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SINGLET OXYGEN GENERATION - ENDOPEROXIDE THERMOLYSIS KINETICS

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A polymeric endoperoxide compound was synthesized, deposited in thin films on a conductive surface, and heated to release excited oxygen ($O_2{}^1\Delta$). The polymer, 1,4-dimethyl-2-vinylnapthalene, was photoperoxidized in 75 percent yield to give the endoperoxide, 2-PVNE. This polymer was then spin-coated onto Pyrex substrates with film thicknesses ranging from 20 to 250 nm. Heating of the polymer to approximately 100°C caused complete release of oxygen. Yield measurements using various film thicknesses revealed that the release of excited oxygen reaches a maximum for films approximately 40 nm thick. Quenching of $O_2{}^1\Delta$ within the napthalene polymer is thought to limit the useful polymer thickness. The percent yield at this optimum thickness, measured optically and with a titration method, was roughly 50 percent. The polymer surface area required for release of one mole of excited oxygen is on the order of 10^4 m^2.

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Introduction

The objective of this research effort is the evaluation of a new concept for the generation of singlet delta oxygen through the use of polymer bound endoperoxides. Currently sparger-type basic hydrogen peroxide-chlorine reactors are used to provide singlet delta oxygen in high yield for laboratory size chemical oxygen-iodine lasers. However, the sparger-type generators are neither scalable to high energy nor capable of space-based or airborne operation.

The solution phase thermolysis reaction of many polyacene endoperoxides is known to yield singlet delta molecular oxygen and the parent hydrocarbon. Generating singlet delta oxygen directly into the gas phase upon thermolysis of solid polymer bound endoperoxides is proposed. For release of singlet delta oxygen into a vacuum or low pressure gas, polymer bound endoperoxides were chosen because of the low vapor pressure of these high molecular weight materials. In concept, the thermolysis of solid endoperoxides offers the promise of a scalable source of singlet delta oxygen which could be used in airborne laser systems. This system of generation has the further advantage of freedom from corrosive chemicals and gas phase contaminants.

The first step in the evaluation of an endoperoxide generator concept is the collection of a data base of kinetic rate constants. Polymer bound endo-peroxides can be used in many different forms--as fibers, sheets or coatings on other substrates. In whatever form it is used, the polymer can be charac-terized by a thickness or distribution of thicknesses (the shortest distance which a liberated oxygen molecule must travel to reach the gas phase). The probability that the excited oxygen molecule will reach the gas phase without first being quenched will depend upon the thickness of the polymer material,

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the speed with which it diffuses out of the polymer, and the fraction of
polymer-singlet oxygen collisions which result in deactivation of excited
oxygen. The rate at which oxygen is liberated from the endoperoxide molecule
will depend on temperature. It is the goal of the endoperoxide research
effort to measure the important kinetic parameters which are instrumental in
the design of an endoperoxide fuelled singlet oxygen generator.

Experimental Program

Materials

Three polymer bound endoperoxides and one endoperoxide salt were synthesized during this project. The latter compound, the lithium salt of [4-methyl-naphthalene-1,4-endoperoxide]-3-propanoic acid, was expected to have a low vapor pressure at elevated temperatures and be suitable for thermolysis chemistry in a low pressure environment. One of the three polymers synthesized was a condensation product of poly(vinyl alcohol) and [4-methyl-naphthyl]-3-propanoic acid.* The polymerization of 1,4-dimethyl-2-vinylnaphthalene (2-PVN) and 1,4-dimethyl-6-vinylnaphthalene,** along with the photoperoxidation of all the compounds mentioned, was carried out at KMS Fusion.***

Preliminary investigations with the lithium salt showed that this compound decomposed at the elevated temperatures necessary to cause oxygen release. Evidence of extensive decomposition was observed in the mass spectrum of the released gas which contained mass peaks associated with carbon containing fragments. The solid lithium salt is apparently difficult to free of adsorbed solvent, and it is possible that the pyrolysis reactions which are observed can be suppressed by a more careful preparation procedure. However, time and funding constraints did not allow for this level of activity so the investigation was abandoned. The polymer formed by ester linkage of the napthylenic propanoic acid with poly(vinyl alcohol), NP-PVA, was then studied.

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* Compound was synthesized in the laboratories of Dr. A. Paul Schaap, Professor of Chemistry, Wayne State University, Detroit, MI.
** The naphthalene compounds were also synthesized by A. Paul Schaap at Wayne State.
*** KMS Fusion, Inc., Ann Arbor, MI

Initial investigation of the endoperoxide of NP-PVA showed that upon thermolysis it released oxygen quantitatively and without degradation of the polymer. The photoperoxidation of this material proved to be difficult. The photoperoxidation procedure uses the dye methylene blue as the sensitizer for the production of singlet delta oxygen which then reacts with the naphthalene group of the polymer at a temperature of 0 C to produce the endoperoxide. The dye was unexpectedly incorporated into the polymer material and inhibited further peroxidation of the polymer. Success in the synthesis of NP-PVA endoperoxide proved to be sporadic, and the supply of material was prematurely exhausted.

The two poly(vinyl naphthalenes) proved much easier to photoperoxidize. The 1,4-dimethyl-2-poly(vinylnaphthylene-1,4-endoperoxide), 2-PVNE, was most extensively investigated. The 6-polyvinyl isomer could only be examined in preliminary fashion because of time and funding limitations. Therefore the kinetic results will focus entirely on 2-PVNE. A complete description of the synthesis of the four materials, as well as their characterization by proton and carbon nuclear magnetic resonance, is included in Appendix A.

Apparatus

The experimental equipment which was used to collect kinetic data is illustrated in Figure 1. The sample chamber is a stainless steel cube Teflon coated on the inside and equipped with ports on all six faces. The chamber was evacuated through one port with a 150 1/s diffusion pump. A butterfly valve at the sample chamber port entrance is used to isolate the sample chamber once it has been pumped down to high vacuum. The endoperoxide was introduced into the chamber as a thin film coating on a 1-in-sq Metavac[*] Pyrex

* Metavac, Inc., Flushing, N.Y.

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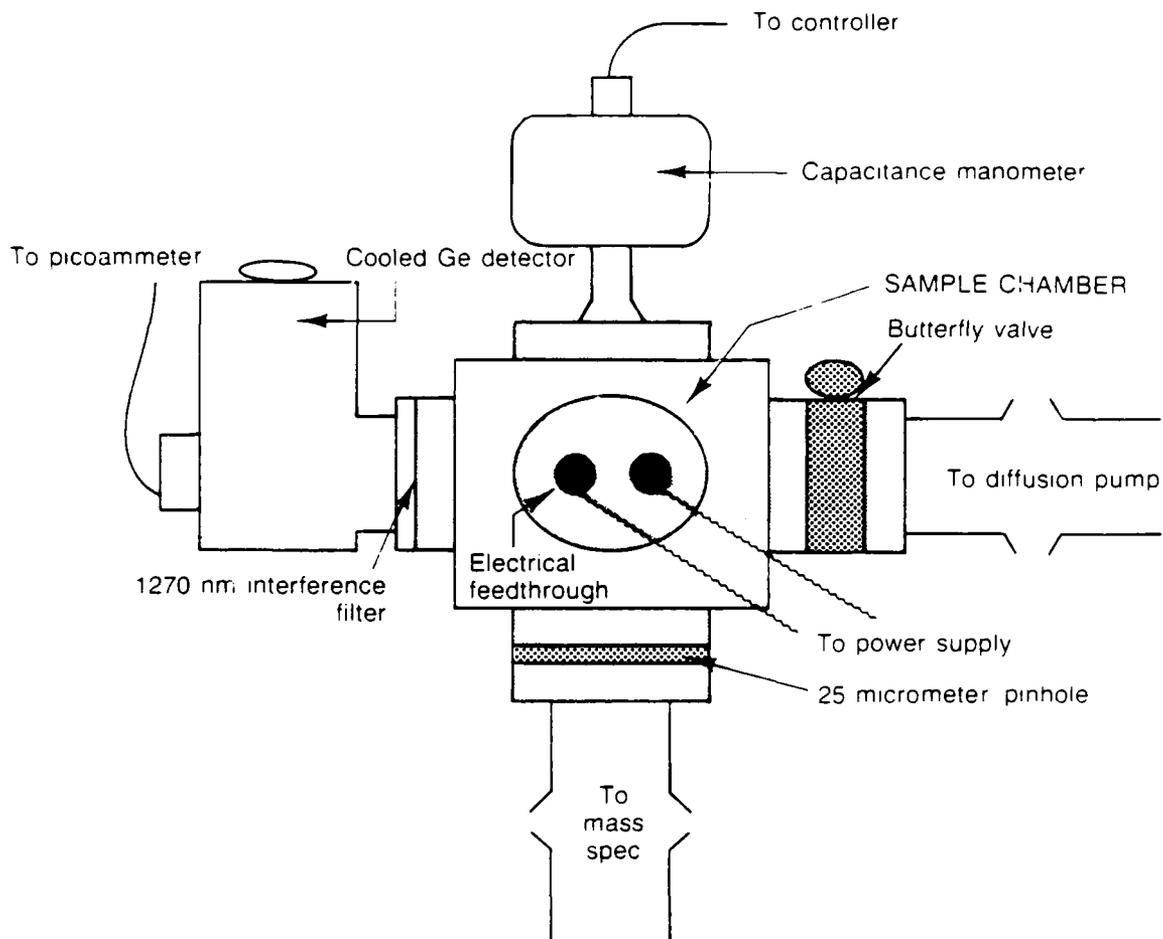
Figure 1. Experimental apparatus.

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substrate, 1/8-in-thick, which was clamped in place between two electrodes from an electrical feed-through flange which occupies a port on the cube. The remaining ports of the cube were fitted with optical windows for viewing luminescence from singlet delta oxygen, an FPI capacitance manometer for determining the quantity of gas released and a 25 μm pinhole connected to a quadrupole mass spectrometer detector.

Primary emission from singlet delta oxygen released in the thermolysis reaction of the endoperoxide was detected with a liquid nitrogen cooled germanium diode equipped with a 1270 nm interference filter. The signal from the germanium diode was amplified with a Keithley 410A picoammeter and then passed through a 10 Hz low pass cutoff filter (to decrease the bandwidth thus improving signal-to-noise) before being recorded on an oscilloscope.

The heating of the endoperoxide was accomplished by passing an electrical current through a thin conductive coating bonded to the surface of the Pyrex substrate. The conductive coating, which consists of a proprietary metal oxide coating with a resistance of 20 to 40 Ω/sq, was deposited on the 1-in-sq Metavac Pyrex substrates. The endoperoxide was deposited directly on top of the conductive metal oxide coating so that the temperature of the endoperoxide film tracked the front surface temperature of the heated plate. Electrical contact was made to the substrate conductive coating using the following procedure (Fig. 2). Copper foil with an adhesive backing was fixed to a 1/8-in-strip at two opposite ends of the plate. The edge of the junction between copper foil and substrate was painted with a conductive (silver-filled) fluorocarbon resin (Acheson Electrode 504), and mechanical contact was made to the copper foil with copper clamps which were attached to the rods of the electrical feed-throughs.

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Endoperoxide Substrate

TOP VIEW

To electrical
feedthrough

Pyrex substrate →

Conductive
metal oxide coating →

To electrical
feedthrough

Endoperoxide film

Teflon mask

Copper electrodes
(clamps)

FRONT VIEW OF SUBSTRATE
WITH TEFLON MASK

Conductively coated
substrate

Silver paint →

Copper foil →

Teflon mask →
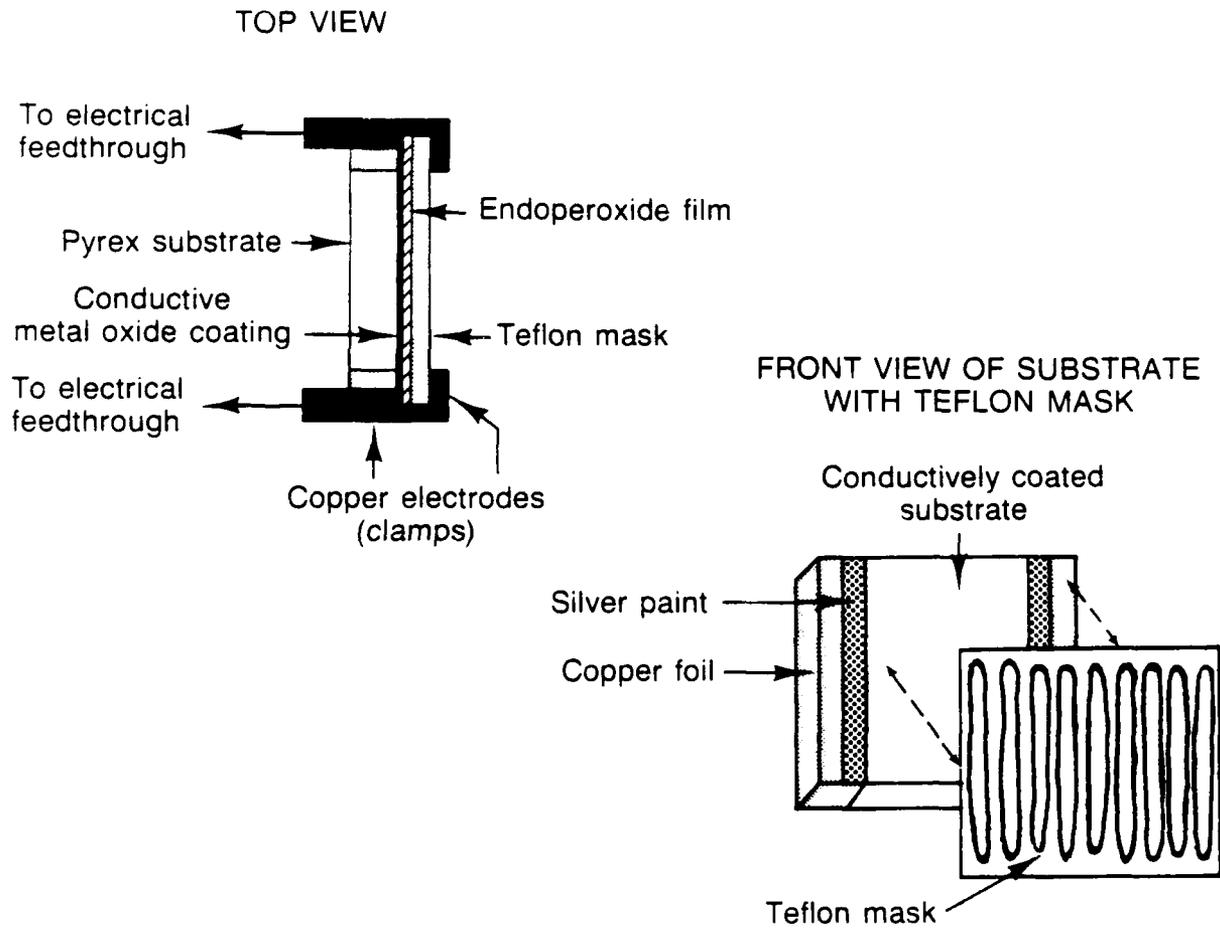
Figure 2. Geometry of the endoperoxide film on the substrate surface.

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The electrical current flowing through the conductive coating on the substrate was controlled so that the temperature of the endoperoxide could quickly be raised to a target temperature and maintain a constant temperature for a period of several seconds. A Kepco ATE 150-3.5M regulated power supply provided the current for the heating of the substrate. The power supply was controlled by an IBM XT computer equipped with a Qua Tech WSB-10 waveform synthesizer board which could be programmed to provide any temporal profile desired. The temporal profile of the pulses has two regions. At early times, the current is held constant at a value as large as is consistent with the resistance of the particular substrate. This results in a maximum heating rate of the substrate. After a period of time, calculated to bring the endoperoxide substrate up to the target temperature, the current decreases at a rate which is proportional to the 1/4 power of time. This region of the heating pulse is designed to maintain the endoperoxide film constant at the target temperature. Appendix B discusses the details of this procedure.

The temperature of the endoperoxide film was monitored with a Vanzetti TM2 Thermal Monitor custom modified to provide a response time on the order of 10 ms. The TM2 consists of a germanium detector complete with appropriate wavelength filtering, radiation collection optics and amplification electronics. The thermal monitor provided a noncontact means of measuring surface temperatures and therefore was used to determine substrate thermal parameters and to test and calibrate the temperature control system. Figure 3 shows an oscilloscope trace of the thermal monitor signal. As the figure shows, with this system it is possible to heat a coating to over 80 C above room temperature in 0.1 s and maintain a constant temperature thereafter. (The maximum time a constant temperature was maintained was 10 s.)

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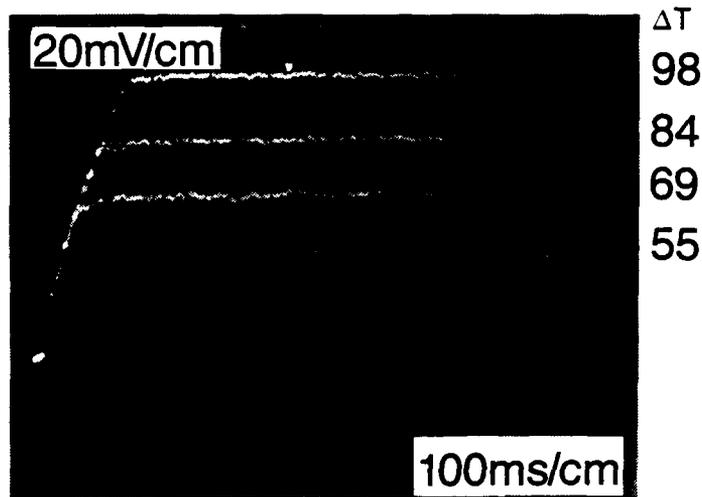
Figure 3. Measured thermal profile of the substrate surface.
Signal from the Vanzetti Thermal Monitor.

The ability to heat an endoperoxide film quickly and then maintain the film at constant temperature has allowed the rate of thermolysis to be examined as a function of temperature. In practice, with the present 525 W power supply, the temperature of the endoperoxide can be raised from room temperature to 130 C in less than 0.2 s. Above this temperature more than half of the endoperoxide will have thermolyzed before the target temperature can be reached and so most of the kinetic measurements were limited to lower temperatures.

Expectations

Before proceeding with a description of the experimental findings, it is instructive to consider a model for endoperoxide thermolysis derived from results of typical solution phase experiments. The first step in the release of singlet oxygen into the gas phase is the elementary endoperoxide thermolysis step. The fission of endoperoxide into a singlet delta oxygen and the

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parent hydrocarbon requires an activation energy of about 1 eV/molecule or about 100 kJ/mole of molecules. A typical value of the rate constant for thermolysis of naphthalene-type endoperoxides is 3 s^{-1} for 1,4-dimethyl-6-poly(vinylnaphthalene-1,4-endoperoxide) in solution at 120 C. This number is calculated from data reported by Saito et al. (Ref. 1). Compared with values for the rate of thermolysis, the rate of diffusion through a thin polymer film is expected to be relatively quick. There are no values available for the diffusivity of singlet delta oxygen in a poly(vinyl naphthalene-1,4-endo-peroxide) however, the diffusivity of ground state oxygen in polystyrene is reported to be 3 x 10^{-6} cm^2/s at 120 C (Ref. 2). In a material in which oxygen has a diffusivity of D, the average time for an oxygen molecule to diffuse an average distance L is approximately t = L^2/2·D. Using the estimate for the diffusivity given, it is found that the average time spent by an oxygen molecule in a 100-nm-thick endoperoxide polymer film after it is released from the endoperoxide but before it reaches the gas-solid interface is about 4 µs. An average distance of 50 nm to the free surface is assumed here.

While the singlet delta oxygen molecule is diffusing through the polymer film it is encountering C-H bonds which are effective quenchers of excited oxygen. The quenching of singlet delta oxygen will compete with the rate of diffusion of excited oxygen out of the polymer. The fraction of oxygen which is released into the gas phase in the singlet delta state will depend on the thickness of the endoperoxide film--the thicker the film the likelier quenching will be a problem. The quenching constant for singlet delta oxygen in solution varies dramatically with solvent environment. In fully halogenated hydrocarbons such as some freons, the lifetime of singlet delta oxygen is on the order of milliseconds. However, in solvents with O-H or C-H

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bonds, the lifetime is much shorter. The poly(vinyl naphthalene) polymers which are being investigated have numerous C-H bonds, and a logical estimate of the lifetime of singlet delta oxygen in these materials is about 10-15 μs. The lifetime in similar materials such as benzene or cyclohexane is about 20 μs at room temperature (Ref. 3) and no more than a factor of 2 decrease in lifetime for a 100 C difference in temperature is expected based on temperature dependence measurements of singlet delta lifetime in chloroform (Ref. 3). From these lifetime estimates, the pseudo-first order quenching rate constant is expected to be the order of 10^5 s^{-1}.

From these above estimates the rate of release of oxygen into the gas phase is expected to be limited by the elementary thermolysis step and not the rate of diffusion through the polymer film. The film thickness can be estimated for which quenching will start to significantly lower the yield of singlet delta oxygen appearing in the gas phase. The average distance which an excited oxygen can diffuse without being quenched is approximately,

$$distance = (2 D t)^{1/2}$$

Using the estimate for the diffusivity, D, and a lifetime, t, of 10^{-5} s a critical thickness of 10^{-5} cm or 100 nm is estimated. This estimate is useful only to guide the experimental approach. It is the goal of this project to acquire the kinetic data necessary to accurately calculate the rate of release of oxygen into the gas phase and the functional dependence of singlet delta oxygen specific yield on polymer thickness.

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Results

Film Deposition and Characterization

Thin films of endoperoxide were deposited on the conductive Pyrex sub-
strates by flowing a solution of the endoperoxide dissolved in methylene
chloride on the spinning substrate. The substrate was mounted on a platform
which was rotated at 19 rps (measured with a General Radio Strobotac). The
concentration of the dissolved endoperoxide determined the film thickness
which is expected to be a linear function of concentration for dilute
solutions. In Figure 4 mean values of film thickness are plotted against
solution concentration values. The thickness measurements were made using a
Dektak Profilometer, and each of the three values of film thickness inc'uded
in Figure 4 is an average of at least nine measurements on four different
plates. From Figure 4, it can be seen that significant deviation from the
expected linear dependence on solution concentration occurs for the thickest
film (1600 nm). Thickness measurements were not made for all of the films
which were tested, but rather it was presumed that the thickness was propor-
tional to solution concentration. Since almost all of the data collected are
with films prepared using dilute solutions (less than 0.4 moles/liter), it is
assumed that the film thickness can be calculated from the parent solution
concentration by multiplying the solution concentration in mg/cc by 8.0 to
give film thickness in nanometers.

