formed while the spectra were recorded. These experiments again demonstrate the participation of small amounts of the pyrrole in free radical reactions. The presence of hydroperoxide accentuates the effect.
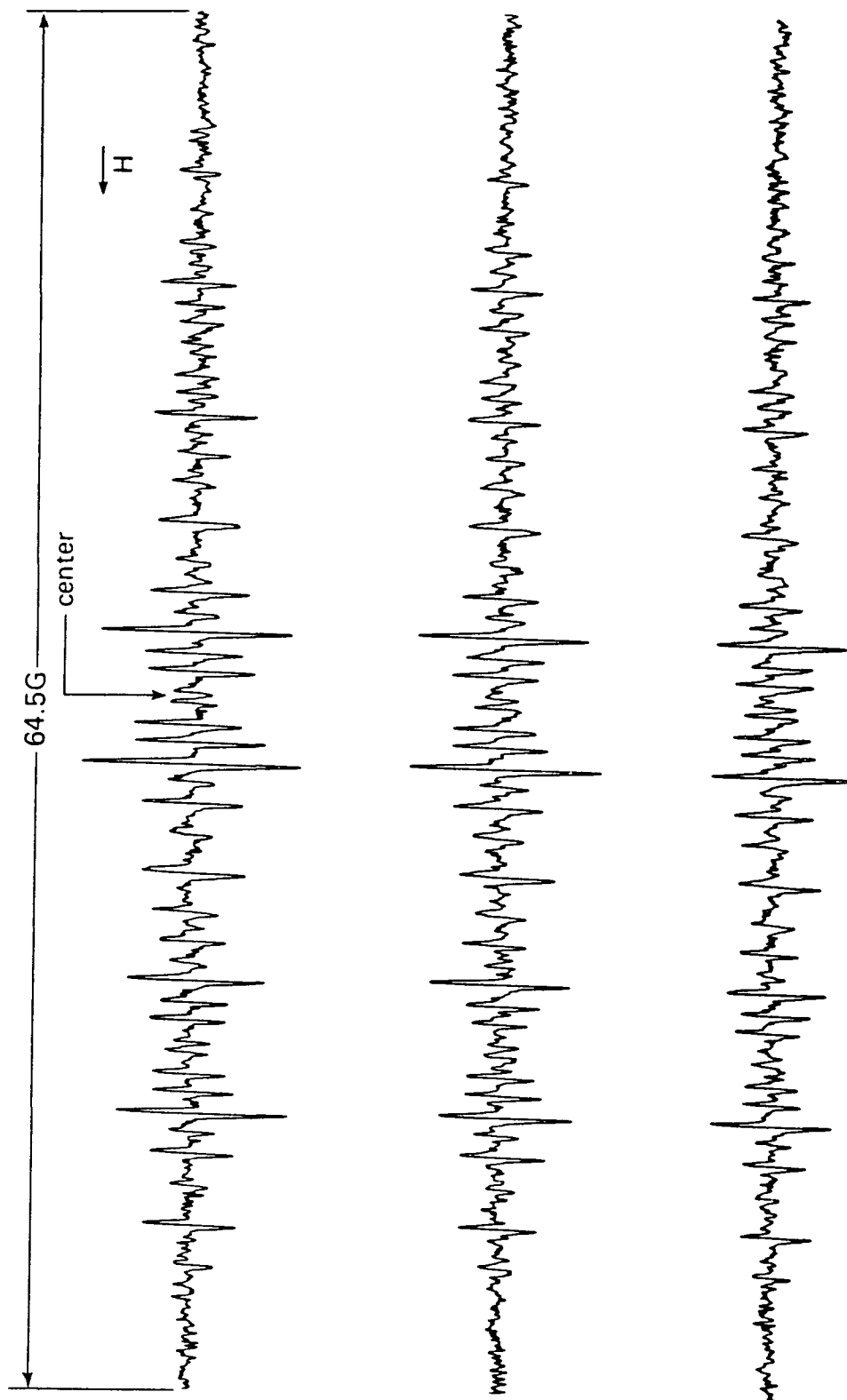
Figure 16

Top: 3% DTBP in toluene at 212°C, 13.8 MPa showing benzyl.
Center: Contains 1% 2,5-dimethylpyrrole.
Bottom: Contains 1% 2,5-dimethylpyrrole and 1% TBHP.

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Finally a sequence of experiments were done with a hydroperoxide using thermal initiation. The top of Figure 17 shows a strong, well resolved spectrum of cumyl from 3% cumene hydroperoxide in cumene at 280°C. The addition of 0.1% 2,5-dimethylpyrrole causes a solid paramagnetic deposit to slowly collect on the heated silica capillary. This appears in the center spectrum of Figure 17 as a wave in the baseline at the center of the spectrum. If the spectrum had been recorded a second time the broad signal from the solid would have become more pronounced because of the extra collection time. Instead, additional pyrrole was added to give a big effect as shown in the bottom spectrum of Figure 17. Upon cooling to room temperature only the broad signal from the solid persists as shown in Figure 18.