Optical spectra of endoperoxide films deposited on quartz plates (the
absorption features of interest occur in the ultraviolet where the Pyrex
substrates strongly absorb) were recorded on a Cary 14 scanning spectro-
photometer. The coated plates were then heated in an oven at 80 C for 1 h
after which the absorption spectrum was again recorded. Figure 5 shows these
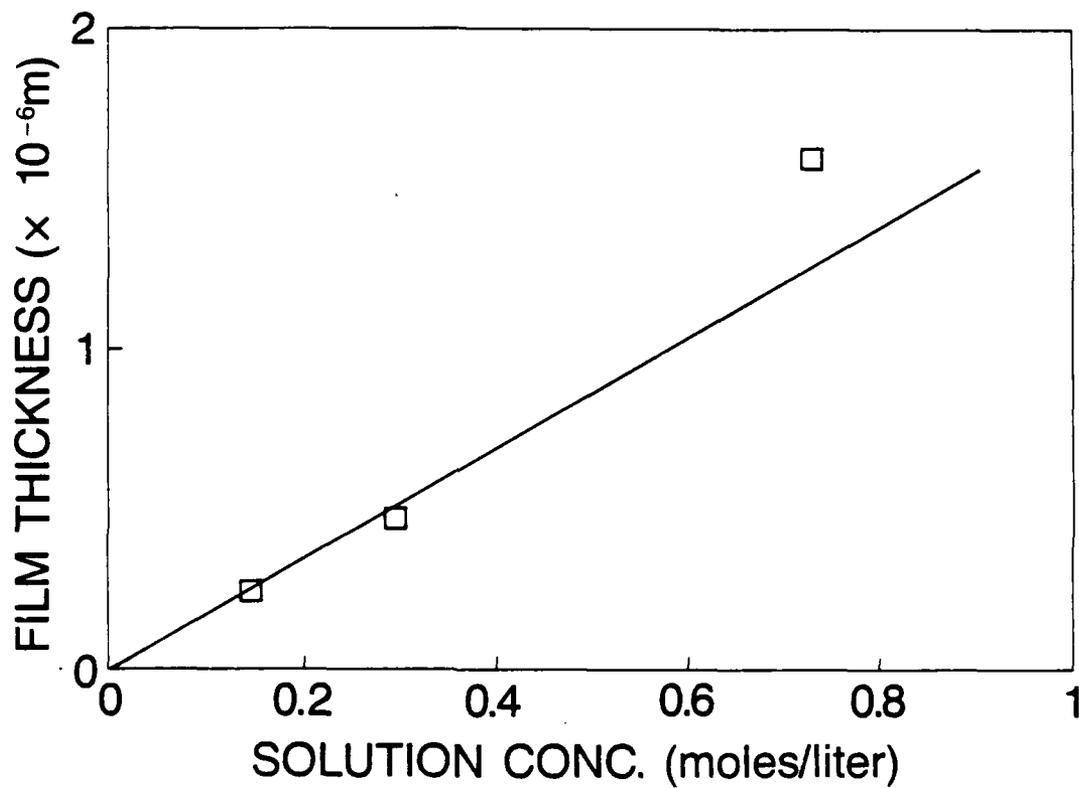
Figure 4.   Thickness of 2-PVN films (measured with a profilometer)
             as a function of spin coating solution concentration.
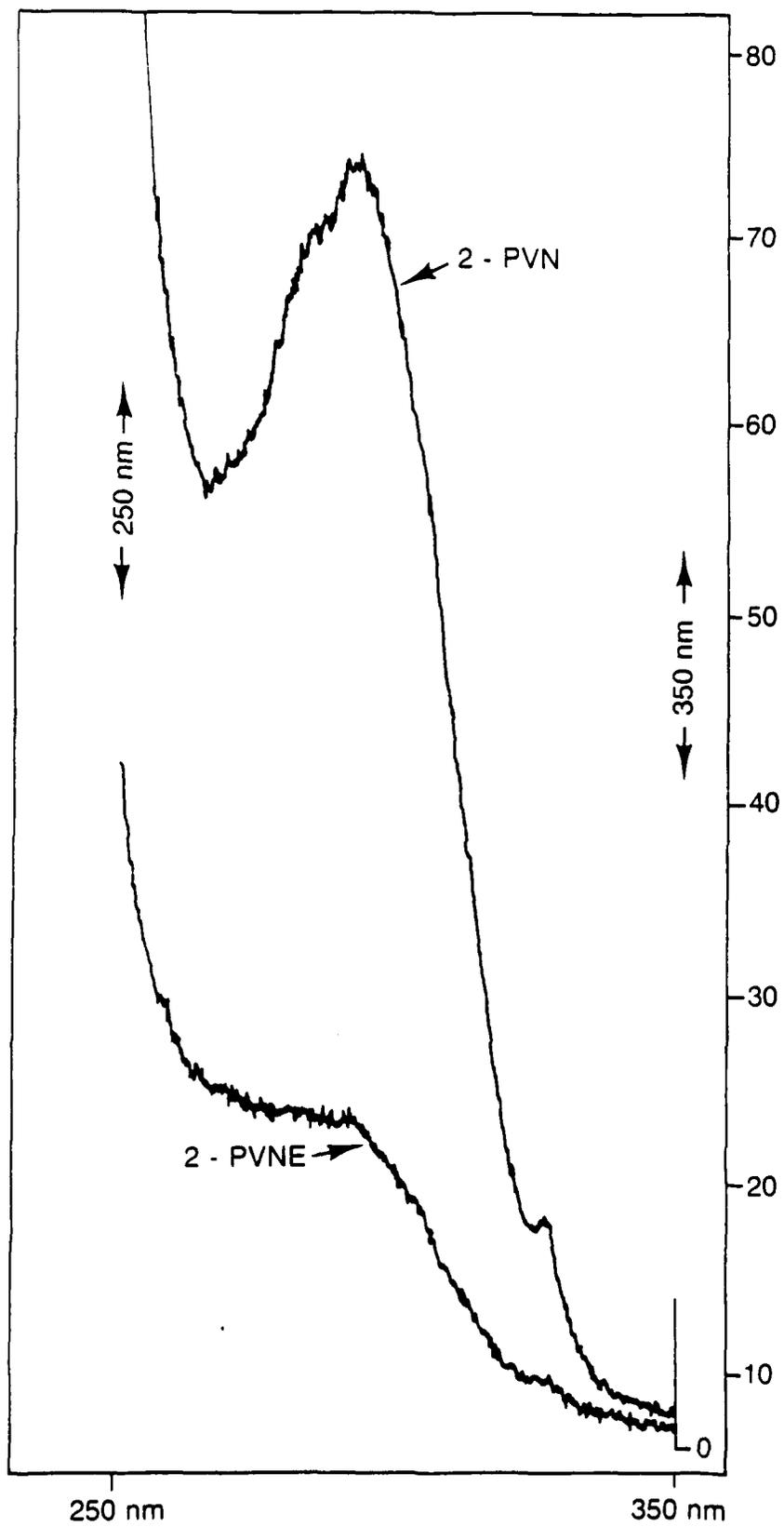
Figure 5. Optical absorption spectra of 2-PVNE and 2-PVN.

absorption spectra for a 240-nm-thick film. Upon thermolysis of the endo-peroxide, a spectral feature emerges with a maximum absorbance in the spectral region around 290 nm. This absorption feature is characteristic of the naphthalene chromophore, and its appearance demonstrates that thermolysis of the endoperoxide film has occurred. The endoperoxide molecule does not show much absorbance at this wavelength and only starts to absorb strongly at shorter wavelengths. The small amount of absorbance which is present at 290 nm in the spectrum of the endoperoxide film is mostly attributed to unoxidized naphthalene. The ratio of absorbance at 290 nm of the endoperoxide film before and after thermolysis gives an estimate of the percent conversion to endoperoxide which was achieved in the synthesis. Using this procedure, 75 percent conversion in the synthesis of 2-PVNE was estimated.

An estimate of the density of the film can be obtained from the absorbance measurements if it is assumed that the absorption coefficient at 290 nm is the same in the film as in solution. From solution measurements a molar extinction coefficient of 5.4×10^3 1/mole-cm at 290 nm for 2-PVN is found. The density of the film can be determined from the absorbance at 290 nm in the following manner. The density is equal to the number of moles (formulas really) of 2-PVNE + 2-PVN in the deposited film multiplied by the formula weight and divided by the volume occupied by the film;

$$\text{density} = \text{moles} \times \text{formula wt/volume} \tag{1}$$

The formula weight is the weighted average of 2-PVN (25%) and 2-PVNE (75%) or 206 g/formula wt. The volume of the endoperoxide film is given by the

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product of its area and thickness. The number of moles can be obtained from absorbance measurements of the thermolyzed 2-PVNE film and is given by:

$$moles = absorbance \times area/extinction\ coefficient \times 1000 \qquad (2)$$

The factor of 1000 in the denominator of the right-hand side of Equation 2 is necessary to convert from liters to cubic centimeters. Table 1 gives the values for density calculated in this manner for three film thicknesses. The density is reasonably constant with an average value of 0.96 g/cm^3

Table 1. Density of 2-PVNE films

Solution Concentration (mg/cm^3)	Absorbance	Density (g/cm^3)
60	1.21	0.96
30	0.65	1.03
15	0.28	0.89

Kinetics of Total Oxygen Release

When a film of 2-PVNE is heated in the sample chamber, oxygen is released causing a rise in pressure. The pressure rise is directly detected with a capacitance manometer and is also measured using the mass spectrometer and a calibrated pinhole (25-μm-dia) to sample the gas in the chamber. Table 2 gives the pressure rise observed for thermolysis of endoperoxide films of several thicknesses measured with the capacitance manometer.

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Table 2. Oxygen release from 2-PVNE

Solution Concentration (mg/cm^3)	Observed Pressure rise (torr)*	Moles of O_2	Calculated Pressure rise (torr)
60	0.084	7.7×10^{-7}	0.080
30	0.040	3.9×10^{-7}	0.040
15	0.019	1.9×10^{-7}	0.020

The pressure rise which will occur if all of the oxygen which is bound in the polymer film as endoperoxide is released can be calculated and compared with the experimental values. The number of moles of oxygen which can be released is equal to the number of formula units of endoperoxide present in the film and is

$$\text{moles of } O_2 = 0.75 \times \text{density} \times \text{area} \times \text{thickness}/206 \qquad (3)$$

where 206 is the formula weight of the endoperoxide film as discussed in the previous paragraph, and the factor of 0.75 accounts for the percent of naphthalene units which were converted to endoperoxide units in the synthesis of 2-PVNE. Finally, the expected pressure rise is calculated using the ideal gas law;

$$\text{pressure} = \text{moles } O_2 \times R \times T/(\text{Volume of chamber}) \qquad (4)$$

* 1 torr = 133 Pa

In this equation, R is the gas constant, T is the absolute temperature and 0.182 l is the measured volume of the sample chamber. It is assumed that the released oxygen equilibrates in temperature with the sample chamber walls which are at 298 K. Table 2 shows the results of this calculation. The close agreement between the measured and calculated values of pressure produced by the release of oxygen is encouraging and supports the validity of the thickness, optical absorbance and capacitance manometer measurements.

A mass spectrum of the released gas shows it to be oxygen with a small (less than 5%) release of a component with a mass peak at 28. This component is probably molecular nitrogen which may be desorbed from the heated plate surface. Figures 7 and 9 show the mass spectra of the released gas in the mass region of 1 to 200 mass units after thermolysis of a 480-nm-thick 2-PVNE film at 130 C. Figures 6 and 8 are mass spectra of the sample chamber gas before the endoperoxide film was heated for purposes of comparison with the mass spectra of the released gas. No evidence has been found for polymer degradation products in these spectra, and the level of pyrolysis (resulting in volatile products) is estimated to be less than 1 percent.

The rate of release of oxygen into the gas phase can be monitored with the capacitance manometer as a function of time. Initially it was thought that using the mass spectrometer in its leak detection mode could provide this information. The quadrupole signal was monitored at mass peak 32, and the analog signal was viewed on an oscilloscope as the 2-PVNE sample was heated. An increase in the quadrupole signal is observed, and the rate of increase changes with the target temperature selected. However, when the apparent rate of release is calculated using the mass spectrometer data, it is significantly less than the same quantity measured by the capacitance manometer. To resolve this discrepancy the response times of both instruments were measured using a

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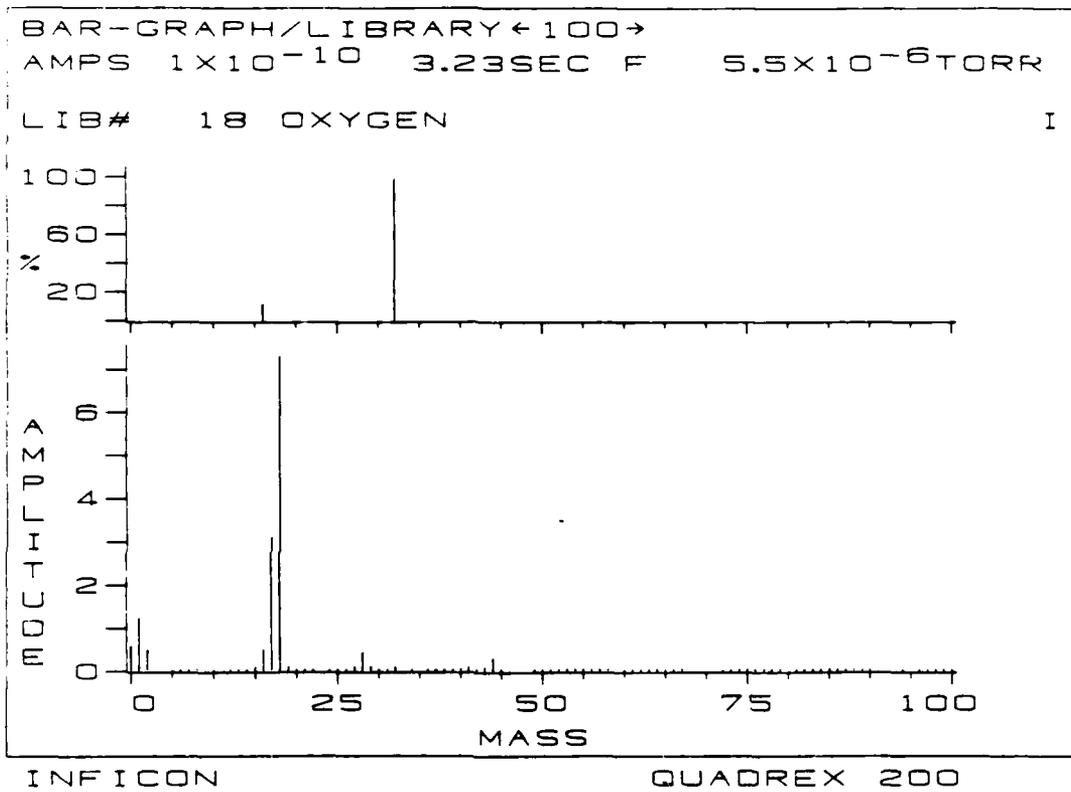
Figure 6. Mass spectrum - baseline 0-100 amu.

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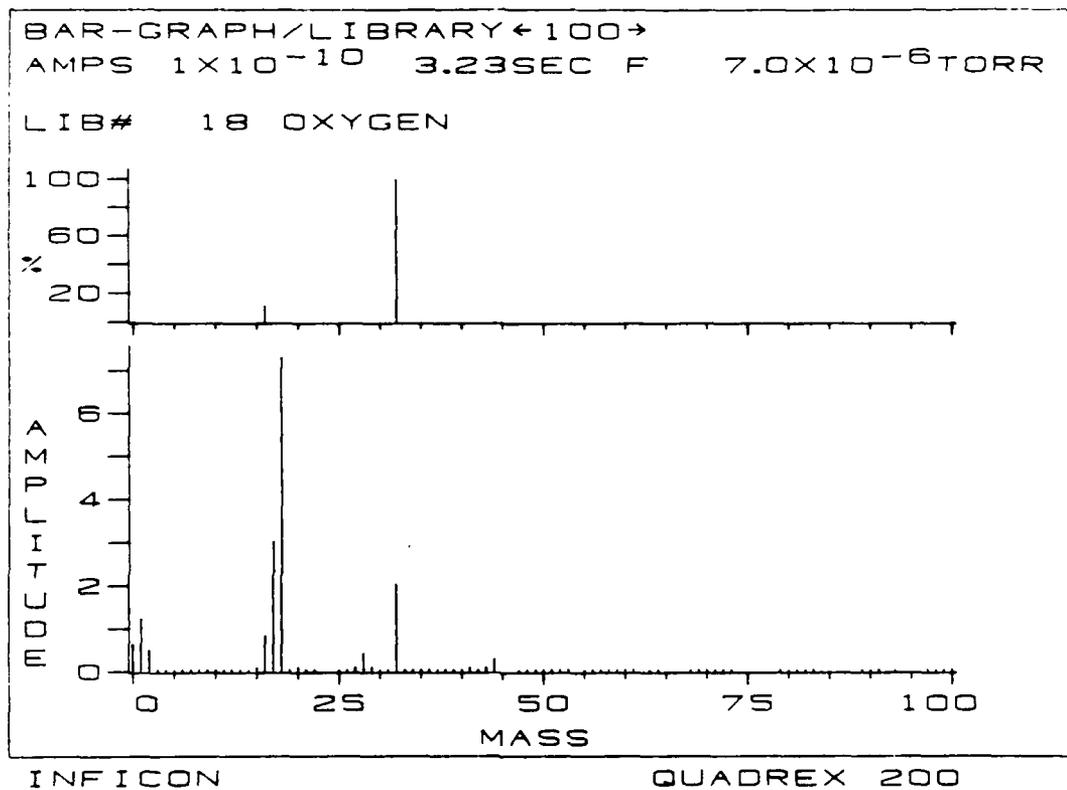
Figure 7.   Mass spectrum - gas released by 2-PVNE, 0-100 amu.
            Temperature of 2-PVNE = 130 C.

BAR-GRAPH/LIBRARY←200→

AMPS 1×10^{-10} 6.43SEC F   5.5×10^{-6}TORR

LIB# 18 OXYGEN

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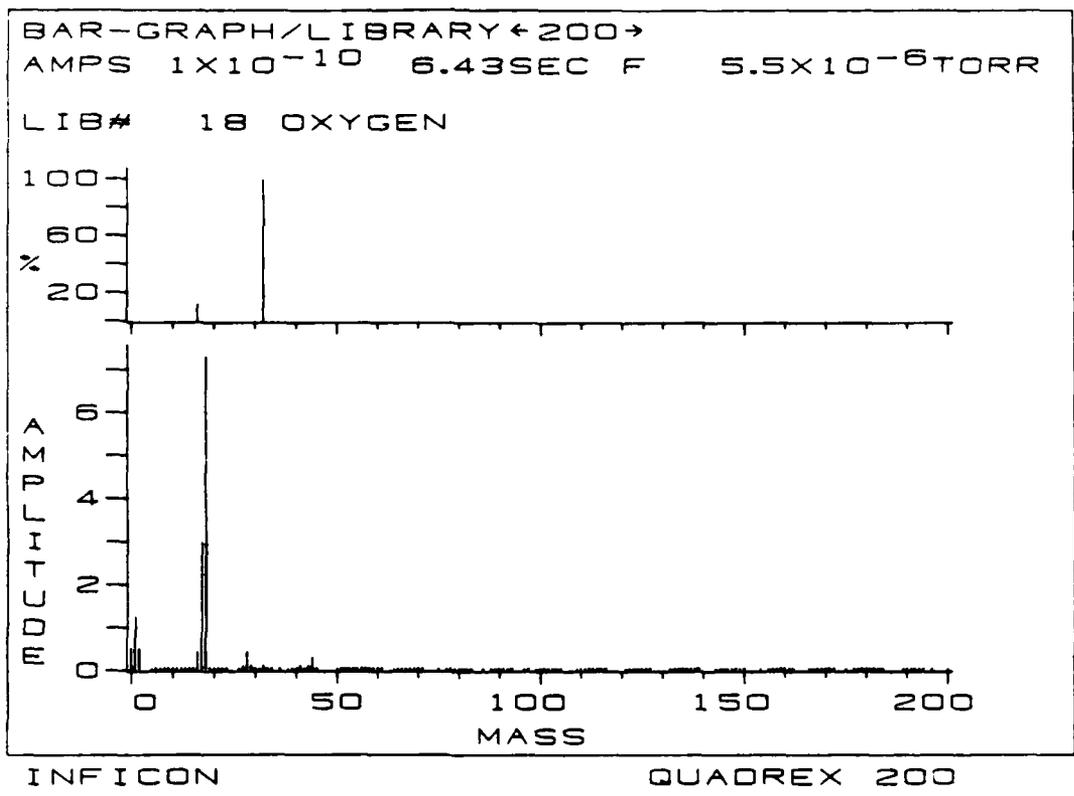
Figure 8.   Mass spectrum - baseline 0-200 amu.
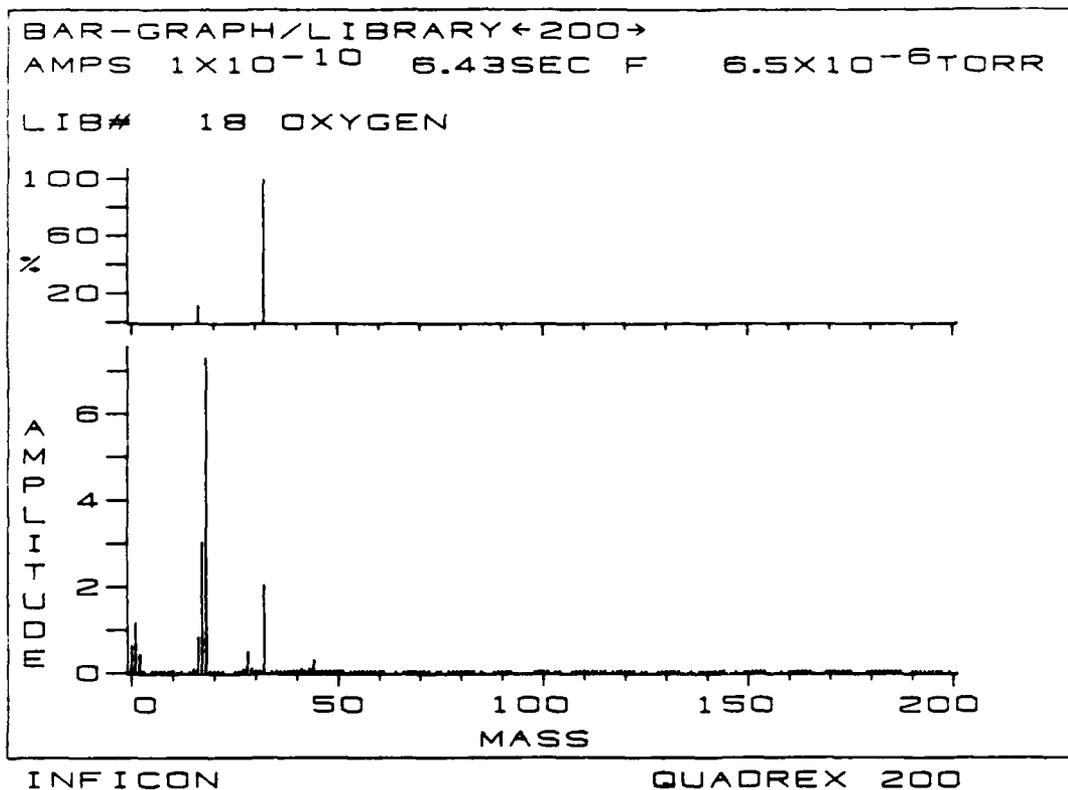
Figure 9.   Mass spectrum - gas released by 2-PVNE, 0-200 amu.
             Temperature of 2-PVNE = 130 C.

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pulsed piezoelectric leak valve (Vacuum General Model 77-10M) which can be gated open for times as short as 2 ms. The pressure pulse which followed the introduction of a 2 ms burst of gas into the sample chamber was recorded with both the capacitance manometer and mass spectrometer. The time for the mass spectrometer to reach 90 percent of its final pressure reading was measured to be 0.5 s. The capacitance manometer, on the other hand, reached the same percent of final pressure in 0.09 s. A review of the kinetic measurements made using the capacitance manometer reveals that the release rates of oxygen from the endoperoxide are of the same magnitude as the response frequency of the mass spectrometer while the capacitance manometer response is fast enough to faithfully record the true release rate.

The release of oxygen from the 2-PVNE film is expected to be described by the following equation,

$$\frac{d\,(O_2)}{dt} = k_{Th}\,[(O_2)^0 - (O_2)] \tag{5}$$

where it is assumed for the moment that k_{Th}, the elementary rate constant for thermolysis of endoperoxide, is the rate limiting step in the release of oxygen from the polymer film. The $(O_2)^0$ is the initial amount of available oxygen (in the form of endoperoxide). Equation 5 is integrated using the following initial conditions. At time t_i when the endoperoxide film has reached target temperature, the amount of oxygen which has been released is $(O_2)_i$. Integrating Equation 5 from time t_i to t and rearranging terms gives

$$\ln\left[\frac{(O_2)^0 - (O_2)}{(O_2)^0 - (O_2)_i}\right] = -\,k_{Th}\,(t - t_i) \tag{6}$$

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A plot of the log function on the left as a function of delayed time $(t-t_i)$ should yield a straight line with a slope of $-k_{Th}$. Figure 10 shows a typical plot from an experiment in which a thin polymer film is heated to 105 C. A linear fit to the data gives the rate constant for release of oxygen at this temperature. When this experiment is repeated with many samples at different temperatures and for several film thicknesses, it is found that over the temperature range of 83 C to 120 C the rate constant changes from 1 s^{-1} to 10 s^{-1}. The rate constant does not appear to depend on thickness in the range of 100 to 400 nm. The absence of a film thickness dependence to the oxygen release rate constant is evidence that the elementary thermolysis rate, and not diffusion out of the polymer, limits the release of oxygen into the gas phase. If the diffusion rate were limiting it would be expected that thinner films would release oxygen more rapidly (since the oxygen has a shorter distance to travel).

The rate constant for thermolysis of naphthalene-type endoperoxides exhibits a strong temperature dependence with an Arrhenius relation of the form,

$$k_{Th} = k_0 \exp(-E_a/RT) \qquad (7)$$

Here k_0 is the pre-exponential factor usually assumed to bear no temperature dependence, E_a is the activation energy, R is the gas constant and T the absolute temperature. A plot of the natural logarithm of k_{Th} against the reciprocal of temperature should give a straight line with a slope of $-E_a/R$ and a y-intercept of $\ln(k_0)$. Figure 11 shows this plot with the linear least squares fit to the data. Data have been included for all three film thicknesses because the variation of k_{Th} with film thickness is not evidenced

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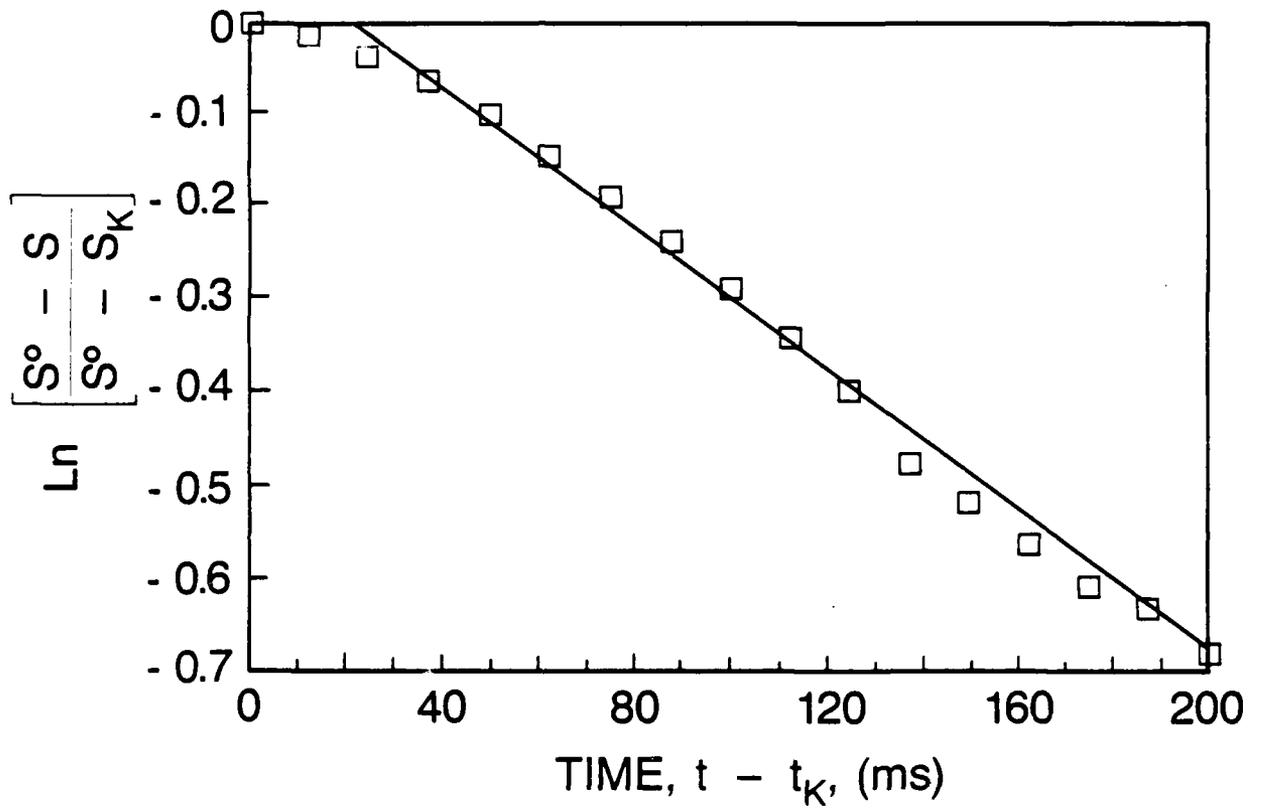
Figure 10. Natural logarithm of capacitance manometer signal (see
text) versus time after the target temperature is reached
$(t-t_k)$. S^o is the signal at long times, S_k is the signal
when the 2-PVNE film has reached target temperature.
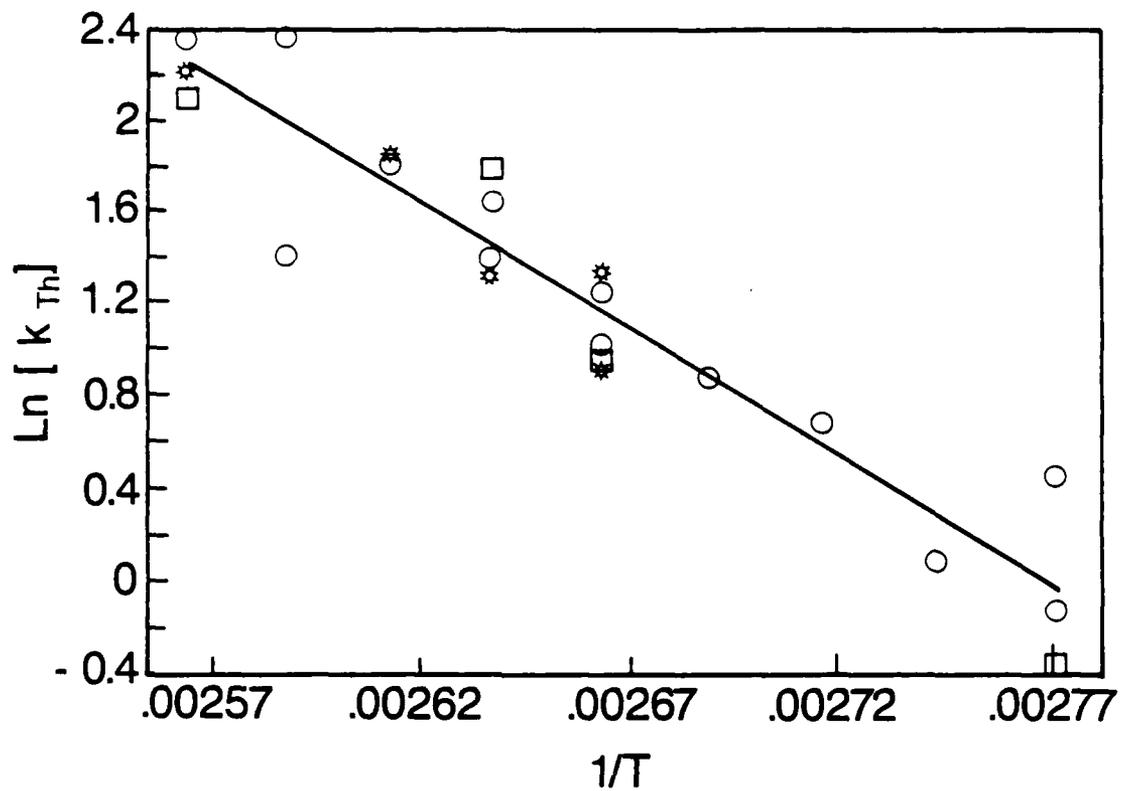
Figure 11. Natural logarithm of the thermolysis rate constant, k_{Th}, versus 1/Temperature.

✿ 15 mg/cc ○ 30 mg/cc □ 60 mg/cc

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by the data (as Figure 11 demonstrates). From the linear least squares fit, a value of 91 ± 7 kJ/mole is obtained for the activation energy of thermolysis and $1.8 \pm 0.4 \times 10^{13}$ s^{-1} for the pre-exponential term. The activation energy observed for the thermolysis of 2-PVNE in solid films is in reasonable agreement with the activation energies of similar compounds thermolyzed in solution. With both E_a and k_o in hand, it is possible to use Equation 7 to predict the release rate of oxygen for any temperature. This information is essential for tne design of a singlet oxygen generator using endoperoxides.

Singlet Delta Oxygen Release

In the last paragraph, the results for the release rate of oxygen from 2-PVNE films were presented. Since neither the capacitance manometer nor the mass spectrometer distinguish between oxygen in the ground state or the singlet delta state, separate measurements of the fraction of oxygen released in the electronically excited singlet delta state must be obtained. This fraction is expected to depend on the ratio of the quenching constant, k_q, for deactivation of singlet delta oxygen by the polymer film and the diffusivity, D, of singlet delta oxygen in the endoperoxide film.

Measurement of the total amount of singlet delta oxygen which enters the gas phase upon thermolysis of the endoperoxide film was made with a cooled germanium diode detector viewing the primary emission of gas phase singlet delta oxygen. To insure that only singlet delta oxygen in the gas phase was detected, the geometry illustrated in Figure 12 was used. The detector, a 1-cm-dia germanium diode (Judson Model J16-D) housed in a liquid nitrogen Dewar flask, was mounted 90 deg to the normal of the sample substrate surface (viewing the edge rather than the front of the substrate) and cooled to liquid

27
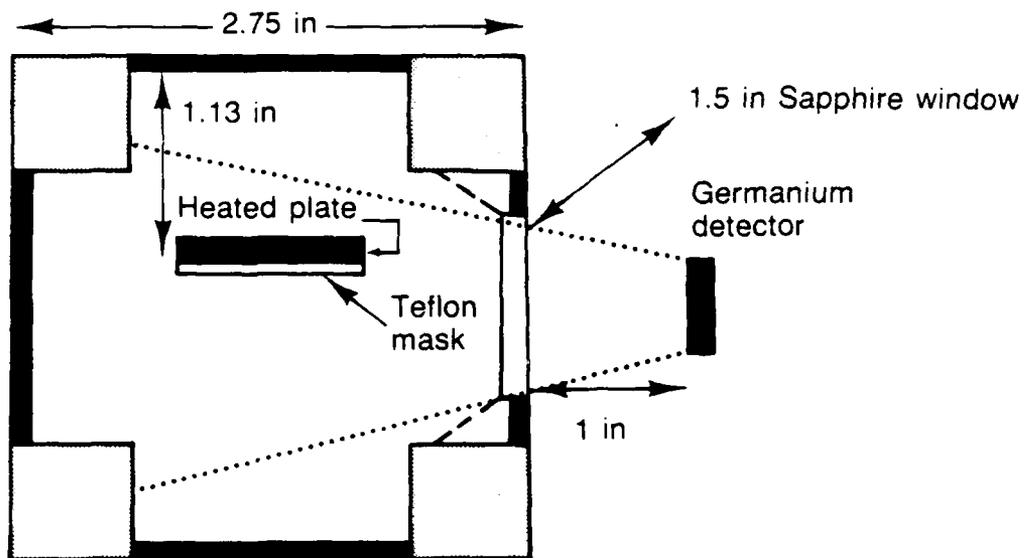
Figure 12. Geometry of singlet delta emission experiments.

nitrogen temperatures. The surface of the plate was masked with a flat 1/16-in Teflon gasket which had 1/16-in-slots cut out every 1/8-in. This grid of Teflon strips was mounted so as to block the sample surface from direct view of the germanium detector. Finally, a thin strip of black plastic tape covered the end of the sample substrate which was in direct view of the detector. These measures were taken to not only block the singlet delta emission originating in the polymer film from direct view of detector but more importantly to decrease the amount of blackbody radiation arriving at the detector surface from the heated substrate. Without these precautions the blackbody radiation signal is the major contributor of noise and limits the level of detectivity to unacceptably large values. The signals observed were less than 5×10^{-11} A whereas the noise equivalent power is calculated to be 1×10^{-11} A at the operating bandwidth of 10 Hz.

The signal from the germanium detector was amplified with a Keithley 410A picoammeter, filtered with a 10 Hz low pass RC filter and displayed on an oscilloscope. Figure 13a shows a photograph of a typical signal obtained upon thermolysis of a 240-nm-thick 2-PVNE film heated to 130 C. Figure 13b shows the background signal, due to blackbody radiation, obtained by reheating the same sample after allowing sufficient time for the substrate to cool from its original heating. This measurement was made with 10 torr of nitrogen buffer gas present in the sample chamber. The buffer gas is necessary because the total yield of gas phase singlet delta oxygen should be measured quantitatively. If the time for diffusion through the buffer gas and out of the field of view of the germanium detector is longer than the response time of the detector and the release time of the thermolysis reaction, the peak signal recorded with the germanium detector will be directly proportional to the total amount of singlet delta oxygen released into the gas phase from

29
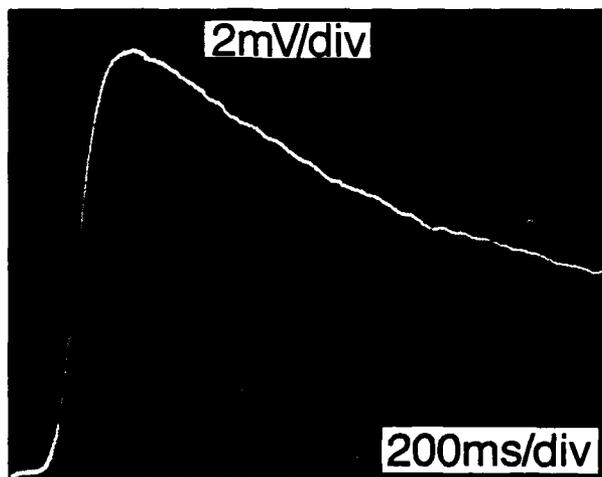
a. 240 nm 2-PVNE film, target
   temperature = 130 C.
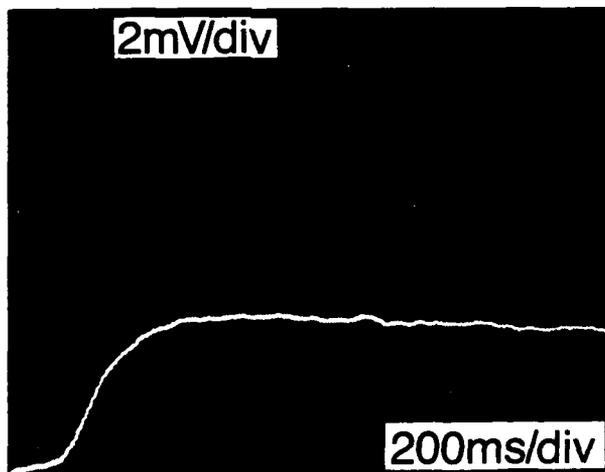
b. Same conditions as in a but 2-PVNE
   film is completely thermolyzed.

Figure 13. Germanium detector signal.

thermolysis of 2-PVNE. As a buffer gas, nitrogen was chosen because of its low rate of singlet delta oxygen deactivation.

Figure 14 shows the detector signals recorded as a function of time (background has been subtracted) for thermolysis of 240 nm films of 2-PVNE at 130 C. The buffer gas pressures were varied over the range of 0 to 760 torr. As anticipated, the signal increases with buffer gas pressure until the time to diffuse outside of the detector's field of view is greater than the release time of singlet delta oxygen into the gas phase. At high pressures (e.g. 760 torr) the signal is reduced. This is probably the result of singlet delta oxygen quenching by either nitrogen or by the energy pooling reaction. In the region of 10 torr the signal is confined to within 3 cm of the substrate surface for the first 0.2 s of its life, and most of the singlet delta oxygen is within the field of view of the detector. Therefore, this buffer gas pressure was selected to use for further studies. Note that the buffer gas is not essential for the release of singlet delta oxygen but is only used for purposes of measuring the singlet delta yield.

As mentioned previously, the percent of released oxygen which enters the gas phase in the singlet delta state is determined by a competition between the rates of diffusion out of the endoperoxide polymer and quenching of the excitation by the polymer. The fraction of oxygen released in the singlet delta state will be a function of the polymer film thickness (because diffusion out of the polymer is more rapid for thinner films). A cooled germanium detector was used to monitor the amount of singlet delta released into a 10 torr nitrogen buffer gas from films of different thicknesses heated to 130 C. Figure 15 shows the results of these measurements along with theoretical curves generated by a simple model. Note that the signal stays constant as the film thickness decreases from 240 nm to about 40 nm and then

31
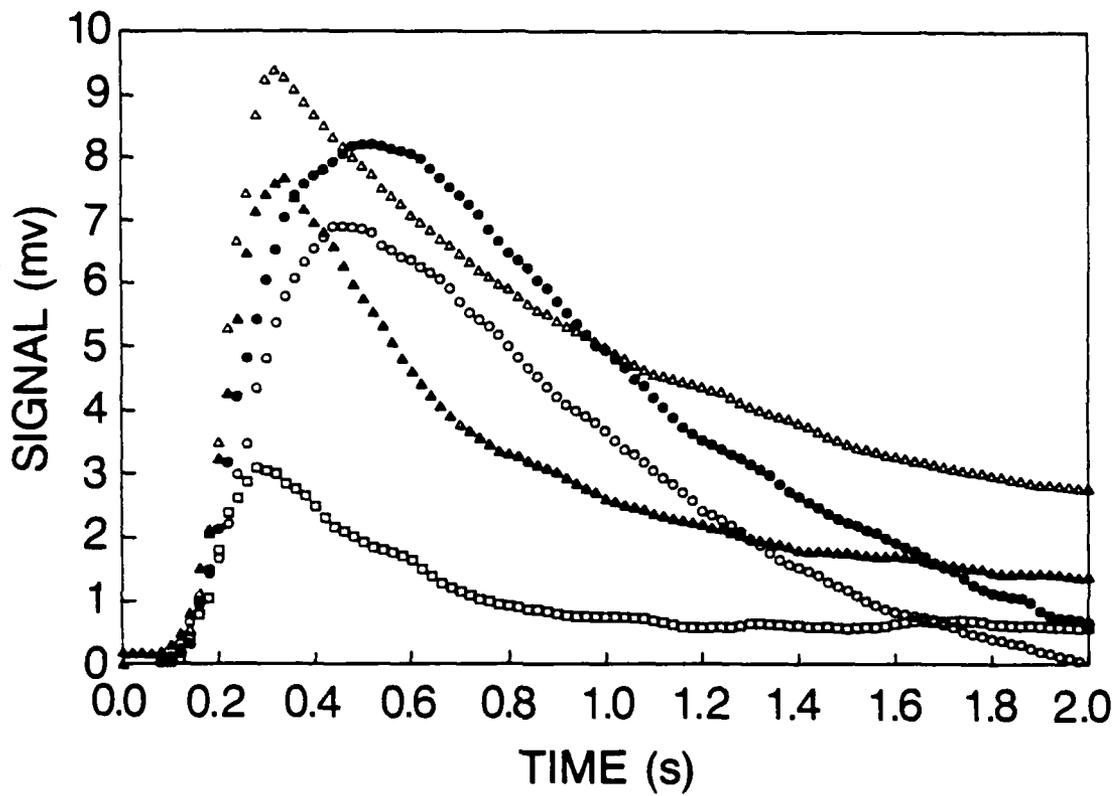
Figure 14. Effect of buffer gas pressure on the germanium detector signal.
○ 0   ● .5   △ 10   ▲ 100   □ 760

32
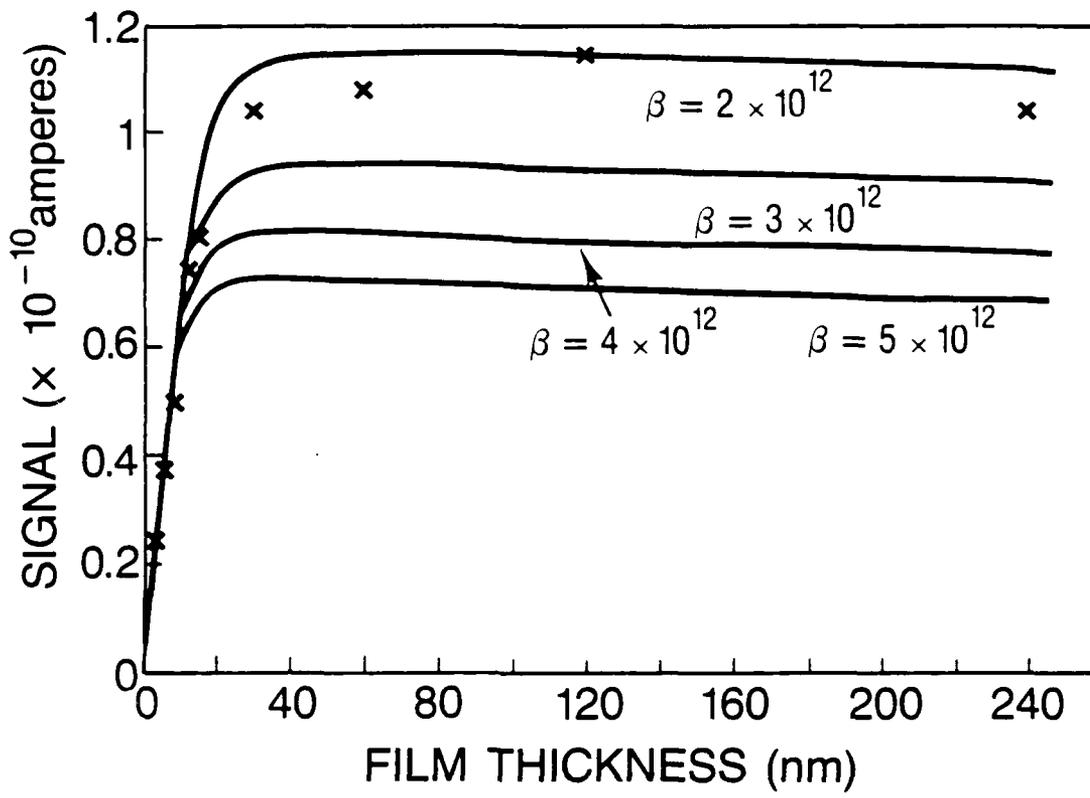
Figure 15. Endoperoxide film thickness dependence (0-250 nm)
of germanium detector signal. Inelastic model.
The parameter β is in units of cm^{-2}.

decreases with a further reduction in film thickness. This behavior can be understood easily if the quenching is thought of as limiting the time a singlet delta oxygen molecule can spend diffusing through the polymer film. This in turn limits the number of oxygen molecules which reach the gas phase still in the excited state to those born within a certain distance of the surface. If the endoperoxide film is made thicker than this distance, the amount of excited oxygen reaching the gas phase will not change and, hence, the primary emission signal (which is proportional to the amount of singlet delta in the gas phase) will remain the same as the film thickness is increased beyond a critical value.