4.6   Experiments with Jet A

A sample of Jet A was obtained from NASA-Lewis Research Center, and attempts were made to observe ESR spectra with a variety of conditions. Neither photolysis at room temperature nor heating to 480°C (1 ml/min flow of sample) gave observable spectra. A sample was air oxidized at 75°C for 22 hours, and neither photolysis at room temperature nor heating to 280°C gave a spectrum. On the other hand, very weak spectra were obtained from a solution of 6% di-$\underline{t}$-butyl peroxide in Jet A. Heating to 212°C gave weak lines at the positions of the stronger dodecyl lines. These lines likely arise from a superposition of spectra from a mixture of radicals of the type $RCH_2\overset{\bullet}{C}HCH_2R'$ formed from long chain aliphatic hydrocarbons. Photolysis at room temperature did not give a peroxy radical spectrum, but there were some extremely weak lines that likely were the same as those better seen at 212°C. As indicated in Section 4.1 it is reasonable to see spectra from the mixture of $RCH_2\overset{\bullet}{C}HCH_2R'$ radicals. It would have also been reasonable to have seen a peroxy radical signal from a mixture because radicals of this type generally consist of a single line at essentially the same g value, but we did not see such a spectrum. The Jet A may have contained an antioxidant which could have been the reason that a peroxy radical signal was not seen.
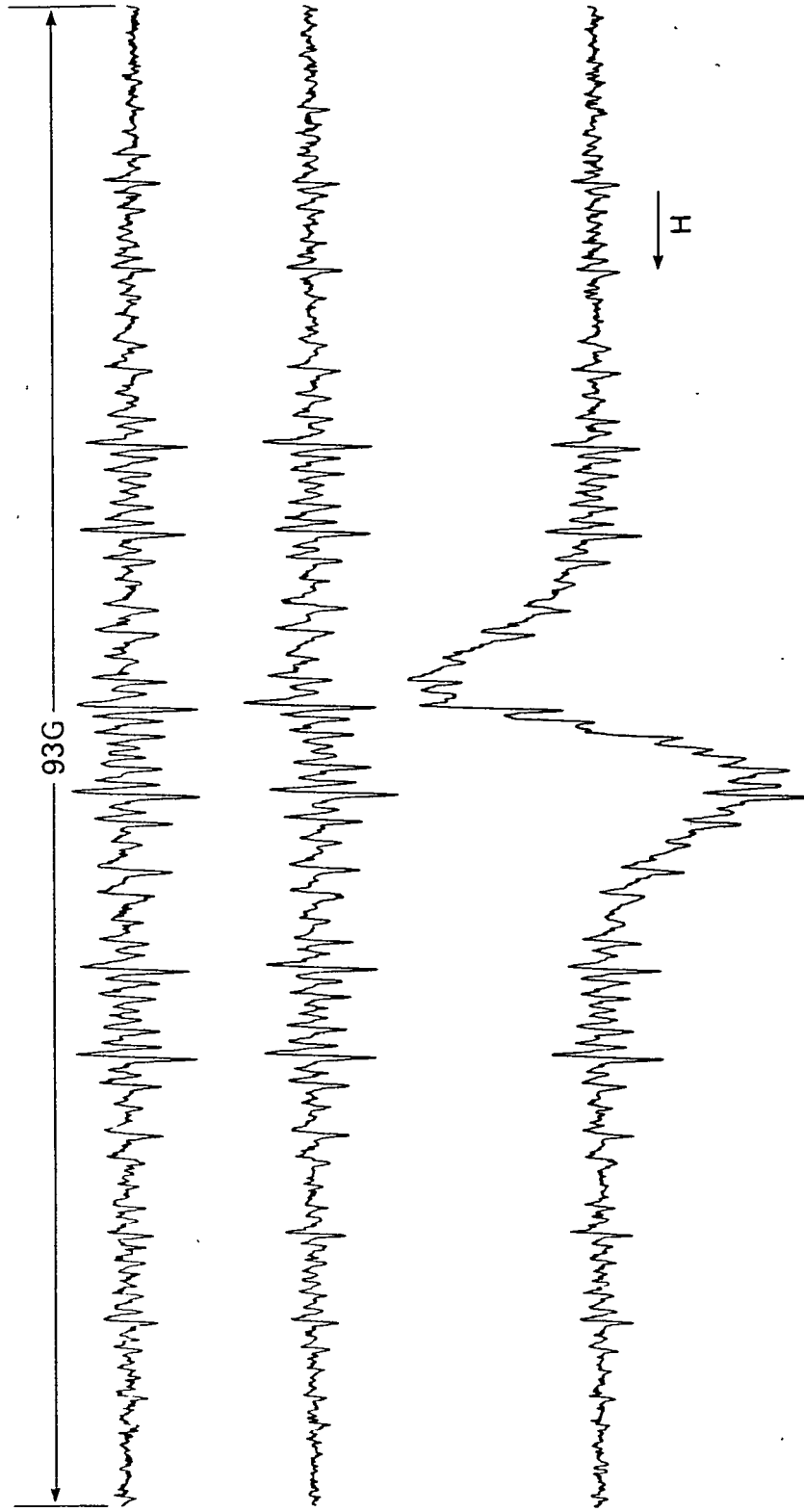
ORNL DWG 83-15614