A more quantitative but still simple calculation of the diffusion and quenching of singlet delta oxygen in a solid material was developed. In Appendix C the two models which were used to evaluate the primary emission experiments are discussed so only the results of those calculations are discussed here. One model, which will be called the elastic model, presumes that singlet delta oxygen is not deactivated by collisions with the metal oxide surface of the Pyrex substrate. The inelastic model simulates just the opposite behavior; all collisions with the metal oxide surface are treated as deactivating. Both models use a fitting parameter, beta, which is equal to the ratio of the quenching rate constant to the diffusivity of singlet delta oxygen in the polymer. A comparison of both of these models with the experimental data can be found in Figures 15 through 18 for film thickness ranges of 0 to 250 nm and 0 to 80 nm. The best fit between the model calculation and the experimental results is obtained for a value of beta of approximately 2 x 10^{12} cm^{-2} (Figures 15 and 16). The value of the diffusivity of oxygen in polystyrene is 4 x 10^{-6} cm^2/s at 130 C. If this same value is used for the diffusivity of singlet delta oxygen in 2-PVNE along with the value for beta,

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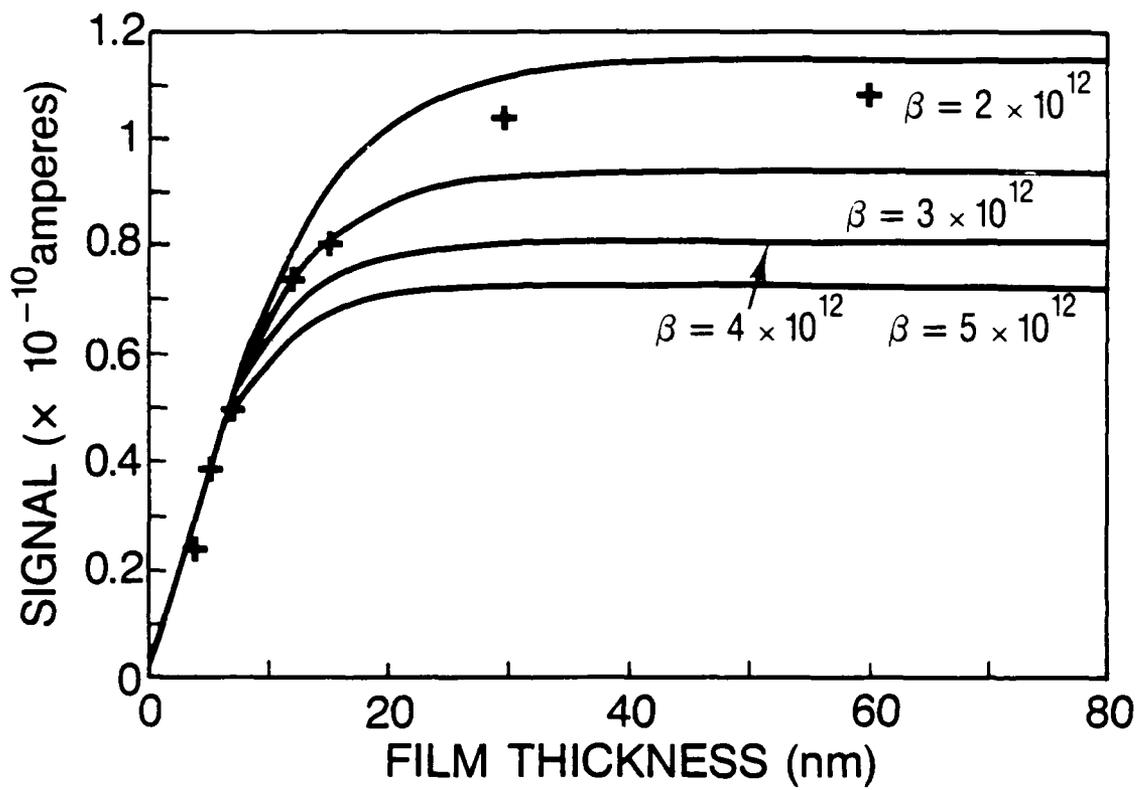
Figure 16. Endoperoxide film thickness dependence (0–80 nm)
of germanium detector signal. Inelastic model.
The parameter β is in units of cm^{-2}.
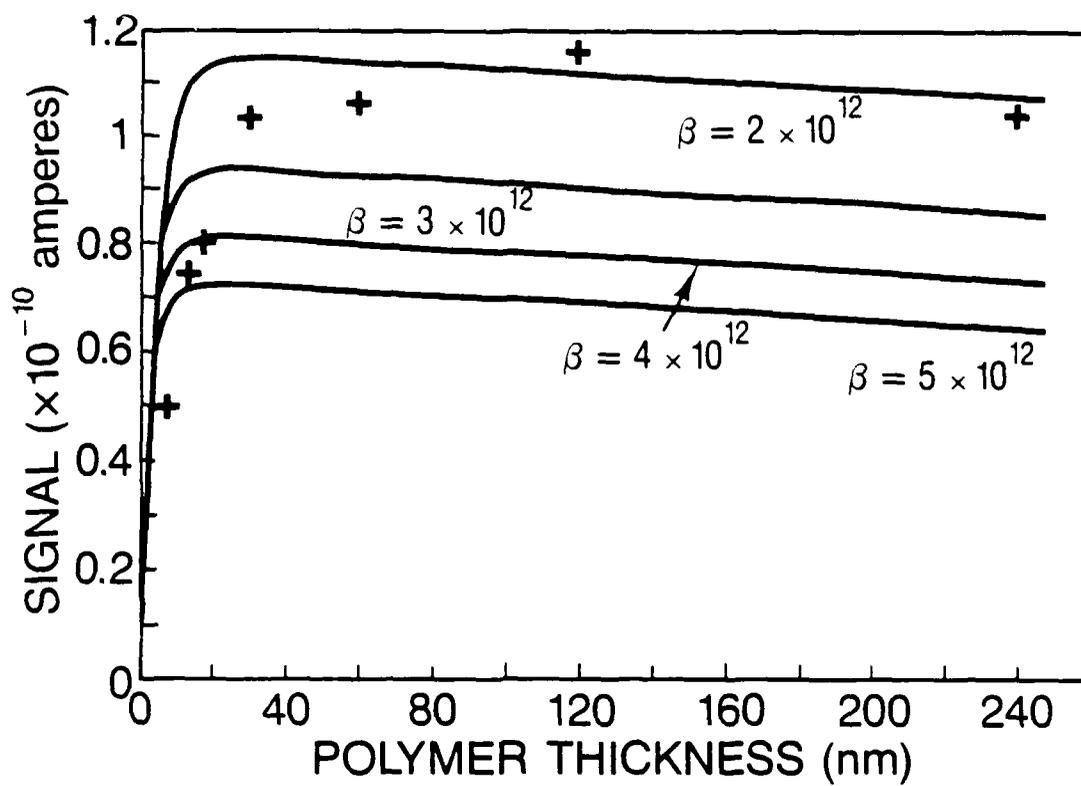
Figure 17. Endoperoxide film thickness dependence (0-250 nm) of germanium detector signal. Elastic model. The parameter β is in units of cm^{-2}.
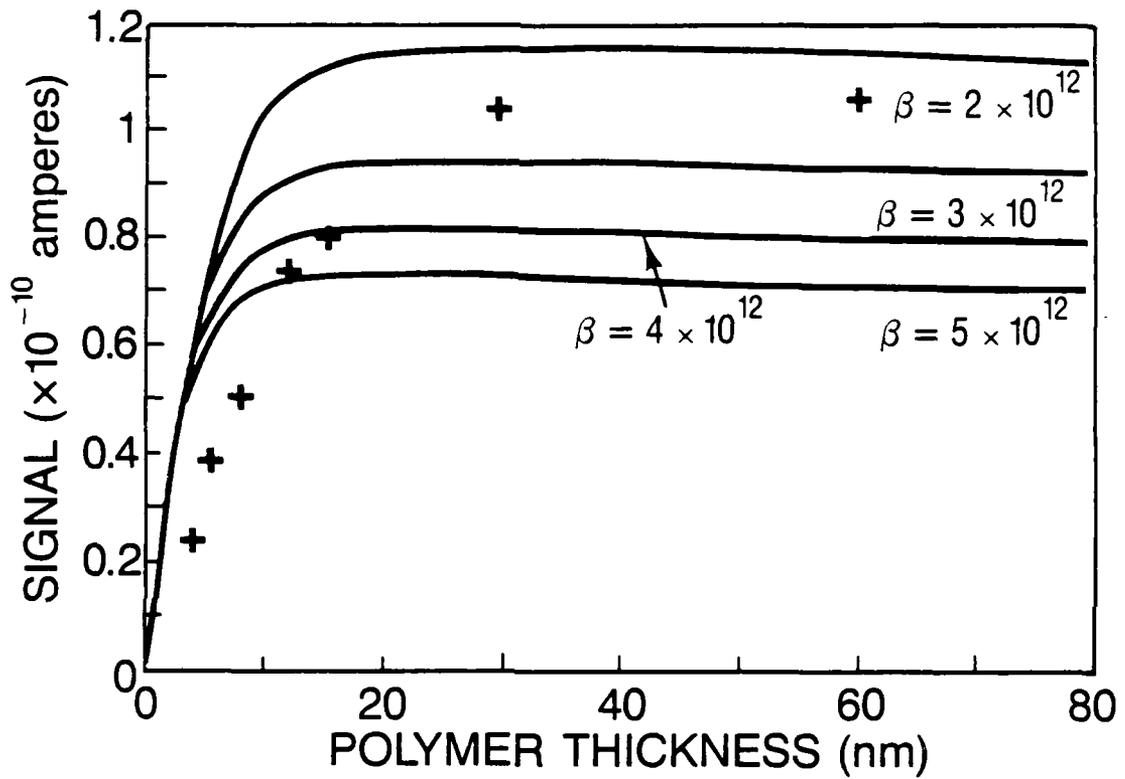
Figure 18. Endoperoxide film thickness dependence (0-80 nm)
of germanium detector signal. Elastic model.
The parameter β is in units of cm^{-2}.

a rather large quenching constant of 8×10^6 s^{-1} is obtained.

The lifetime derived from the calculated quenching constant is 0.1 μs which is almost two orders of magnitude smaller than lifetimes observed for singlet delta in hydrocarbon solvents at room temperature. It is possible that the diffusivity of singlet delta oxygen in 2-PVNE is significantly smaller than the value presumed. If there is significant probability of singlet oxygen recombining with naphthalene molecules to produce endoperoxide molecules, the diffusivity will be much lower than estimated. In this situation, the observed diffusivity will include the time that singlet oxygen remains trapped in the form of newly generated endoperoxide as well as the actual diffusion time of the free singlet delta molecular oxygen. It is also possible that the quenching rate is a factor of approximately 100 larger than expected, or the temperature dependence of quenching rate is stronger than expected. Finally, the value of beta is obtained from a fit of the theoretical yield curves obtained from the diffusion equation and the experimental germanium detector signals which were recorded. If the calibration factors which convert the germanium detector signal to a value for the total singlet oxygen released into the gas phase are in error, the experimental numbers which are compared with the theoretical values may be in error. However, the experimental values are not expected to be inaccurate by more than 20 percent.

Discussion

Thermolysis of endoperoxides potentially offers a convenient, reliable, and clean source for singlet delta oxygen which is used in the oxygen iodine chemical laser. The goal of the Phase I effort in the endoperoxide project was to acquire sufficient data to assess the possibility of designing a singlet delta oxygen generator fuelled by endoperoxides. This goal has been achieved and the design and construction of a singlet delta oxygen generator is now possible. This section summarizes what has been learned in the Phase I effort and what direction future research should take.

Present Knowledge

The kinetics of singlet oxygen release in three solid endoperoxides has been investigated. The lithium salt of 3-(4-methyl-1-naphthalene-1,4-endoperoxide) propanoic acid decomposed upon heating in a vacuum and was not investigated further. The condensation polymer, NP-PVA, released oxygen quantitatively upon heating to modest temperatures, but because of difficulties with the photoperoxidation synthesis and the limited availability of this polymer, this material was not pursued further. Instead, attention was focussed on 2-PVNE which was more readily photoperoxidized.

The study of 2-PVNE was detailed and fairly complete. Several accomplishments can be listed:

1. 2-PVN was photoperoxidized with 75 percent yield. That is, 75 percent of the naphthalene units were oxidized to endoperoxide units.

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2. Thin films (with reproducible thicknesses) were deposited on glass substrates. It was found that the film thickness scales linearly with the concentration of dilute 2-PVNE solutions (less than 0.4 moles/liter.

3. It was found that oxygen is released into the gas phase upon thermolysis of 2-PVNE in 100 percent yield.

4. The rate of release of oxygen into the gas phase was found to be independent of 2-PVNE film thickness (for submicrometer thick films). This is interpreted to mean that the molecular thermolysis rate is being measured; all other rates, such as diffusion, must be much faster.

5. The rate constant for release of oxygen into the gas phase was found to have an activation energy of 91 ± 7 kJ/mole and a pre-exponential of $1.8 \pm 0.4 \times 10^{13}$ s^{-1}.

6. The fraction of released oxygen gas which is electronically excited was measured and found to depend markedly on 2-PVNE film thickness.

An understanding of how the fraction of released oxygen gas which is electronically excited varies with film thickness is crucial for the design of a singlet oxygen generator. This quantity is difficult to measure accurately and a brief discussion of those measurements is in order. The quantity of singlet delta oxygen released into the gas phase was measured by monitoring emission at 1270 μm using a cooled, large area germanium detector. Several

features of these measurements confirm the assertion that the emission observed is really singlet delta oxygen released into the gas phase from endoperoxide.

1. The size of the emission signal depends upon buffer gas pressure in a manner which is explainable if our hypothesis is correct.

2. Reheating the 2-PVNE film, or heating a 2-PVN film for the first time, does not produce a primary emission signal.

3. The emission measured with the germanium detector occurs in the spectral neighborhood of 1270 μm where the primary emission of singlet delta oxygen is expected.

The peak signal from the germanium detector was measured for a series of 2-PVNE films of different thicknesses. It was found that the primary emission signal remains relatively constant for films in the thickness range of 240 to 40 nm and decreases monotonically with film thickness for films less than 40 nm thick. This behavior is predicted by even simplistic models based on the one-dimensional diffusion equation. The results are in agreement with those of a simple diffusion calculation which assumes that the substrate surface adjacent to the 2-PVNE film deactivates all excited oxygen molecules which collide with it. The calculations have one adjustable parameter which is the ratio of the quenching constant to the oxygen diffusivity. When this ratio assumes the value of 2×10^{12} cm^{-2}, the calculations agree well with the experimental data.

On the strength of the good fit achieved by the model calculations with the experimental data, the model can be used to calculate the fraction of singlet delta oxygen appearing in the gas phase as a function of film

thickness. This calculation is straightforward and involves calculating the number of moles of singlet delta oxygen released and dividing this number by the total number of moles of endoperoxide (available singlet oxygen). Figures 19 and 20 show the result of this calculation when a value of 2×10^{12} cm^{-2} is chosen for the adjustable parameter, β. Two things are immediately apparent upon perusing these figures. (1) The fraction of singlet oxygen does not become interesting (large) until film thicknesses of 40 nm or less are examined. This results in the large value of k_q/D required to fit the experimental data; a value more than two orders of magnitude larger than expected. At present, there is no information as to whether the quenching constant is extremely rapid or the diffusivity of oxygen in 2-PVNE/2-PVN is unexpectedly slow. (2) The maximum singlet delta oxygen yield which can be had is 0.5. This limit is imposed by the assumption in the calculations that every excited oxygen which collides with the metal oxide coated substrate is deactivated. Because one half of the diffusing excited oxygen molecules do collide with the substrate, the largest yield which can be expected from a film deposited on a highly quenching substrate is 0.5. One reason why this substrate may be effective as a singlet oxygen quencher is that the surface (which a singlet oxygen molecule sees when it diffuses through 2-PVNE to the substrate surface) is electrically conductive. Electrically conductive metal surfaces are known to efficiently quench singlet oxygen. Because the metal oxide surfaces are also electrically conductive, it is expected that these surfaces may be as effective at quenching singlet oxygen as are metal surfaces.

The results of the primary emission experiments are encouraging for the development of a singlet oxygen generator. While the small thickness values necessary to achieve a large fraction of singlet delta oxygen are somewhat

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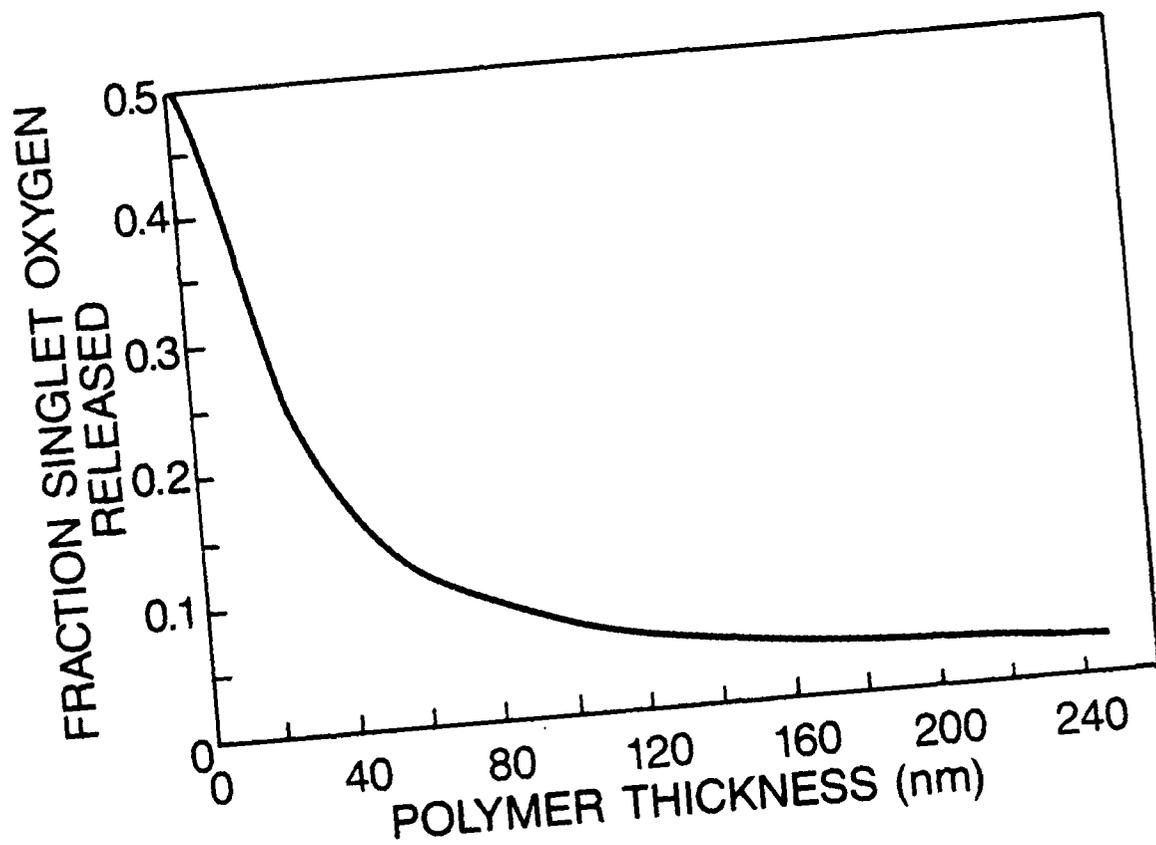
Figure 19. Calculated fraction of singlet delta oxygen release as a function of film thickness (0-250 nm). $\beta = 2.0 \times 10^{12}$ cm^{-2}.

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FRACTION SINGLET OXYGEN RELEASED

0.5

0.4

0.3

0.2

0.1

0   20   40   60   80

POLYMER THICKNESS (nm)
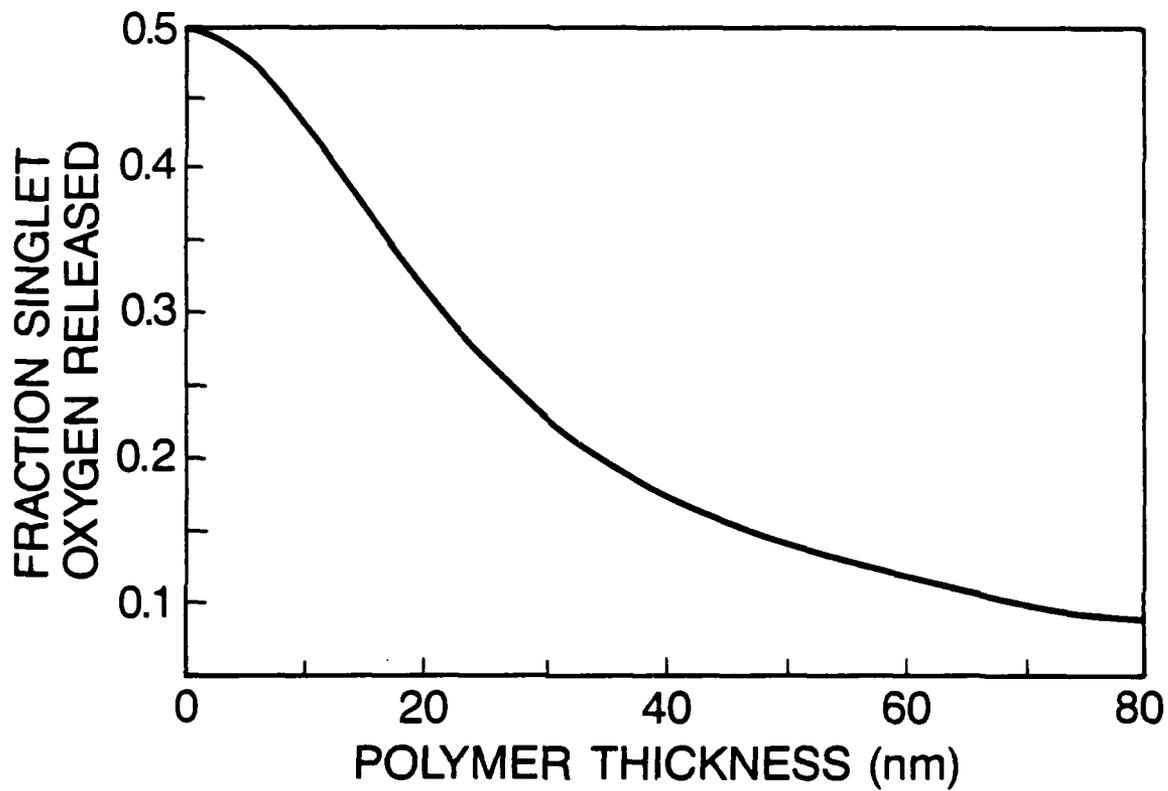
Figure 20. Calculated fraction of singlet delta oxygen release as a function of film thickness (0 - 80 nm). $\beta = 2.0 \times 10^{12}$ cm^{-2}.

disappointing (a factor of 100 times thicker films was expected), it is
believed that 20-40 nm materials can be manufactured and used. One deceptive
aspect of the results is the limit of 0.5 as the maximum yield of singlet
delta. This limit only applies when the film is deposited on a perfect
quenching surface. Such a surface would be avoided in an actual generator
design and limiting yields of 1.0 are possible.

Future Directions

Several extensions from the current endoperoxide research project are now
possible. First of all, the primary emission experiments which measure the
number of moles of singlet delta oxygen released into the gas phase are
crucial to the design of a viable endoperoxide fuelled singlet oxygen gener-
ator. These measurements are not believed to be greatly in error; however,
because of the importance of these measurements, and because the experiments
did not use absolute calibration of the primary emission detector, calibration
measurements are necessary. Calibration of the germanium detector can be done
with an electron spin resonance spectrometer.

Given the present state of knowledge of the thermolysis kinetics of
2-PVNE, it is possible to design a laboratory scale generator. Because the
fraction of singlet delta oxygen released severely depends on film thickness,
high surface area (small thickness) materials will have to be used. It would
be much easier to design a laboratory scale generator with thicker materials,
however, the benefits of demonstrating that a small-scale generator can be
constructed using endoperoxide fuels are substantial and design of this
generator should begin as soon as possible.

Finally, an effort to make materials which do not quench singlet oxygen
as quickly as 2-PVNE should be carried out in parallel with the design of a

high surface area endoperoxide fuelled singlet oxygen generator. Partially or fully halogenated poly(vinylnaphthalene) or poly(vinylanthracene) may show a singlet oxygen quenching rate constant much diminished from its value in the 2-PVNE/2-PVN films. The lifetime of singlet oxygen in fully halogenated hydrocarbon solvents such as the freons is on the order of milliseconds at room temperature. This is two to three orders of magnitude longer than the singlet delta oxygen lifetime in normal hydrocarbon solvents. The synthesis of halogenated hydrocarbon endoperoxides should be pursued, because a simple order of magnitude decrease in the quenching rate constant from its value in 2-PVNE would make the construction of a generator much easier. It would also be desirable to investigate the singlet delta oxygen release kinetics of 6-PVNE (the vinyl group attached to the 6-position of the naphthalene ring). This material is not expected to differ substantially from the 2-PVNE material. However, because 6-PVNE has been synthesized and is available and because the measurement procedures needed to do this work are now fairly routine, the acquisition of the important rate constants for the thermolysis of 6-PVNE would be straight-forward and easily accomplished. The endoperoxide project would benefit by increasing the data base of thermolysis reactions of endoperoxides. It is possible that future endoperoxide fuelled generators may benefit by a mixture of endoperoxide materials. The larger the data base of different endoperoxides, the more flexibility there is the design of singlet oxygen generators.

It is recommended that a diversified approach to further endoperoxide work should be considered. This could involve

- the design and construction of a singlet oxygen generator
- calibration of the primary emission experiments
- development of new endoperoxides with the goal of finding higher performance materials.

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Appendix A: Synthesis of Endoperoxide Materials

1. Synthesis of NP-PVA.

The synthesis of the ester of poly(vinyl alcohol) and 3-(4-Methyl-1-naphthalene)propanoyl chloride to give the naphthalenic polymer NP-PVA was carried out at the laboratories of Professor Paul Schaap at Wayne State University.* The following procedure was used by Dr. Schaap for this synthesis (see Fig. 21).

Spectral Characterization of Materials: Proton and carbon NMR spectra were acquired on a Nicolet QE-300 spectrometer using deuteriochloroform as solvent.

1-Chloromethyl-4-methylnaphthalene: Paraformaldehyde (120 g) was dissolved in a mixture of glacial acetic acid (270 ml) and concentrated hydrochloric acid (375 ml) at 50 $^\circ$C. The temperature was raised to 90-95 $^\circ$C, after which phosphoric acid (175 ml) and 1-methylnaphthalene (290 g) were added dropwise. The mixture was stirred at 90-95 $^\circ$C for 5 h after which time TLC on silica with methylene chloride indicated that the reaction was complete. The reaction mixture was diluted with saturated aqueous sodium chloride (150 ml) and extracted with methylene chloride (150 ml). The methylene chloride layer was then washed with saturated sodium bicarbonate, washed three times with water, and dried over sodium sulfate. After evaporation of the solvent, the oily material was distilled under vacuum to give a solid product. This solid was crystallized from n-hexane to give 255 g (66%): mp 55-6 $^\circ$C; proton NMR δ 2.660 (s, 3H) 4.998 (s, 2H), 7.216-7.240 (m, 1H), 7.363-7.387 (m, 1H), 7.511-7.610 (m, 2H), 8.001-8.031 (m, 1H), 8.125-8.157 (m, 1H).

* Dr. A. Paul Schaap, Professor of Chemistry, Wayne State University, Detroit, MI

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Figure 21. Synthetic route to NP-PVA polymer.

Ethyl 3-(4-methyl-1-naphthylene)-2-carboethoxypropanoate:
Sodium (11.5 g, 0.5 mol) was dissolved in absolute ethanol (400 ml) under
argon. To this solution, diethyl malonate (83 g, 0.53 mol) was added drop
wise. After a clear solution was obtained, 1-chloromethyl-4-methylnaphthalene
(100 g, 0.53 mol) was added and the mixture was stirred at reflux. After 3.5
h, TLC analysis on silica with methylene chloride indicated that the reaction
was complete. The solid sodium chloride that had formed was filtered away and
the ethanol was evaporated from the solution. The remaining yellow liquid was
vacuum distilled to give a pale yellow oil (70 g, 52%): bp (0.7 torr) 190-200
^{0}C; ^{1}H NMR (CDCl$_3$) δ 1.05 (t), 2.52 (s), 3.73 (m), 4.08 (q), 7.55 (s), 7.50
(m), 8.00 (m), IR (neat) 3050, 2975, 1720, 1590, 1440 cm^{-1}.

Ethyl 3-(4-methyl-1-naphthalene)propanoate: Ethyl 3-(4-methyl-
1-naphthylene)-2-carboethoxypropanoate (24 g, 0.076 mol), sodium chloride (6
g, 0.10 mol) and water (12 g, 0.67 mol) were stirred together in N,N-dimethyl-
formamide (240 ml) at reflux. TLC on silica with methylene chloride indicated
that the reaction was done in 24 h. The solution was diluted with water (1 L)
and extracted with ethyl ether (4 x 500 ml). The ether layers were washed
with water (1 L), dilute copper (II) nitrate solution (250 ml) to remove
residual dimethylformamide and water (1 L). The solution was dried with
magnesium sulfate and evaporated to a yellow oil. The oil generally was used
without further purification, although column chromatography with hexane and
ethyl acetate followed by crystallization from hexane and methylene chloride
arforded white crystals (19 g, 93%): mp 35-37 ^{0}C; ^{1}H NMR (CDCl$_3$) 1.21 (t),
2.68 (m), 3.56 (m), 4.85 (q), 7.28 (s), 7.53 (m), 8.07 (m); IR (CDCl$_3$) 3070,
2980, 1725 (s), 1475, 1465, 1440 cm^{-1}.

3-(4-Methyl-1-naphthylene)propanoic acid: Crude ethyl 3-4(4-methyl-1-
napthalene)propanoate (19 g, 0.079 mol) was dissolved in methanol (50 ml). To

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this solution was added a solution of potassium hydroxide (4 g, 0.071 mol) in water (50 ml). This mixture was stirred at reflux until complete as indicated by TLC on silica with methylene chloride. Heating was stopped and the methanol was evaporated. The resulting aqueous basic solution was acidified with 2N hydrochloric acid until no more white solid precipitated. The solid was filtered and was dried by dissolving in ethyl acetate, drying the ethyl acetate solution with magnesium sulfate and evaporating the solvent. The crude white product was recrystallized repeatedly from methylene chloride to give white crystals (15 g, 89%) of constant melting point: mp 158-159 ^{0}C (lit. mp[112] 158 ^{o}C); ^{1}H NMR (CDCl$_3$ + DMSO-d$_6$ δ 2.69 (m), 5.40 (t), 7.31 (s), 7.56 (m), 8.10 (m); IR (KBr) 3000 (b), 2930, 1915 (s), 1605, 1525, 1430 cm^{-1}.

3-(4-Methyl-1-naphthalene)propanoyl chloride: The acid chloride was prepared from 21.4 g of the acid and an excess (20 ml) of thionyl chloride. The reaction solution was stirred at 50 ^{o}C after which the liquid was removed under vacuum. The resulting solid was dissolved in n -hexane and the residual solid separated by filtration to remove unreacted acid. Removal of the solvent gave the acid chloride which was used for the reaction with PVA.

Polymer[Acid chloride + Poly(vinyl alcohol)]: 5.0 g of acid chloride and 1.0 g of PVA (mw - 3000, 75% hydrolyzed) were mixed and subsequently heated as a melt at 160 - 165 0 ^{o}C for 5 min. After the reaction the material was taken up in methylene chloride and any remaining solid filtered off. Removal of the solvent under vacuum provided the polymer.

2. Synthesis of 1,4-dimethyl-2-vinylnaphthalene and 1,4-dimethyl-6-vinyl-napthalene.

Both of the title monomers were synthesized and characterized in Dr. Schaap's laboratories at Wayne State University.* The following procedures were used for their synthesis and analysis (see Fig. 22).

Spectral Characterization of Materials: Proton and carbon NMR spectra were acquired on a Nicolet QE-300 spectrometer using deuteriochloroform as solvent.

1-Chloromethyl-4-methylnaphthalene: Paraformaldehyde (120 g) was dissolved in a mixture of glacial acetic acid (270 ml) and concentrated hydrochloric acid (375 ml) at 50 $^\circ$C. The temperature was raised to 90-95 $^\circ$C, after which phosphoric acid (175 ml) and 1-methylnaphthalene (290 g) were added dropwise. The mixture was stirred at 90-95 $^\circ$C for 5 h after which time TLC on silica with methylene chloride indicated that the reaction was complete. The reaction mixture was diluted with saturated aqueous sodium chloride (150 ml) and extracted with methylene chloride (1500 ml). The methylene chloride layer was then washed with saturated sodium bicarbonate, washed three times with water, and dried over sodium sulfate. After evaporation of the solvent, the oily material was distilled under vacuum to give a solid product. This solid was crystallized from n-hexane to give 255 g (66%): mp 55-6 $^\circ$C; proton NMR δ 2.660 (s, 3H), 4.998 (s, 2H) 7.216-7.240 (m, 1H), 7.363-7.387 (m, 1H), 7.511-7.610 (m, 2H), 8.001-8.031 (m, 1H), 8.125-8.157 (m, 1H).

1,4-Dimethylnaphthalene: To a solution of 1-chloromethyl-4-methyl-naphthalene (50 g) in dry dimethylsulfoxide (350 ml) was added sodium borohydride (15 g) in portions [This reaction is extremely exothermic.
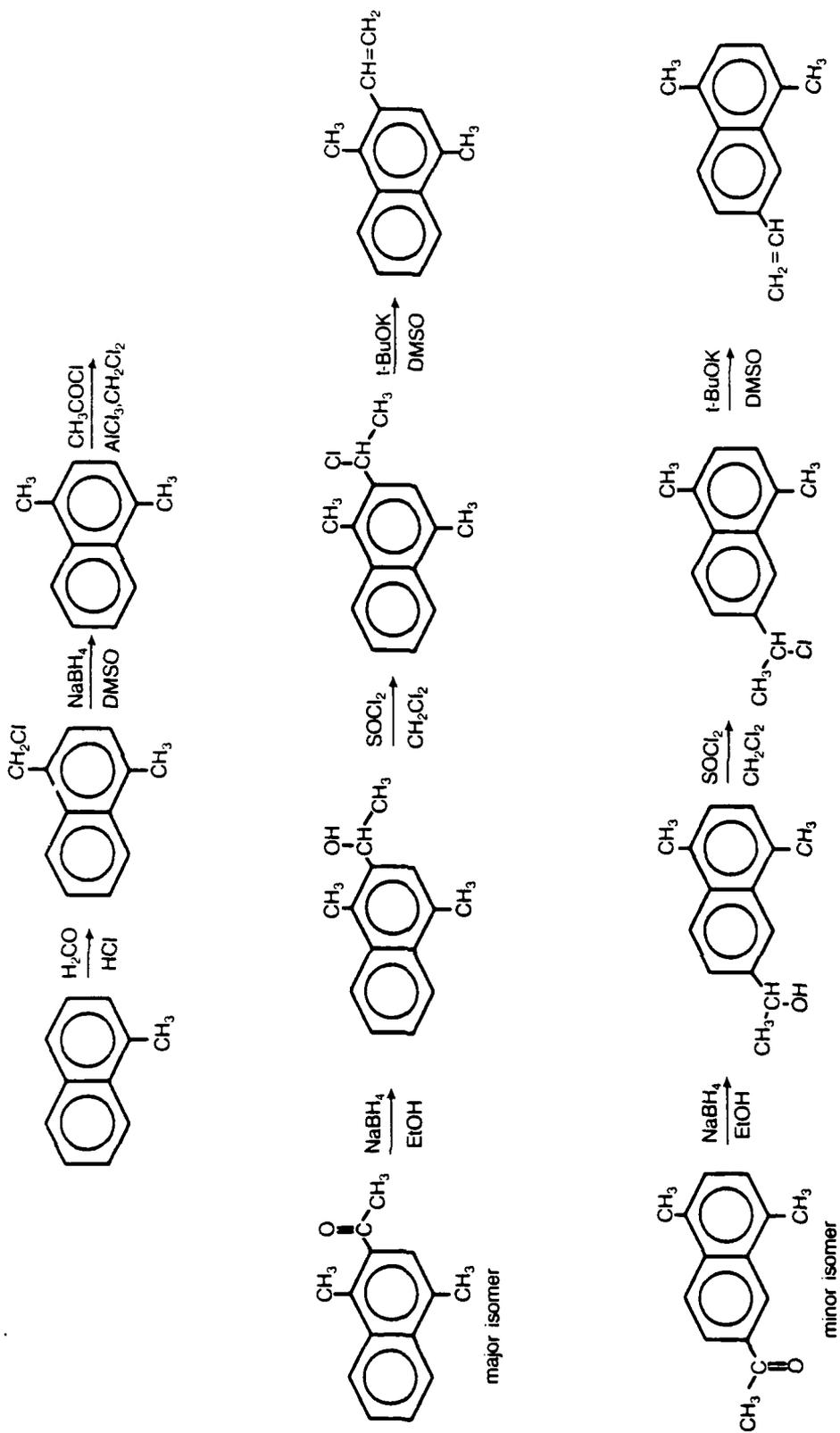
SYNTHETIC ROUTE

Figure 22. Synthetic route to 2-PVN and 6-PVN.

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Addition of NaBH$_4$ should be in small portions. The reaction may be cooled by ice-water]. The reaction mixture was stirred for two hours and cooled to room temperature. The excess sodium borohydride was destroyed by slow and careful addition of 2N hydrochloric acid until the frothing ceased. The mixture was diluted with water and extracted with methylene chloride (3 x 500 ml) and washed three times with water. The methylene chloride layer was dried over sodium sulfate and evaporated to give 39 g (95%) of a yellow oil which was used in the next step without further purification: proton NMR δ 2.653, 6H), 7.197 (s, 2H), 7.498-7.531 (m, 2H), 7.983-8.015 (m, 2H); carbon NMR δ 19.284, 124.650, 125.328, 126.256, 132.309, 132.728.

Friedel Crafts Acylation of 1,4-Dimethylnaphthalene: Anhydrous aluminum chloride (18 g) and acetyl chloride (10 ml) were stirred in methylene chloride (150 ml) until most of the aluminum chloride had dissolved. A solution of 1,4-dimethylnaphthalene (20 g) in methylene chloride (50 ml) was added quickly but carefully. The solution turned black immediately. The reaction mixture was stirred for 2 h at room temperature. TLC on silica with n-hexane indicated that the reaction was complete. The reaction mixture was poured into ice-water containing 100 ml of conc HCl. The methylene chloride layer was washed three times with water and the solvent evaporated to give 22 g (88%) of a yellow oil. The NMR of the crude material showed the presence of three products in a ratio of 65:25:10. Two major products were separated by column chromatography on silica gel (230-400 mesh) by using n-hexane/ethyl acetate (95:5) as an elvant. major isomer: 1,4-dimethyl-2-acetonaphthone, mp 53-54 $^{\circ}$C, proton NMR [Fig. 23] δ (s, 3H), 2.670 (s, 3H), 2.738 (s, 3H), 7.370 (s, 1H), 7.550-7.601 (m, 2H), 7.963-8.004 (m, 1H), 8.128-8.170 (m, 1H); carbon NMR 15.511, 19.365, 30.894, 124.472, 124.537, 125.771, 126.844, 131.335, 132.355, 133.036, 133.393, 136,859, 204.444.

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1,4-dimethyl-2-acetonaphthone
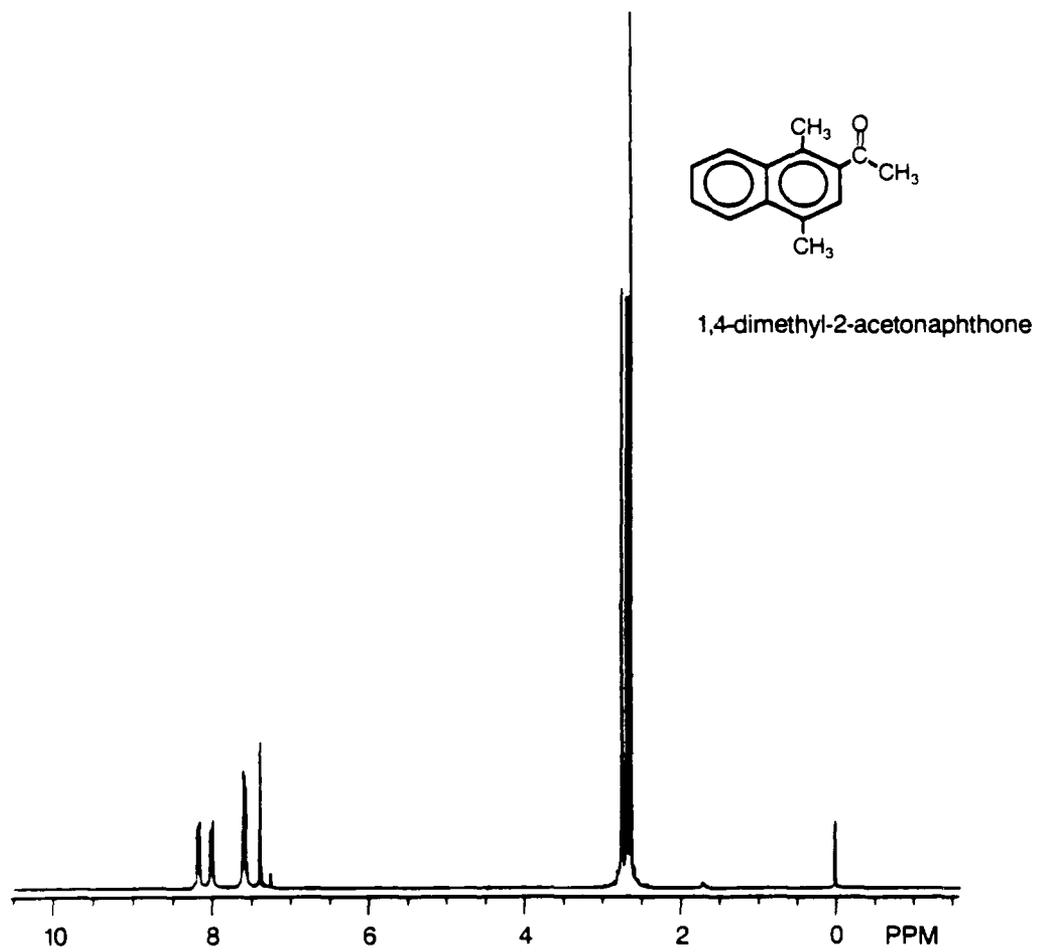
Figure 23. Proton NMR spectrum of 1,4-dimethyl-2-acetonaphthone.

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1,4-Dimethyl-6-(1-hydroxyethyl)naphthalene: To a solution of 1,4-dimethyl-6-acetonaphthone (1.3 g) in dry ethanol (75 ml) was added sodium borohydride (1.1 g). After allowing this solution to stand for 36 h at room temperature, the solvent was evaporated, the material dissolved in methylene chloride (150 ml) and this solution washed three times with water. After drying over anhydrous sodium sulfate and evaporating the methylene chloride, the resulting oily material was crystallized from n-hexane to yield 1.0 g: mp 71-73 $^{\circ}$C, proton NMR [Fig. 24] δ 1.572 (d, 3H, 6.3 Hz), 7.157-7.213 (m, 2H), 7.500-7.535 (m, 1H), 7.935-7.989 (m, 2H); carbon NMR δ 19.305, 25.230, 70.763, 120.711, 123.105, 125,132, 126.174, 126.603, 132.175, 132.316, 132.570, 142.607.

1,4-Dimethyl-2-(1-hydroxyethyl)naphthalene: Prepared as described for 1,4-dimethyl-6-(1-hydroxyethyl)naphthalene from 2.0 g ketone and 2.0 g NaBH$_4$ to yield 1.6 g, mp 82-84 $^{\circ}$C, proton NMR [Fig. 25] δ 1.500 (d, 3H, 6.3 Hz), 1.919 (bs, 1H, OH, D$_2$O exchangeable), 2.589 (s, 3H) 2.670 (s, 3H), 5.392 (q, 1H, 6.3 Hz), 7.467-7.545 (m, 3H), 7.957-7.983 (m, 1H), 8.041-8.073 (m, 1H); carbon NMR δ 13.384, 19.468, 24.312, 67.152, 123.560, 124.507, 124.638, 125.151, 125.618, 127.207, 132.017, 132.586, 132.877, 139.872.

1,4-Dimethyl-2-(1-chloroethyl)naphthalene: To a solution of 1,4-dimethyl-2-(1-hydroxyethyl)naphthalene (5.8 g) in methylene chloride (50 ml) was added a solution of thionyl chloride (5 ml, excess) in methylene chloride (30 ml). The resulting solution was stirred overnight at room temperature. TLC on silica showed the reaction to be complete. The solvent and excess thionyl chloride were removed under reduced pressure. The oily liquid was crystallized from n-hexane to yield 5.25 g: mp 52-53 $^{\circ}$C, proton NMR [Fig. 26] δ 1.912 (d, 3H, 6.6 Hz), 2.678 (s, 6H), 5.678 (q, 1H, 6.6 Hz), 7.510-7.554

1,4-dimethyl-6-(1-hydroxylethyl)
naphthalene
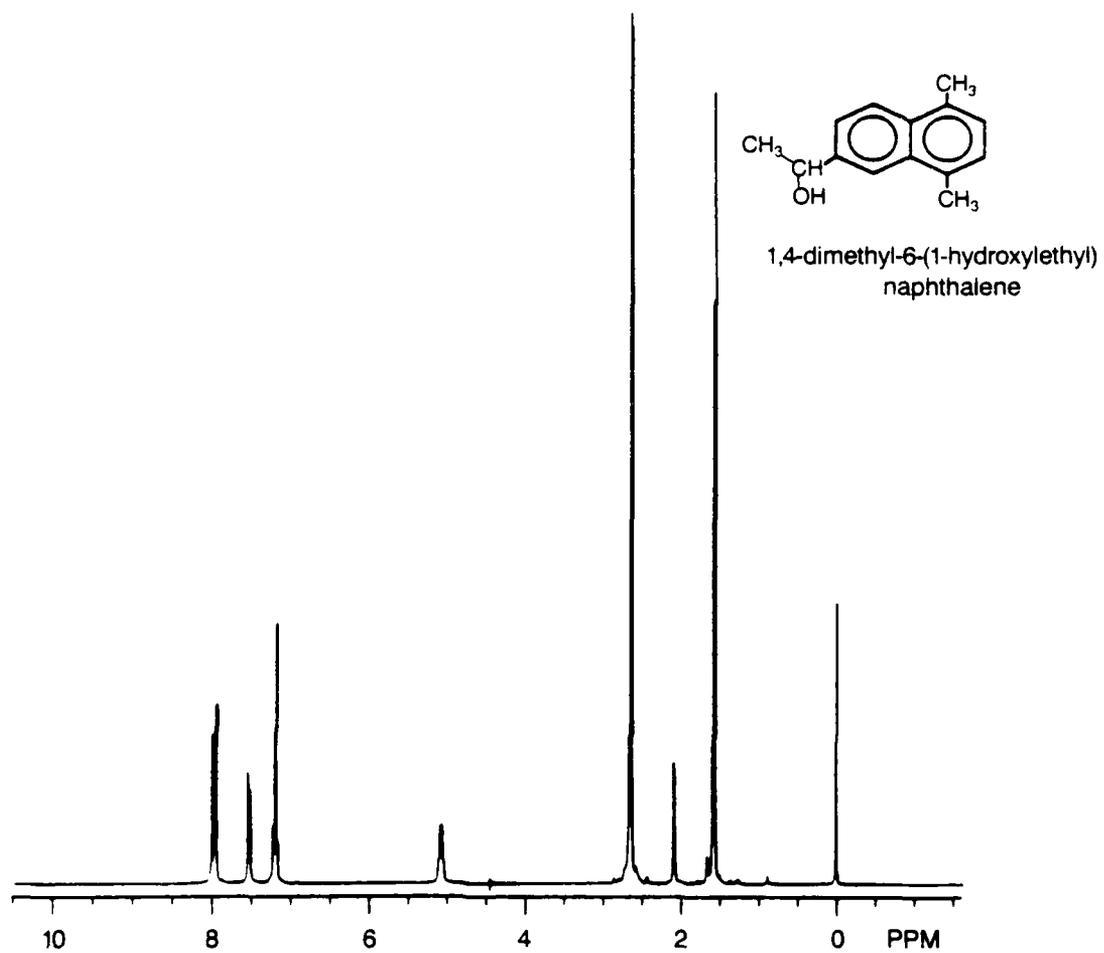
Figure 24.   Proton NMR spectrum of 1,4-dimethyl-6-(1-hydroxyethyl)
   naphthalene.