93G

H

Fig. 17. Top: 3% CHP in cumene at 280°C, 13.8 MPa.
Center: Contains 0.1% 2,5-dimethylpyrrole.
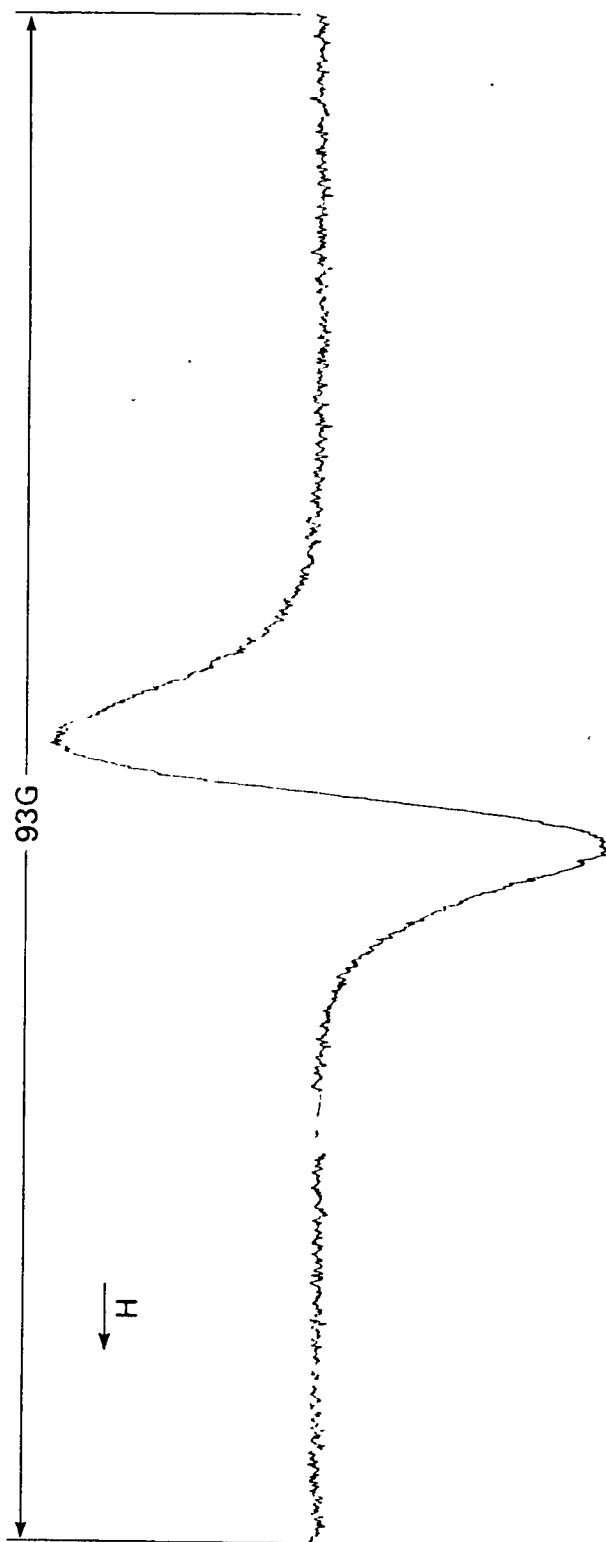Bottom: Contains 0.5% 2,5-dimethylpyrrole.

Fig. 18. Spectrum at room temperature, 13.8 MPa of deposit from 3% CHP and 0.5% 2,5-dimethylpyrrole in cumene at 280°C after cooling to room temperature and rinsing with cumene.

We would not expect to see a spectrum from a mixture of short lived aromatic radicals because these spectra, in general, would not have lines that superimpose.