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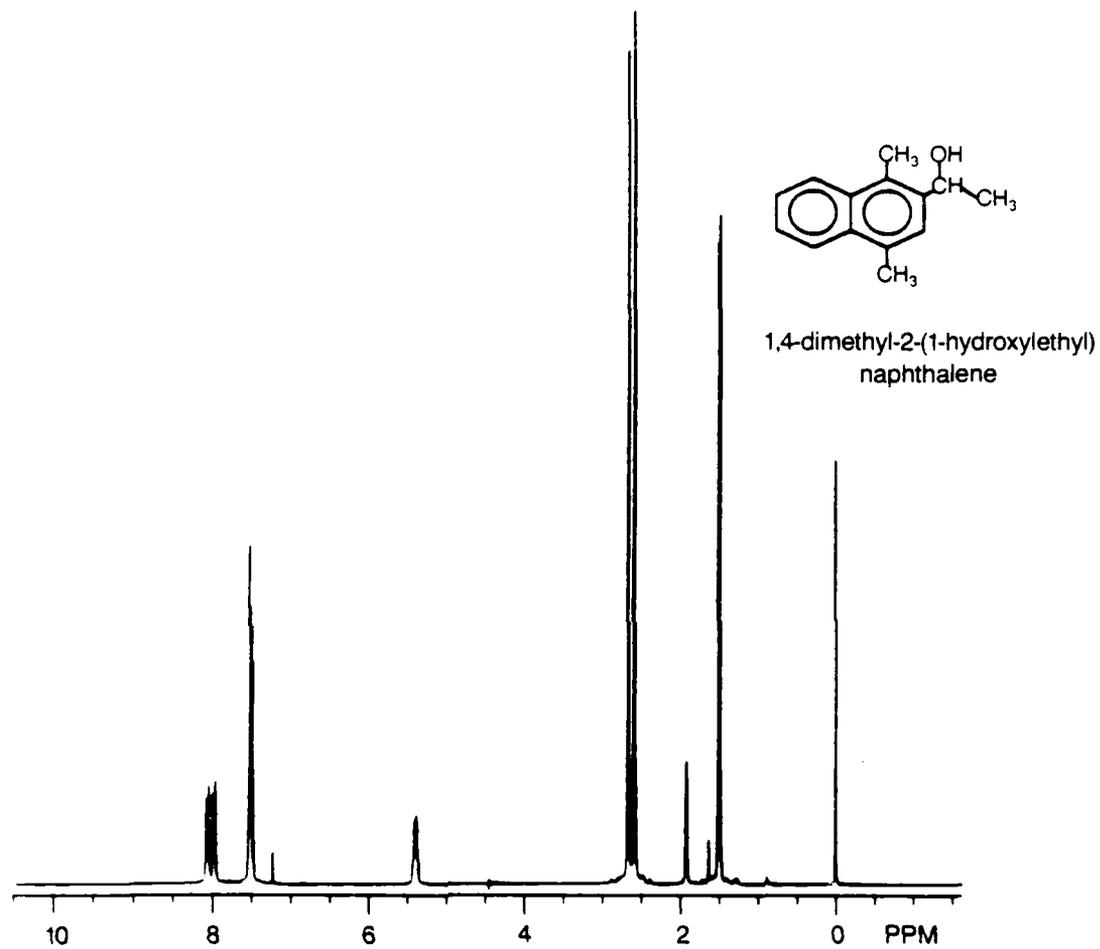
Figure 25.   Proton NMR spectrum of 1,4-dimethyl-2-(1-hydroxyethyl)
             naphthalene.
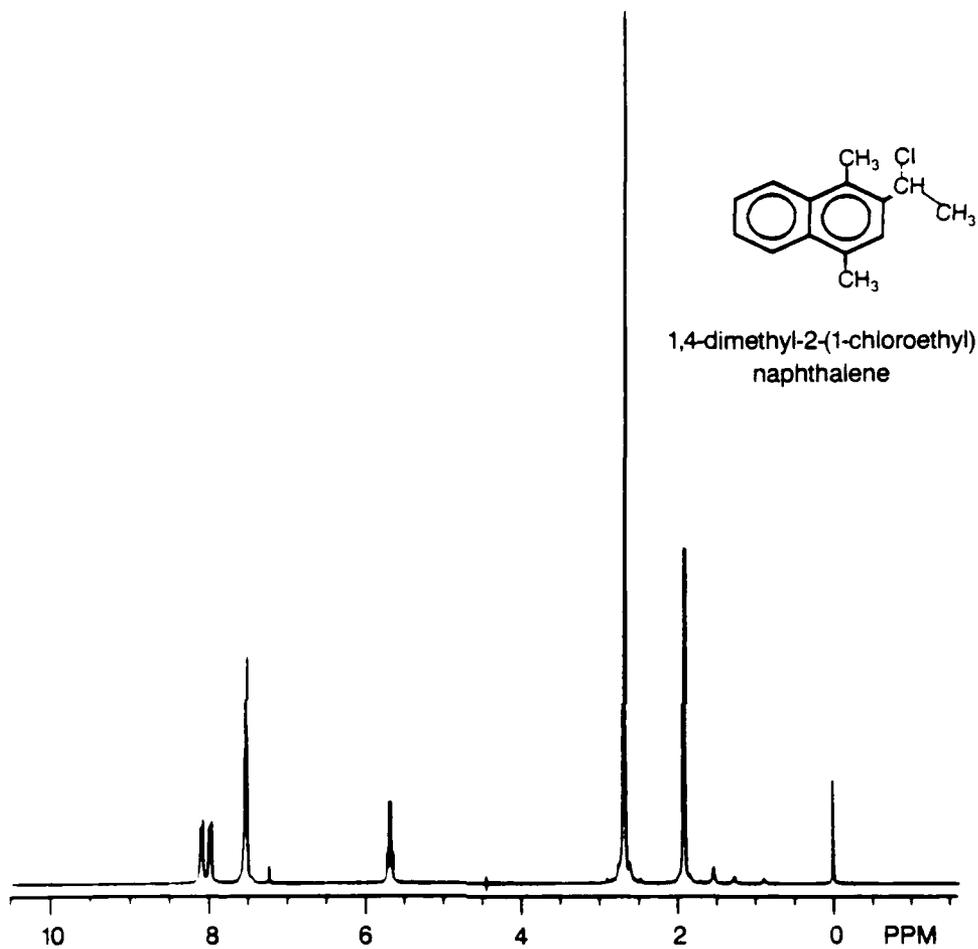
Figure 26.   Proton NMR spectrum of 1,4-dimethyl-2-(1-chloroethyl) naphthalene.

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(m, 3H), 7.957-7.989 (m, 1H), 8.069-8.101 (m, 1H); carbon NMR δ 13.642, 19.533, 25.961, 55.826, 124.199, 125.554, 125.096, 125.762, 125.932, 128.540, 132.404, 132.726, 132.895, 136.593.

1-4-Dimethyl-6-(1-chloroethyl)naphthalene: Prepared as described for 1,4-dimethyl-2-(1-chloroethyl)naphthalene from 2.2 g of 1,4-dimethyl-6-(1-hydroxyethyl)naphthalene and 4 ml of thionyl chloride: yield 2 g of an oil.

1,4-Dimethyl-2-vinylnaphthalene: To a solution of 1,4-dimethyl-2-(1-chloroethyl)naphthalene (9.0 g) in 150 ml of dimethylsulfoxide was added potassium t-butoxide (5.0 g) in portions. The reaction mixture was stirred at room temperature for 3 h and then poured into water (600 ml). This aqueous solution was extracted with methylene chloride (2 x 400 ml). The organic layer was then washed four times with water and dried over anhydrous sodium sulfate. After evaporation of the solvent the oily material was purified by chromatography over silica gel using n-hexane as elvant to give 4.2 g of material, mp 44-45 $^{\circ}$C; proton NMR [Fig. 27] δ 2.641 (s, 3H), 2.657 (s, 3H), 5.380 (d of d, 1H), 5.712 (d of d, 1H), 7.227 (d of d, 1H), 7.460-7.528 (m, 3H), 7.940-8.086 (m, 2H); carbon NMR δ 14.098, 19,395, 115.663, 124.514, 124.650, 124.924, 125.253, 129.068, 131.917, 132.998, 135.620.

1,4-Dimethyl-6-vinylnaphthalene: Prepared as described for 1,4-dimethyl-2-vinylnaphthalene from 4.0 g of 1,4-dimethyl-6-(1-chloroethyl)naphthalene and 2.5 g potassium t-butoxide in 75 ml of DMSO: 2.3 g mp 48-9 $^{\circ}$C; proton NMR [Fig. 28] δ 2.631 (s, 3H), 2.647 (s, 3H) 5.330 (d, 1H, 10.8 Hz), 5.878 (d, 1H, 17.7 Hz), 6.921 (d of d, H, 10.8 Hz, 17.7 Hz), 7.140-7.216 (m, 2H), 7.650-7.850 (m, 1H), 7.888-7.957 (m, 2H); carbon NMR δ 19.264, 122.507, 123,374, 124.983, 126.394, 126.710, 132.243, 132.484, 132.810, 134.429.
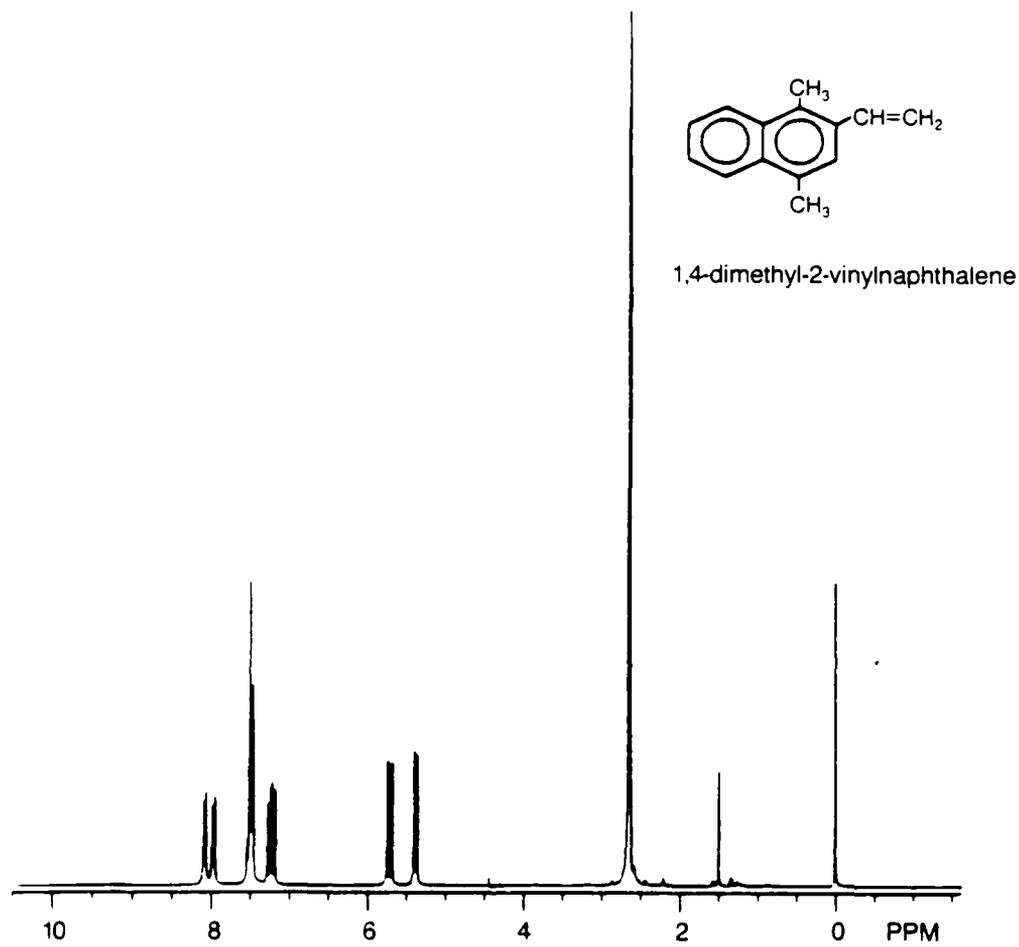
Figure 27. Proton NMR spectrum of 1,4-dimethyl-2-vinylnaphthalene.
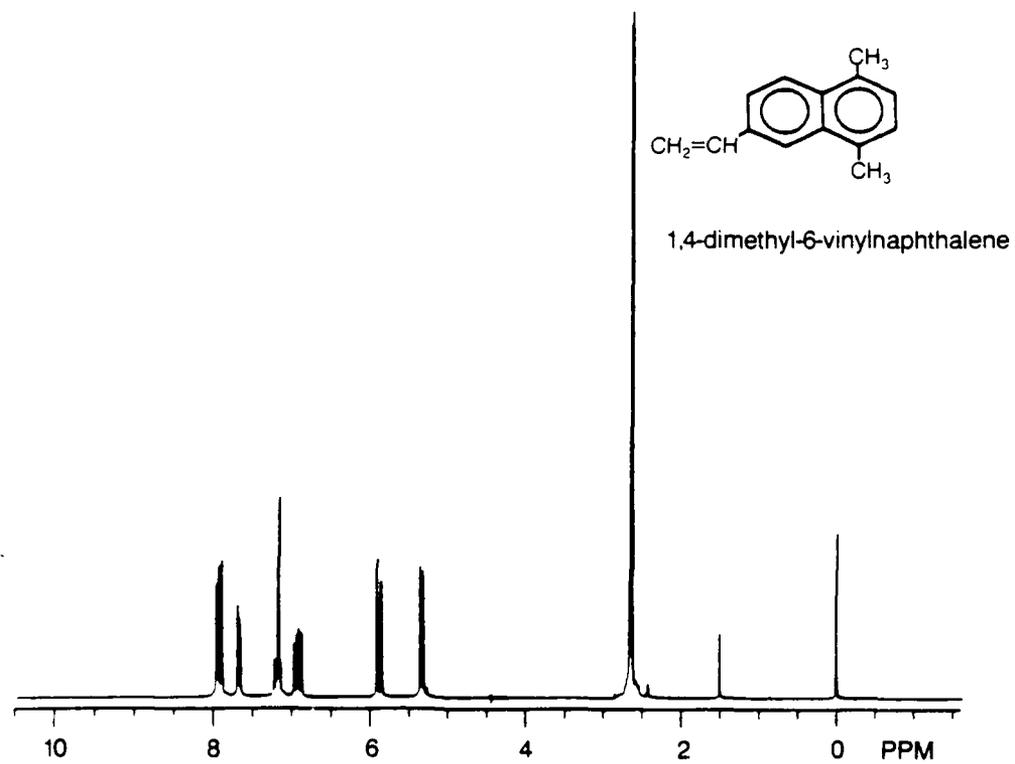
Figure 28.   Proton NMR spectrum of 1,4-dimethyl-6-vinylnaphthalene.

3. Synthesis of Lithium 3-(4-methyl-1-naphthalene-1,4-endoperoxide) propanoate.

The lithium salt was synthesized by Dr. Schaap* from the endoperoxide of the appropriate propanoic acid as follows. To 0.535 g of 3-(4-methyl-1-naphthalene-1,4-endoperoxide)propanoic acid in 4 ml of dry THF at 0 C under argon was added slowly 1 equivalent of 10.5 M n-BuLi (0.238 ml). After the addition was complete, the solvent was removed under vacuum to yield the lithium salt of the acid.

4. Polymerization of 1,4-dimethyl-2-vinylnaphthalene and 1,4-dimethyl-6-vinylnaphthalene.

The following procedure was developed and used at KMS Fusion** for polymerization of the title monomers. A solution of the monomer (2.0 g) and the free radical initiator, AIBN (0.2 g) in degassed benzene (50 ml) was heated to 80-90 C for approximately four hours. Benzene was then added to keep the newly formed polymer in solution. The dropwise addition of the polymer solution to methanol (> = 200 ml) precipitated the polymer, a white solid, which was filtered.

5. Photo-peroxidation of polymer bound substituted naphtnalene.

The following procedure for synthesis of endoperoxides was carried out at KMS Fusion.** A solution of the dye, methylene blue, in methylene chloride was prepared with sufficient concentration of the dye so that the solution had an absorbance of from 1 to 2 at 590 nm. The polymer (2-3 g) was dissolved in 70-80 ml of dye solution, and molecular oxygen was bubbled through the

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** KMS Fusion, Inc., Ann Arbor, MI

reaction mixture while being illuminated with a 250 watt Westinghouse

Ceramalux sodium lamp. The reaction mixture was cooled in an ice bath

throughout the 4-8 hours of irradiation. The extent of photoperoxidation was

determined by periodic UV spectrophotometric analysis of an aliquot of the

reaction mixture. A significant decrease in the absorbance of the naphthalene

peak at 290 nm signaled the end of the reaction. The irradiation was stopped,

and the reaction solution was washed with charcoal three or four times to

remove the methylene blue. Evaporation of most of the solvent and addition of

pentane in copious quantities served to precipitate the endoperoxide. The

endoperoxide was filtered and dried in a desiccator. The solid was stored at

reduced temperature in a freezer. For 1,4-dimethyl-2-(polyvinylnaphthalene-

1,4-endoperoxide) the yield was 90 per cent of 75 per cent peroxidized

material.

Appendix B: Constant Temperature Surface-Power Requirements.

In order to investigate the temperature dependence of the thermolysis
reaction of thin films of polymeric endoperoxide, it is useful to have good
control of the temperature of the film. Ideally, it is desirable to raise the
temperature to a target value instantly and maintain the film temperature
constant at that value indefinitely. Because the polymer film is supported by
a glass substrate, heating the surface of the substrate will result in heating
of the film. However, the energy deposited on the surface of the glass sub-
strate in order to raise the temperature of the film will raise the temper-
ature of the whole glass substrate through the transport of heat into the
interior of the glass. The power requirements needed to raise the temperature
of a substrate surface to an arbitrary value and maintain it at that value
will be examined here.

In order to easily model the diffusion of heat from the surface of a
glass plate into its interior, the plate is considered to be semi-infinite
(the surface being heated is at $x = 0$, the other surface is infinitely far
away). This assumption will cause no problems if the time of the experiment
is less than the thermal diffusion time,

$$\text{diffusion time} = (L^2/2\alpha)^{1/2} \tag{1b}$$

Here L is the plate thickness and α is the thermal diffusivity. For a 1/8-in-
thick plate and a thermal diffusivity of 6×10^{-3} cm^2/s for glass, the
diffusion time is estimated to be on the order of 3 s. Another assumption
implicit in the model is that the thermal conductivity and thermal diffusivity are
independent of temperature over the temperature range of interest.

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The complete thermal behavior of the glass substrate surface can be obtained from the solution of the thermal diffusion equation in one dimension,

$$\frac{dT}{dt} = \alpha \left[\frac{d^2T}{dx^2} \right] \tag{2b}$$

using the boundary conditions $T(0,t) = T_0$ and $T(\infty,t) = 0$. Here α is the thermal diffusivity and $T(x,t)$ is the temperature at a distance of x from the surface at time t. The solution to Equation 2b with these boundary conditions is

$$T(x,t) = T_0 \; \text{erfc} \left[\frac{x}{2(\alpha t)^{1/2}} \right] \tag{3b}$$

where erfc(z) is the complementary error function of z. The quantity of interest is the power input at the surface ($x = 0$). The power is easily calculated from the flux at the surface by multiplying by the surface area. The flux at $x = 0$ is

$$F_0(t) = -K \left. \frac{dT}{dx} \right|_{x=0} \tag{4b}$$

where K is the thermal conductivity of the substrate. Differentiating Equation 3b as prescribed in Equation 4b and multiplying by surface area, A, the power required to maintain the surface of the substrate at the temperature T_0 is obtained.

$$P_0(t) = K \, A \, T_0 / (\pi \alpha \{ t - t_1 \})^{1/2} \tag{5b}$$

Here t_1 is the time of the start of the heating pulse. Because the actual glass substrate surface is heated by electrical power delivered through a conductive surface coating of resistance, R, the voltage across the conductive coating must change in time as

$$V(t) = (K\ T_0\ A\ R)^{1/2} \cdot (\pi\alpha(t-t_1))^{-1/4} \qquad (6b)$$

Inspection of Equation 5b reveals that the power delivered to the plate becomes infinite as t approaches t_1. Because the power supply used in the experiments reported here is limited to an output power of 525 watts, an initial period of time is required to heat the surface to the target temperature before the analysis presented above can be employed. Therefore, Equation 2b must be used to calculate the time required to reach a given target temperature.

If a constant power is delivered to the surface of a semi-infinite slab, the temperature rises in time as

$$T(t) = (2\ P_0/A\ K) \cdot (\alpha\ t/\pi)^{1/2} \qquad (7b)$$

Solving Equation 7b for t yields the delay time needed to reach a prescribed temperature with a constant input power of P_0 at the surface. Equation 7b can also be used to determine the ratio of constants $\alpha^{1/2}/K$. The thermal conductivity and the thermal diffusivity appear as this ratio in all the equations of interest. The ratio can be experimentally determined by measuring the surface temperature of the substrate as a function of time and then plotting the surface temperature against the square root of time. A linear plot

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results, and, from the slope of this plot the ratio of thermal constants is determined to be 3.1×10^{-4} $m^2Ks^{1/2}J^{-1}$ for the Pyrex plates.

It is necessary to discuss briefly how the transition from Equation 7b to 5b is handled. Using Equation 7b, a time is calculated for heating the substrate surface (and the polymeric film) to the target temperature. Equation 5b then specifies the power requirements for maintaining the plate at constant temperature, however the definition of t_1 for this equation must still be elucidated. At the transition time $t - t_{tr}$, the flux calculated from Equation 7b must equal the flux calculated from Equation 5b: there must not be a discontinuity in time for the energy flux at the surface. Substituting $t = t_{tr}$ into Equation 5b and letting the flux equal the value determined from Equation 7b for T = the target temperature yields an equation which can be solved for t_1 in terms of t_{tr},

$$t_1 = t_{tr}[1 - 4/\pi^2] \qquad (8b)$$

With this value for the initial time, t_1, Equation 2b can be used to calculate the power or voltage needed to maintain a constant temperature. This procedure is only an approximation and will approach the ideal case for times long compared with t_1.

Appendix C: Diffusion of Singlet Oxygen in 2-PVNE.

The diffusion and quenching of singlet delta oxygen in a thin film of 2-PVNE may be a complex process. One complication of the process is the changing nature of the polymer matrix; it changes from 2-PVNE to 2-PVN as the thermolysis reaction proceeds. To better understand some of the features of the thermolysis process, an attempt is made to simulate the release of singlet delta oxygen from heated 2-PVNE films with simple mathematical models. The polymer film is treated as a homogeneous material characterized by a single, constant diffusivity, D, and a thickness, S. It is assumed that at time $t = 0$ singlet delta oxygen is instantly generated uniformly throughout the film. Singlet oxygen can escape from only one of the film surfaces, the front surface; the back surface is in contact with a conductive metal oxide surface. Collisions of singlet delta oxygen with the back surface either result in deactivation of the excited oxygen, in which case the collision is called inelastic, or result in reflection of the excited oxygen back into the polymer film without deactivation, in which case the collision is called elastic. In the simple mathematical model presented, the collisions of singlet delta oxygen with the back surface are treated as either all elastic or all inelastic.

The problem of thermal diffusion in a slab with parallel boundaries is discussed by Carslaw and Jaeger (Ref.4). A slab is considered to occupy a space from -L to +L with the boundary conditions $T = 0$ at $x = -L$ and +L. The initial temperature (T) is T_0 throughout the slab. The analogous problem in mass diffusion considers a slab with an initial concentration of diffusing species, c_0, uniformly dispersed at time $t = 0$ and with the boundary conditions $c = 0$ at $x = -L$ and +L. Here c is the concentration of the

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diffusing species of interest. If the species of interest is singlet delta oxygen, the flux of this species crossing the boundary at $x = +L$ into the gas phase is given by the flux at this surface which can be written down from analogous thermal diffusion problem with the substitutions; heat flux/thermal conductivity becomes molar flux/diffusivity, temperature becomes concentration, and thermal diffusivity becomes singlet oxygen diffusivity. With these substitutions the molar flux at $x = L$ is given by, (Ref. 4)

$$Flux\big|_{x=L} = \left[\frac{2 \, D \, C_0}{L}\right] \sum_{n=0}^{\infty} e^{-D(2n+1)^2 \pi^2 t / 4L^2} \tag{1c}$$

Equation 1c presumes that the singlet oxygen molecules have an infinite lifetime. The flux in Equation 1c must be multipled by the probability that the oxygen molecule is still excited, $\exp\{-k_q t\}$. Here k_q is the pseudo first order quenching constant associated with deactivation of singlet delta oxygen by the polymer. Finally, this lifetime corrected flux is integrated over all time to give,

$$N = \frac{8}{\pi^2} C_0 \, A \, L \sum_{n=0}^{\infty} \left[\frac{1}{(2n+1)^2 + \dfrac{4 \, k_q}{\pi^2 D} L^2}\right] \tag{2c}$$

Included in Equation 2c is the area of the boundary surface across which singlet oxygen diffuses before reaching the gas phase. The result is n, the total number of singlet delta oxygen molecules which enter the gas phase. Equation 2c has one adjustable parameter, $\beta = k_q/D$, the ratio of the quenching constant to the molecular diffusivity of singlet delta oxygen in 2-PVNE. The sum in Equation 2c was evaluated numerically for a range of values of L. The calculation was repeated for several values of the adjustable parameter giving a family of curves of singlet delta oxygen release as a function of film thickness.

The manner in which L is related to the endoperoxide film thickness will determine whether the back surface is modeled as deactivating or non-deactivating. If the thickness, S, is chosen to be equal to L, with the front surface at +L and the back surface at $x = 0$, the calculation prescribed by Equation 2c will support an elastic model. The inelastic model results from the choice of $2L = S$, and the resulting value of n is 1/2 the value calculated from Equation 2c in the limit of infinitesimal film thickness.

Equation 3c is used to calculate the total number of moles of singlet delta oxygen released into the gas phase as a function of film thickness (with either of the two assignments for L). The experimental data is given in terms of amperes of current from a cooled germanium detector. It remains to convert one to the other for purposes of comparison between the theoretical calculations and the experimental results. Here, the results of the theoretical calculations are converted to units of signal currents. The calculated signal current is given by,

$$
\text{Signal} = (0.5) \times (1.56 \times 10^{-9}) \times (2.6 \times 10^{-4}) \times (.57) \\
\times (.72) \times (1.7 \times 10^{-3}) \times N \tag{3c}
$$

The first term on the right is the responsivity of the germanium detector, the second term is energy of one photon at 1270 nm, the third term is the radiative rate constant, the fourth term corrects for the transmission of the interference filter, the fifth term allows for reflection losses at four surfaces (the sapphire windows on the sample chamber and on the dewar of the germanium detector), and, finally, the sixth term is the fraction of photons collected by a 1-cm-dia surface 6 cm from the source of photons. The last factor assumes that all the singlet delta is collected at the center position of the substrate. This is not a severe approximation and any reasonable

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distribution of excited oxygen will give approximately (within 10%) the same result.

The results of these calculations are presented in the main body of this report as a family of curves of signal strength versus film thickness with β as the adjustable parameter. Both assignments of L are treated, and the experimental results are compared with the elastic and inelastic theoretical models.

Supplement 1: Singlet Oxygen Yield Measurements.

Executive Summary

The primary objective of this series of experiments was to determine the fraction of oxygen released into the gas phase in the singlet delta state upon thermolysis of 2PVNE. To this purpose DMF or TME was allowed to selectively react with singlet oxygen and the extent of this reaction was assayed by mass spectrometry. The results of this analysis were compared when TME and DMF were used as singlet oxygen titrants in the determination of fractional singlet oxygen yields derived from 19-nm-thick 2PVNE films. When TME was used, a fractional singlet oxygen yield of only 0.11 was measured, whereas a yield of 0.3-0.4 was measured with DMF. The substantially lower yield found for TME is not unexpected; the reaction rate constant of singlet oxygen with TME is a factor of 20 slower than with DMF and a slower reaction rate provides more time for the quenching of oxygen by the buffer gas, by TME itself, and by the walls of the sample chamber.

The extent of reaction of singlet oxygen with DMF was measured using two methods. The primary oxygen mass peak at $m/e=32$ and the primary DMF peak at $m/e=96$ were used to analyze the fraction, F, of singlet oxygen produced by thermolysis of 2PVNE. Agreement between the two methods was not completely satisfactory; the fraction of singlet oxygen calculated from $m/e=32$ data is 0.4 ± 0.08 which is substantially larger than 0.3 ± 0.02 calculated from the $m/e=96$ data, though the standard deviation on the former is comparable to the extent of disagreement. Because the primary DMF peak at $m/e=96$ is less

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subject to interference by fragmentation of other molecules, the change in ion current at this mass peak was monitored in subsequent analysis.

The fraction of oxygen entering the gas phase in the singlet delta state depends markedly on the thickness of the 2PVNE film. A simple model for singlet oxygen diffusion and quenching in the polymer film is found to agree very well with the mass spectrometry results. The model employs a fitting parameter, k_q/D, which is the ratio of the pseudo-first-order rate constant for singlet oxygen quenching by the polymer to the diffusivity of singlet oxygen in the polymer. The value of this ratio when a good fit is achieved with the experimental data is determined by the values which are assumed for two other parameters, the intrinsic yield of singlet oxygen, ϕ, and the probability that a singlet oxygen molecule will be quenched when it encounters the Nesatron surface - polymer interface, γ. The fractional singlet oxygen yield at the limit of zero film thickness is found to be close to 0.5 in the present series of experiments. This constrains ϕ to values between 0.5, when $\gamma = 0$, and 1 when $\gamma = 1$.

In previous work the fractional yield of singlet oxygen released from 2PVNE films was calculated from photometric measurements of emission at 1.27 μm and examined as a function of 2PVNE film thickness. Agreement of the photometric results with model calculations and with the DMF titration results is quite good. The same values of k_q/D used to fit the titration data also furnish a good fit between model calculations and photometric results.

From the agreement of model calculations with fractional singlet oxygen yield results, it is not possible to determine the extent of singlet oxygen quenching at the polymer - Nesatron interface since a good fit is obtained

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over the full range of this parameter. Overcoating the Nesatron surface with silicon monoxide was found to have no observable effect on the fractional singlet oxygen yield. From this we conclude that surface trapped or free charge carriers are not involved in the quenching of singlet oxygen at the Nesatron/2PVNE interface. It may be that the quenching probability of singlet oxygen at the Nesatron surface is unusually high as a result of hydroxyl groups attached to the metal oxide surface. If this is the case a silicon monoxide overcoating would not be expected to provide much protection from quenching since this surface also has surface hydroxyl groups which could participate in the quenching of singlet oxygen.

Introduction

Thermolysis of the endoperoxides of many polycyclic aromatic hydrocarbons has been shown to result in efficient conversion of thermal energy to electronic excitation of the product oxygen molecule.[1] Recently, solid films of 1,4-dimethyl-2-poly(vinylnaphthalene-1,4-endoperoxide), 2PVNE, were reported to quantitatively release oxygen into the gas phase upon heating. The fraction of the oxygen which was electronically excited to the singlet delta state was found to vary markedly with 2PVNE film thickness in agreement with a simple model of molecular diffusion and quenching in the polymer solid. The fraction of oxygen released into the gas phase in the singlet delta state was determined from luminescence measurements of the excited oxygen at 1270 nm detected with a liquid nitrogen cooled germanium photodiode.[2]

There are difficulties with the determination of singlet oxygen yields from photometric data. The photometric signal is proportional to the number of luminescing species present at any one time rather than the integral amount of species produced. This problem was circumvented in our previous work[2] by releasing the singlet oxygen quickly into a 10 Torr buffer gas which served to confine the excited oxygen to the viewing region of the detector for a period of time comparable to that required for thermolysis of the 2PVNE and release of O_2 from the polymer film. Under these conditions the peak germanium detector signal is proportional to the total amount of singlet oxygen released into the gas phase. Unfortunately the large number of physical constants required to convert the germanium detector signal to an absolute measure of luminescing species population renders the accuracy of the yield determination suspect. Uncertainties connected with the spatial

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distribution of singlet delta oxygen in the sample chamber, the effective f

number of the optical setup, the responsivity of the detector, the radiative

rate constant for the singlet delta to the ground state triplet sigma transi-

tion all contribute to the uncertainty of the calculated singlet oxygen

yield.

A more direct measure of the singlet oxygen yield can be obtained by

preferentially reacting the singlet oxygen molecule with another chemical

species and assaying the reactants or products. This method was previously

used to measure the singlet oxygen density in a microwave discharge gas flow.

Gleason et al.[3] measured the rate constants for the reaction of singlet delta

oxygen with tetramethylethylene (TME) and 2,5-dimethylfuran (DMF) using a

gas-liquid chromatograph to separate reactants from products and quantify the

amount of material reacted. Their findings suggested that DMF physically

quenched singlet delta oxygen at about the same rate with which it reacted,

whereas TME, though having a reaction rate with singlet delta oxygen which

was about 4 times slower than DMF, reacted quantitatively. The rate

constants reported by these workers for the reaction of singlet delta oxygen

with DMF and TME are 3.7×10^8 $cm^3 mol^{-1} s^{-1}$ and 1×10^8 $cm^3 mol^{-1} s^{-1}$, respectively.

Huie and Herron,[4],[5] measured the rate constants for the same reactions

of singlet oxygen with DMF and TME using mass spectrometry to detect the

reactants and products. DMF was found to react quantitatively with singlet

oxygen, in contrast with results reported by Gleason et al.[3] The rate

constants which Huie and Herron report[5] are 1.5×10^{10} $cm^3 mol^{-1} s^{-1}$ and 7.7×10^8

$cm^3 mol^{-1} s^{-1}$ for DMF and TME, respectively. These rate constants are signifi-

cantly larger than some earlier reported values and the differences have been

attributed to the presence of atomic oxygen in the gas flow in earlier

studies. The effects of atomic oxygen were minimized in the studies reported by Huie and Herron by addition of NO_2 to the singlet oxygen flow.[5]

In this paper we report the fractional yield of singlet delta oxygen released from 2PVNE films determined by reaction of the excited oxygen with TME and DMF. Using mass spectrometry to assay the quantity of DMF reacted, the singlet oxygen yield is found to be in substantial agreement with previous photometric determinations.

Experimental

The preparation of 2PVNE, its deposition as thin films on resistive glass plates and the heating of the endoperoxide films were described in detail in reference 2. For the present series of experiments 2PVNE was spin coated directly on the electrically resistive metal oxide layer (about 30 ohms per square) of one eighth inch thick Nesatron plates (Nesatron is a glass substrate with an electrically resistive coating obtained from PPG Industries). The passage of an electrical current through the resistive Nesatron coating heated the surface of the glass plate and the adjacent endoperoxide film. The thermolysis area was limited to 3.2 cm^2 by etching 1.5-inch-square Nesatron plates in hydrochloric acid which left a resistive strip in the center of the plate as shown in Figure 29. Aluminum strips 1-micrometer-thick were vacuum deposited on two sides of the thermolysis area providing a high conductance current path to the electrically resistive metal oxide coating. Copper rods in physical contact with the aluminum strips were connected to a Kepco ATE 150-3.5M programmable power supply which provided the electrical power needed to heat the thermolysis area of the Nesatron plate. For one series of experiments the resistive coating of the Nesatron
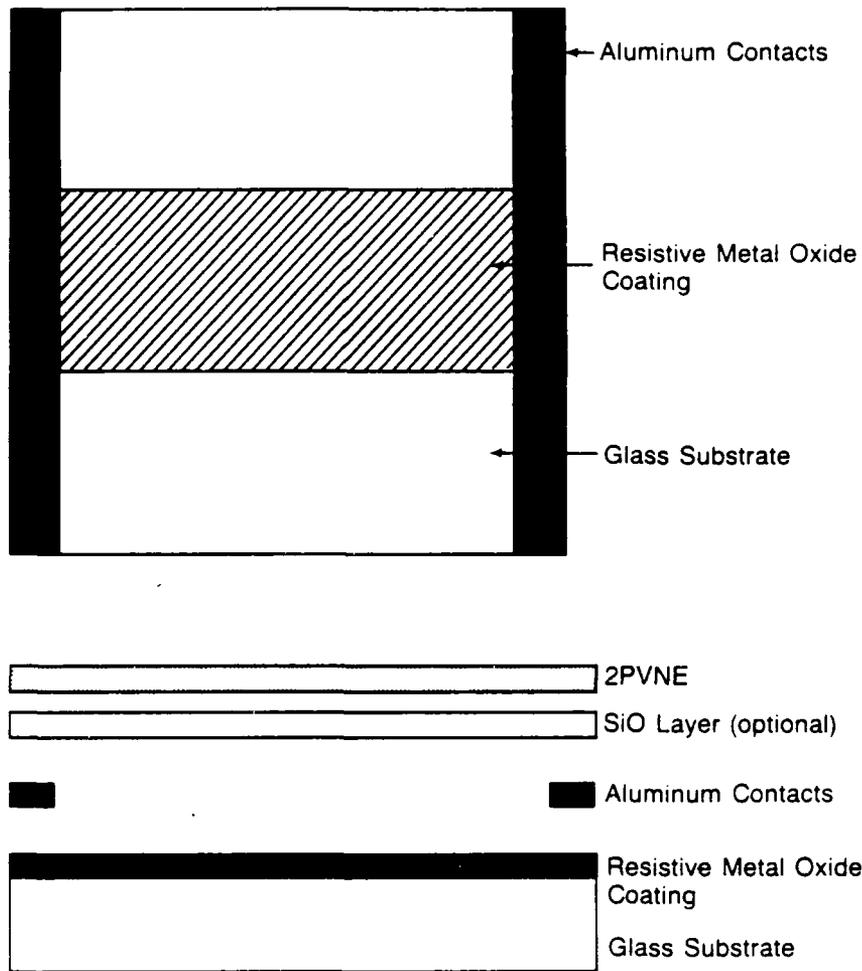
Figure 29. The heated substrate on which 2PVNE is deposited.

plate was overcoated with 0.1 micrometers of silicon monoxide to provide an insulating surface on which the endoperoxide was then deposited.

The experimental apparatus which was used to measure the singlet oxygen yield upon thermolysis of the endoperoxide films is illustrated in Figure 30. A sample chamber with an internal volume of 14.5 cm³ was constructed from Teflon to minimize deactivation of singlet delta oxygen on the walls of the container. The Nesatron plates coated with 2PVNE were mounted to the sample chamber with vacuum sealing provided by an O ring. The sample chamber along with the gas handling manifold was evacuated with a 150 l/s diffusion pump and filled with roughly 50 millitorr of reactant (DMF or TME) and 0.5 Torr of N_2. The nitrogen buffer gas was added in order to slow the rate of diffusion of singlet oxygen to the walls of the sample chamber. The pressure in the manifold was accurately measured after each gas addition with a 1 Torr Baratron capacitance manometer (Type 127AA) calibrated by the manufacturer.

After addition of reactant (DMF or TME) and nitrogen, the sample chamber was isolated from the gas handling manifold with a Teflon valve and the sample substrate was then heated by passing a current through the resistive metal oxide coating resulting in the thermolysis of the adjacent 2PVNE film. A 25-micron-diameter pinhole mounted to a port in the sample chamber provided a slow leak of the sample gas to the ionization section of a UTI Model 100C Quadrupole mass spectrometer equipped with an electron multiplier ion sensor. The detector section of the mass spectrometer was evacuated with a Leybold-Heraeus turbopump (Turbovac 50).

Tetramethylethylene (Aldrich Chemical) and 2,5-dimethylfuran (Aldrich Chemical) were purified by distillation and kept refrigerated until just
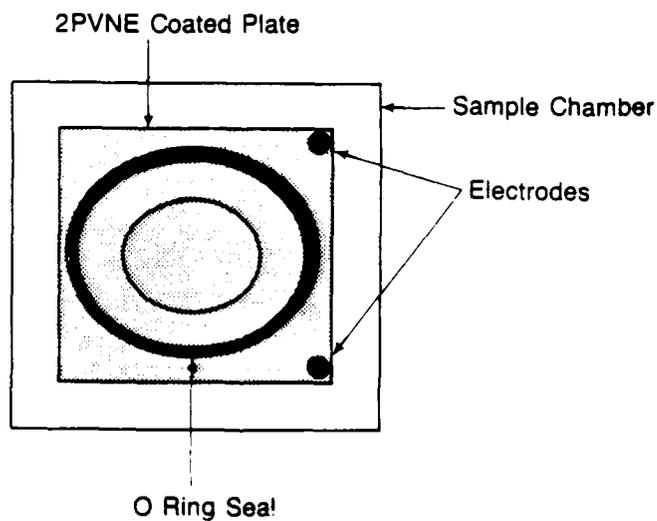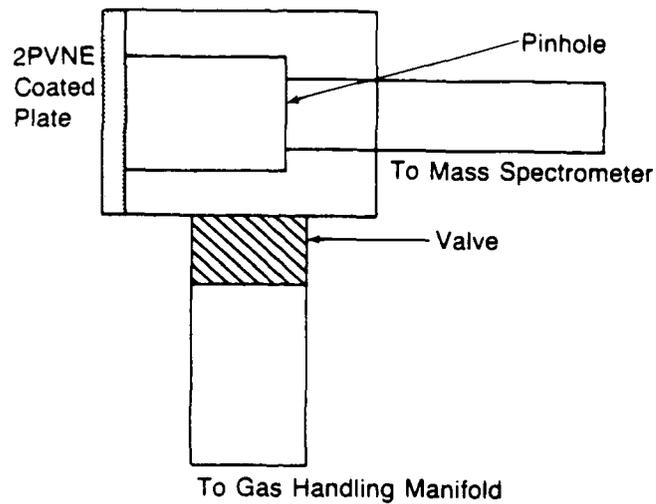
Figure 30. The experimental apparatus for measuring singlet oxygen yield
upon thermolysis of 2PVNE.

prior to use. The polymeric endoperoxide, 2PVNE, was prepared from the monomer and peroxidized as described in reference 2.

Results

The total amount of oxygen (both ground state and electronically excited) released into the gas phase upon thermolysis of a 19-nm-thick 2PVNE film was measured for a series of six samples. The film was heated to 88 C for five seconds and the change in the ion current at m/e=32 was recorded. The mass spectrometer was calibrated for molecular oxygen by recording both the ion current at m/e=32 and the sample chamber pressure as pure oxygen was metered into the sample chamber. The number of moles of oxygen released into the gas phase was determined by first multiplying the mass spectrometric ion current change at m/e=32 by the calibration factor to give the partial pressure of O_2 in the sample chamber and then using the ideal gas law (the gas was assumed to be thermally equilibrated with the sample chamber walls). Dividing the number of moles of O_2 thus calculated by the area of the 2PVNE thermolysis region (3.2 cm²) gave 5.33 0.22 x 10^{-9} moles/cm² for a 19-nm-thick 2PVNE film.

The number of moles of oxygen released from the 2PVNE film per unit area can be independently determined from 1) the fraction of 2PVN which has been converted to endoperoxide (this is measured by solution phase absorption spectrophotometry), 2) an average density of 1 g/cm³ (supported by data in reference 2), 3) the average formula weight of the polymer and 4) the film thickness determined from the coating solution concentration (using a previously determine correlation of 8.4 nm of film thickness for each 1 g of 2PVNE per liter of solution).[2] This calculation gives an oxygen yield of

6.27×10^{-9} moles/cm² which is about 15 per cent larger than the value determined by mass spectrometric assay of O_2.

The fraction of oxygen released in the singlet delta state upon thermolysis of 2PVNE was measured by reaction of either DMF or TME with singlet oxygen. The extent of the reaction was determined by observing the change in time of the mass spectrometer ion current when the quadrupole filter was set to pass a particular mass to charge ratio (m/e) associated with the O_2 ion or with a reactant or product fragment ion. From the mass spectrometric signal, the number of moles of singlet oxygen released into the gas phase, n*, was calculated. The fractional yield was then obtained by dividing n* by n, the total number of moles of O_2 released. The value of n is found by assuming that n is directly proportional to film thickness and using the value of 5.33×10^{-9} moles/cm² measured for a 19-nm-thick film.

When DMF is used to titrate singlet oxygen, the amount of singlet oxygen released into the gas phase can be independently determined from the data acquired at several mass peaks, including the primary product signal at m/e=128, the primary oxygen signal at m/e=32 and the primary DMF signal at m/e=96. The appearance of a product peak in the mass spectrum at m/e=128 upon titration of singlet oxygen by DMF has been reported by others[4] but was not observed in our experiments. Changes in the ion current at m/e=32 and m/e=96 were observed, however, and these changes were used to measure the singlet oxygen yield.

The change in ion current at the primary oxygen mass peak (32) upon thermolysis of 2PVNE, $S_0(32)$, is proportional to the total amount of oxygen released (both electronically excited and ground state) when DMF is absent from the sample chamber. When DMF is present in the sample chamber, the

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primary oxygen signal is diminished in magnitude from $S_0(32)$. With an excess of DMF, the change in ion current, $S(32)$, is proportional to the sum of the oxygen released into the gas phase in the ground state and that oxygen released into the gas phase in the singlet state which is quenched to the ground state without reaction with DMF. The latter was assumed to be negligible.

The fractional yield of oxygen released into the gas phase in the singlet delta state is equal to $1 - S(32)/S_0(32)$. From ion current changes at m/e=32 the fractional yield was calculated to be $0.40 \pm .08$ for 19-nm-thick 2PVNE films heated to 88 C for 5 seconds. The determination of this quantity can be in error if either the reactant, DMF, or the reaction product fragments to give an ion current at m/e=32 and if these contributions are not equal.

The singlet oxygen yield also can be determined from the change in ion current at the primary DMF mass peak upon release of singlet oxygen into the sample chamber. This method is less troubled by possible competing fragmentation channels than is the determination using the primary oxygen mass peak. The ion current at m/e=96 was measured over the course of the 2PVNE film thermolysis and the fractional change was computed. The initial partial pressure of DMF was measured with a capacitance manometer and the number of moles of DMF in the sample chamber was computed using the ideal gas law. This value when multiplied by the fractional change in m/e=96 ion current gives the number of moles of DMF consumed in the reaction with singlet oxygen. The number of moles of singlet oxygen released into the gas phase, n^*, is taken to be equal to the DMF consumed in the reaction. The fraction of singlet oxygen released then is simply the ratio of n^* to the total number

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of moles of oxygen released, both electronically excited and in the ground state. The latter was determined in a separate set of experiments in which DMF was absent from the sample chamber and the change in the ion current at m/e=32 was recorded (vide supra). Using the m/e=96 ion current signal, the calculated value of the fractional yield of singlet oxygen is 0.30 ± 0.02 when a 19-nm-thick 2PVNE film is thermolyzed by heating to 88 C for 5 seconds. This value obtained from measurements of the primary reactant mass peak compares with 0.40 ± 0.08 which was obtained from measurements of the ion current at the primary oxygen peak (m/e=32).

The fractional yield which is calculated from the m/e=96 data will underestimate the true fraction of oxygen released into the gas phase in the singlet delta state if the product (presumed to be an endoperoxide of DMF) formed by reaction of singlet oxygen with DMF fragments in such a manner so as to give an ion with a mass to charge ratio of 96. The extent of this problem was assessed by reacting all the DMF in the sample chamber with sing-let oxygen to give DMF-O_2 and measuring the change in m/e=96 ion current. Since the thermolysis of a 19-nm-thick 2PVNE film results in the release of enough singlet oxygen to consume about 6 millitorr of DMF, the addition of only 2 millitorr of DMF to the sample chamber ensured that ample singlet oxygen was present during the course of the experiment to react with all the DMF. Figure 31 shows the result of this experiment. The ion current (m/e=96) drops to about five of the DMF present in the sample chamber. If the DMF-singlet oxygen product contributed significantly to the ion current at m/e=96, a dramatic decrease in the mass spectrometric signal such as seen in Figure 31 would not be observed. Therefore, the value of the singlet
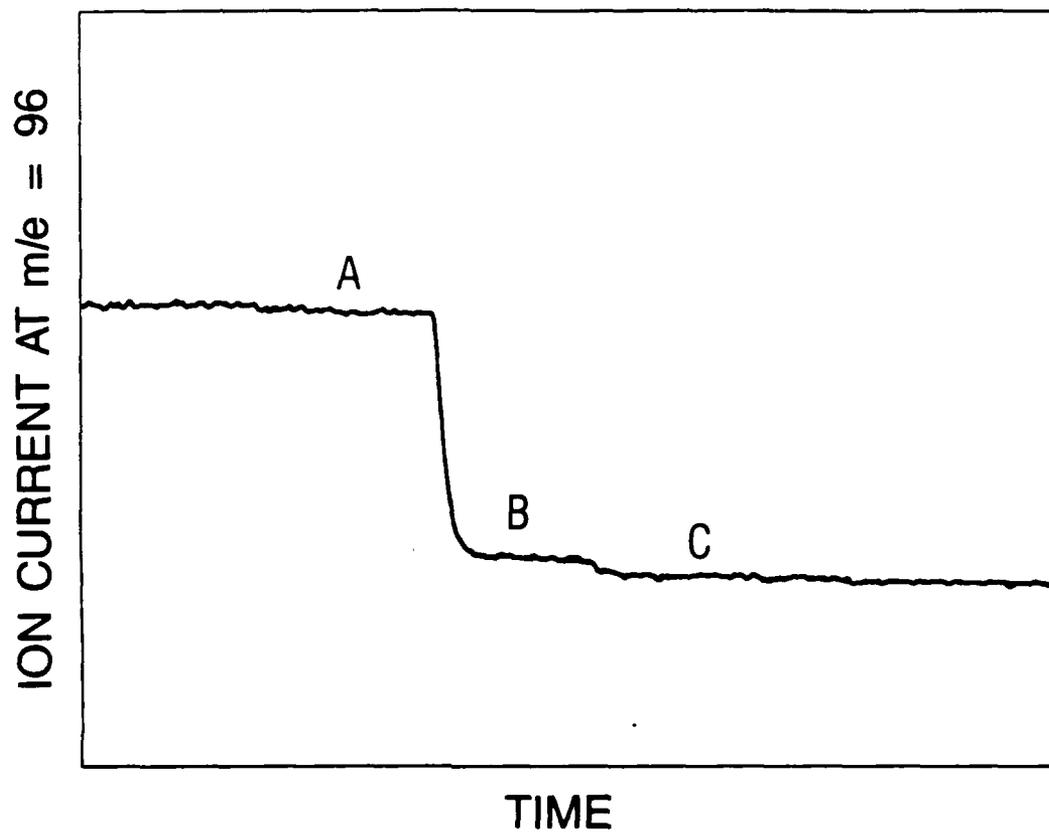
Figure 31. The decrease in ion current at the primary DMF mass peak (96)
upon release of singlet oxygen from 2PVNE.
A: Before thermolysis, B: after thermolysis, C: after
sample chamber evacuation.

oxygen yield calculated from the fractional change in ion current at m/e=96 is probably not reduced from the true value by more than 5 per cent as a consequence of fragmentation of DMF-O_2.