Pyrolysis of Jet A gives an observable spectrum. Very weak sharp lines are obtained at 530° with the customary sample flow rate of 1 ml/min which gives a contact time of less than 5 seconds. By prolonging the contact time by using flow rates of 0.1 ml/min and even stopping the flow an extremely strong spectrum may be obtained at temperatures lower than 530°C. The spectrum is from stable free radicals that can also be observed at room temperature after they have been formed at temperatures above 400°C. The spectrum obtained at 480°C with a sample flow rate of 0.1 ml/min is shown in Figure 19. The major contribution to the spectrum comes from the phenalenyl (perinaphthenyl) radical which is a very stable radical and which has been observed in a variety of pyrolyzed organic systems.[8] It has also been found[9] in pyrolyzed petroleum hydrocarbons.
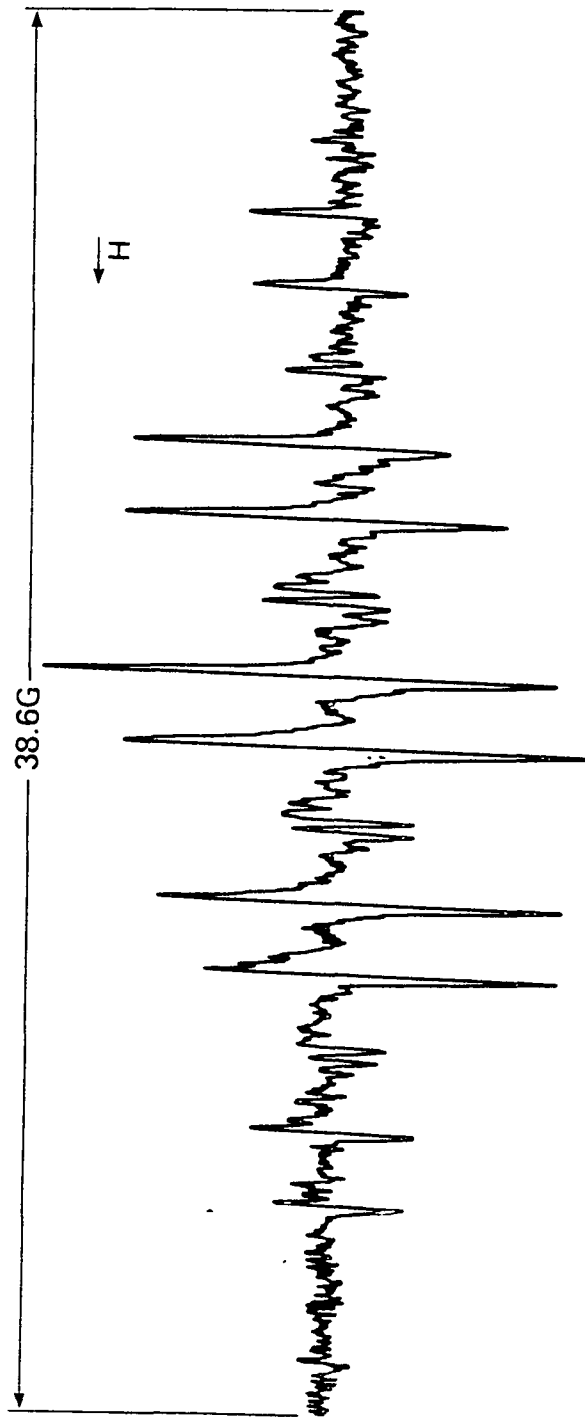
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Fig. 19. Jet A fuel pyrolyzed at 482°C, 17.2 MPa.

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15. Supplementary Notes

16 Abstract

Free radicals have been studied by electron spin resonance (ESR) using model compounds that are representative of constituents of jet fuels. Radical formation has been initiated with peroxides and hydroperoxides by using UV photolysis at and near room temperature and thermal initiation at higher temperatures. Both oxygen free and air saturated systems have been studied. n-Dodecane has frequently been used as a solvent, and a mixture of n-dodecyl radicals has been made with a peroxide initiator in n-dodecane (free of oxygen) thermally at 212° C and photolytically at room temperature. Hydrogen abstraction from the 3,4,5 and 6-positions gives radicals that are sufficiently alike that their spectra are essentially superimposed. The radical formed by abstraction of hydrogen from the 2-position gives a different spectrum. ESR parameters for these radicals have been measured. The radical formed by abstraction of a primary hydrogen was not observed. Similar radicals are formed from n-decane. A variety of exploratory experiments have been carried out with systems that give free radical spectra to which has been added small amounts of 2,5-dimethylpyrrole. The pyrrole frequently lowers the steady state concentration of free radicals, and in some systems there is an accompanying formation of paramagnetic solid. Photolytic systems seem especially susceptible to solid formation, and there is some indication that the presence of hydroperoxides enhances the effectiveness of the pyrrole.

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