The singlet oxygen yield can be measured only when an excess of reactant (DMF or TME) is present in the sample chamber and under these conditions the amount of DMF which reacts with singlet oxygen should be independent of the initial amount of DMF. Several experiments were performed with differing amounts of DMF (at least twice the amount required to fully react with all the singlet delta oxygen released) loaded into the sample chamber to substantiate this conjecture. Figure 32 shows the number of moles of DMF consumed upon release of singlet oxygen as a function of initial DMF partial pressure The amount of DMF consumed in the reaction is not significantly affected by the initial partial pressure of DMF as long as at least a two-fold excess of DMF is initially present.

The amount of DMF consumed upon thermolysis of a 19-nm-thick 2PVNE film was measured over a fairly restricted range of substrate temperature, 81 C to 92 C, to assess whether small inadvertent variations in temperature which may occur among a series of experiments can result in significant changes in the measured singlet oxygen yield. Figure 33 shows the variation of the amount of DMF consumed as a function of substrate temperature. From 81 C to 88 C this fraction does not change. A small increase may occur when the temperature is raised to 92 C but the variation in the experimental data is comparable to the observed increase.

TME has previously been used as a titrant for singlet oxygen, however, because the reaction with singlet delta oxygen is much slower than with DMF, more opportunity exists for singlet oxygen deactivation either by collisions

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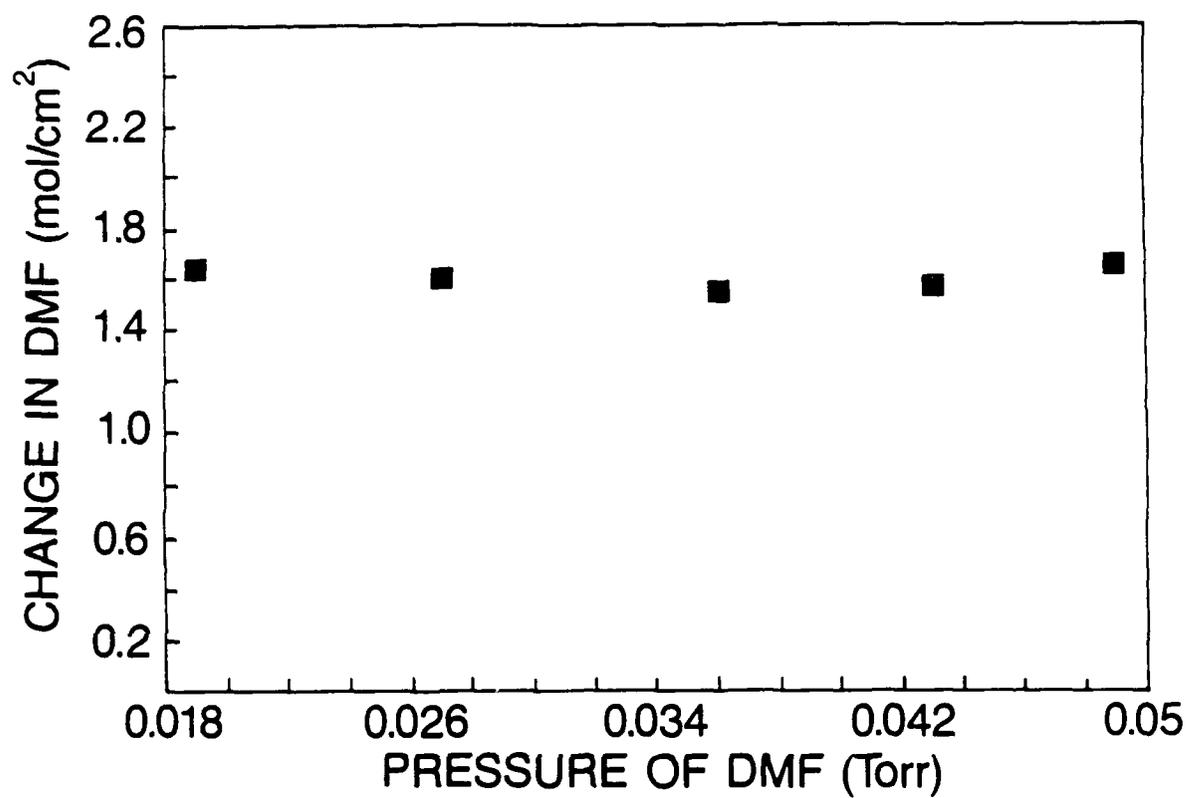
Figure 32. The number of moles of DMF consumed upon release of singlet oxygen from 2PVNE per unit area of endoperoxide film as a function of DMF partial pressure.

90
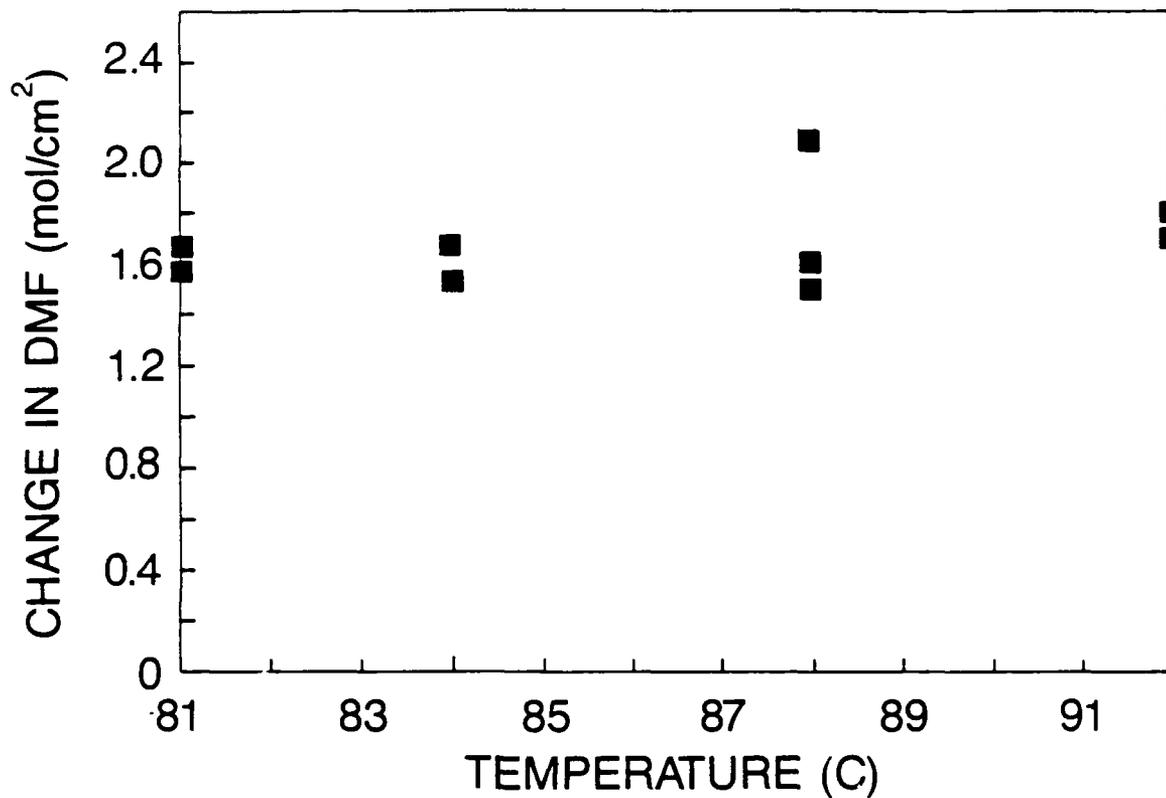
Figure 33. The number of moles of DMF consumed upon release of singlet oxygen from 2 PVNE per unit area of endoperoxide film as a function of thermolysis temperature.

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with TME, collisions with the buffer gas, or by deactivation on the walls of the sample chamber (particularly the endoperoxide film surface). In a series of experiments TME replaced DMF as the chemical reactant in the singlet oxygen yield determination. An increase in ion current at m/e=83 was observed upon thermolysis of 2PVNE and was attributed to the $C_6H_{11}^+$ ion resulting from the fragmentation of the addition product of singlet oxygen to TME. A decrease in ion current upon reaction of TME with singlet oxygen was observed at the primary TME peak at m/e=84 and at the fragment peak at m/e=69. The yield of singlet oxygen from thermolysis of a 19 nm 2PVNE film heated to 88 C for 5 seconds was calculated from the fractional decrease in ion current at m/e=84 and 69 and was found to be 0.11 in both cases. This compares with 0.30 measured using the same procedure - fractional decrease in reactant ion current - with DMF as the chemical titrant.

In previous experiments in which a germanium detector was used to photometrically determine the yield of singlet delta oxygen it was found that the fraction of singlet oxygen released into the gas phase varied markedly with film thickness. The primary motivation for the present series of experiments was to verify these measurements with a technique which could give a more accurate measure of the singlet oxygen yield. The fraction of singlet oxygen released into the gas phase upon thermolysis of 2PVNE at 88 C was measured as a function of film thickness using DMF to assay the amount of released singlet oxygen and recording the change in ion current at m/e=96. The results of this study are plotted in Figure 34 for the range of film thickness of 0 to 50 nm. The error bars attached to these results are the standard deviations from the mean of at least five separate samples for each film thickness which was studied.
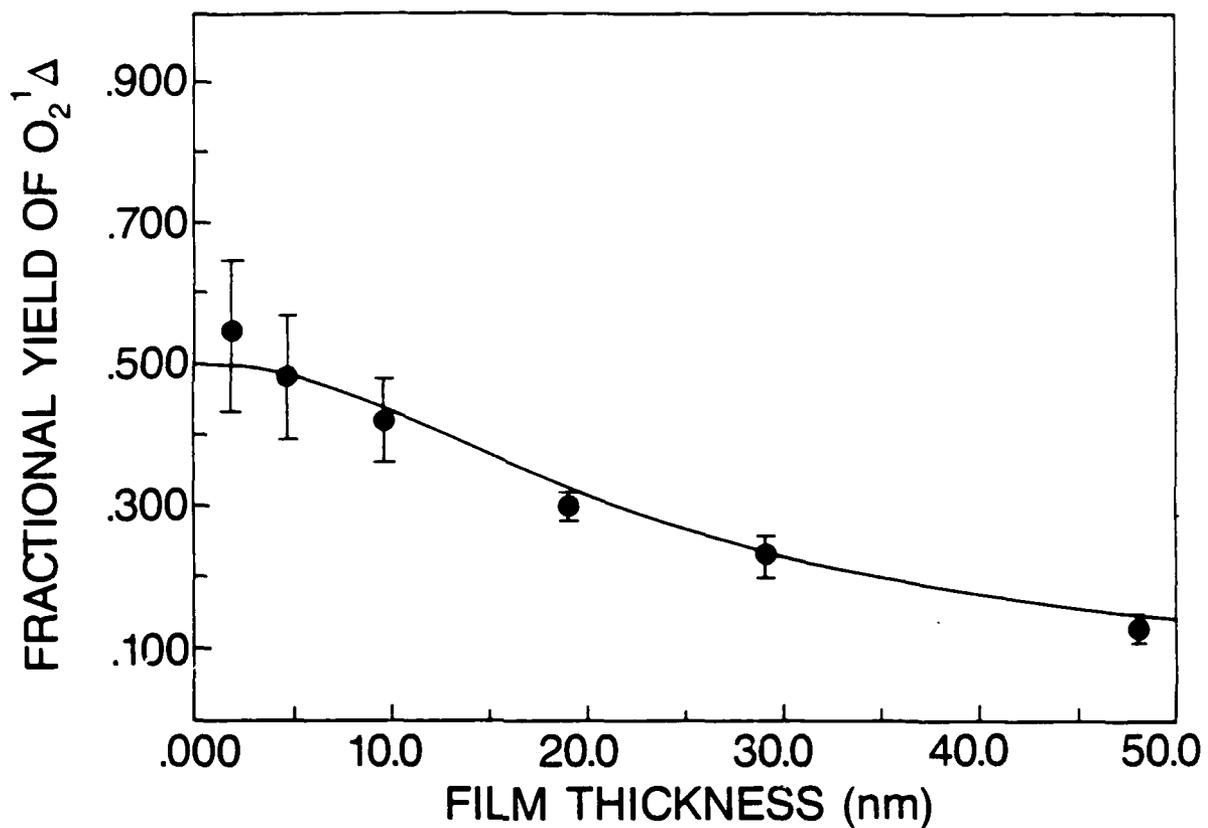
Figure 34. The fraction of oxygen released into the gas phase in the singlet delta state as a function of 2PVNE film thickness.
●, experimental results determined from mass spectrometric analysis of the primary DMF mass peak:
_____, model calculation results (see text).

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The solid curve in Figure 34 was calculated from a diffusional model described in reference 2 which includes a pseudo-first-order singlet oxygen quenching rate. The fraction of oxygen released from a film of thickness T in the singlet delta state is given by

$$F = \frac{8\phi}{\Pi^2} (1 - \gamma/2) \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2 + \left(\frac{k_q}{D}\right) T^2 \left[\frac{2}{\Pi} (1-\gamma/2)\right]^2} \qquad (1S)$$

The ratio of the quenching rate constant, k_q, to the diffusivity of singlet oxygen in the polymer film, D, is an adjustable parameter of the model. Two other parameters implicit in the model as described in reference 2 are included in equation 1S; the probability, γ, that a singlet oxygen molecule will be quenched at the 2PVNE/Nesatron interface and the intrinsic yield, ϕ, of singlet oxygen upon thermolysis of the endoperoxide moiety in the polymer.

In principle both γ and ϕ in equation 1S can range from 0 to 1, however the asymptotic value of the measured fractional yield at zero film thickness is close to 0.5 and therefore limits the intrinsic yield to values between 0.5 and 1. The incorporation of the $(1-\gamma/2)$ factor in equation 1S is not rigorously justified except at the limiting values of 0 and 1 which correspond with the elastic and inelastic models discussed in reference 2. The solid curve in Figure 34 was calculated assuming that both γ and ϕ are unity. A good fit with the experimental data is achieved when $k_q/D = 2 \times 10^{12}$ cm^{-2}. An equally good fit is obtained for $\phi = 0.5$ and $\gamma = 0$, however, inspection of equation 1S shows that with these choices for ϕ and γ, the adjustable parameter, k_q/D, must be reduced by a factor of 4 to give the same dependence of the fractional yield, F, on film thickness.

The results of singlet oxygen yield measurements obtained by chemical reaction of singlet oxygen with DMF (measured by following the decrease in ion current at m/e=96) compare favorably with the yields obtained from germanium detector measurements previously reported. Figure 35 shows the germanium detector measurements of the fractional singlet oxygen yield as a function of film thickness but over a larger range of film thickness (0 to 250 nm) than was studied with the chemical reaction method. The data is reasonably well fit by model calculation results (solid curve in Figure 35) using the same value of k_q/D and the same choices for γ and ϕ that were used for the model calculation results of Figure 34.

It is not possible to determine the extent of quenching of singlet oxygen at the polymer/Nesatron interface from the fitting of model calculations with the measured singlet oxygen yields as inspection of equation 1S makes clear. Equally good agreement is obtained at the extremes of the range of γ (0 and 1) if ϕ is allowed to vary from 0.5 to 1.0. It may be argued that the conducting metal oxide coating on Nesatron contains a wide distribution of impurity charge carrier trapping sites as well as mobile electrons which could interact with the excited oxygen providing an unusually effective quenching surface for singlet oxygen excitation. This argument favors a quenching probability and an intrinsic yield both close to unity.

An experiment was performed to determine the extent to which charge carriers in the Nesatron coating act as quenchers of singlet oxygen. A silicon monoxide coating of 100 nm was deposited on top of the resistive metal oxide coating of Nesatron and the endoperoxide film was spin coated on top of this electrically insulating layer. Figure 36 shows the fractional yield of
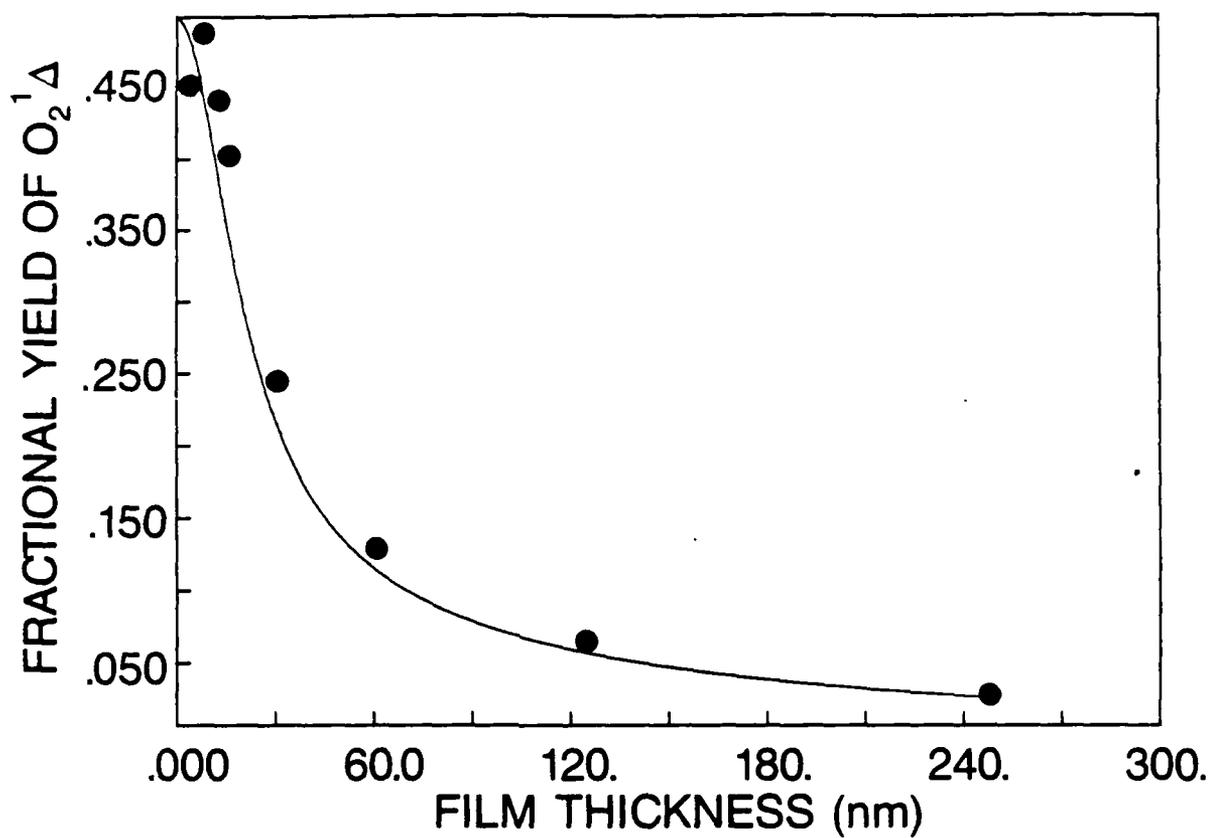
Figure 35. The fraction of oxygen released into the gas phase in the singlet delta state as a function of 2PVNE film thickness. ●, experimental results determined from photometric data; ___, model calculation results (see text).

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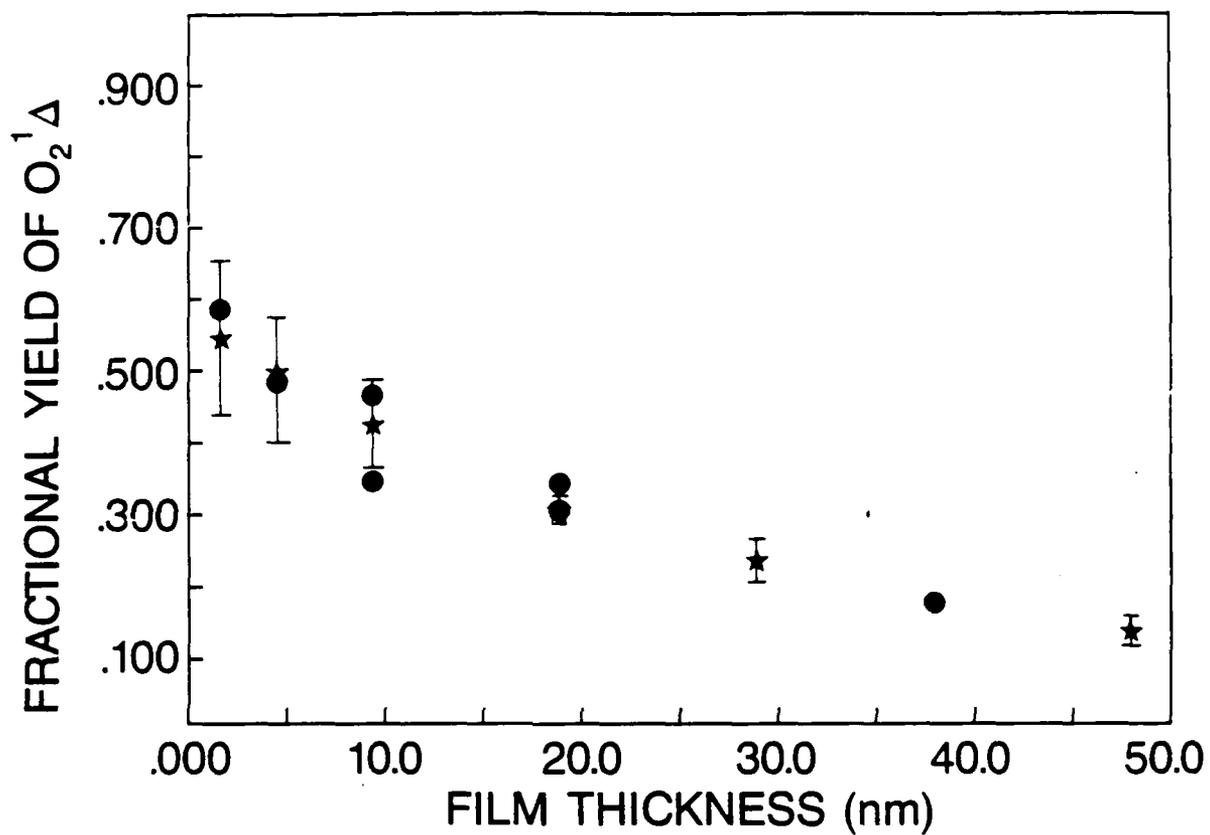
Figure 36. Fractional yield of singlet delta oxygen as a function of
2PVNE film thickness. Experimental results were determined
from mass spectrometric analysis of the primary DMF mass peak.
* - 2PVNE/Nesatron interface. ● - 2PVNE/SiO/Nesatron
interface.

singlet oxygen as a function of 2PVNE film thickness obtained when the polymer was coated on silicon monoxide and also includes the measurements presented in Figure 34 where 2PVNE was deposited directly on the bare Nesatron surface. No significant difference between the two sets of measurements is apparent suggesting that if the Nesatron surface is in fact an effective quencher for singlet oxygen the quenching mechanism probably does not involve charge carriers.

Summary and Discussion

The amount of oxygen released by a 19-nm-thick film of 2PVNE determined by mass spectrometric assay is 5.33×10^{-9} moles/cm^2. This value is about 15 per cent below that which is calculated from film thickness, mass density, and fractional conversion of the naphthalene moieties to endoperoxide in the film. A 15 per cent disagreement in total oxygen yield is not surprising considering the complexity of the experiment and the number of assumptions required for these estimates. Possible sources of error are the estimate of the area of 2PVNE which is heated (this area was taken to be equal to the area of the etched Nesatron metal oxide coating), the film thickness, the mass density of the film and the per cent conversion of naphthalene to endoperoxide. It should be noted that the fractional yield measurements reported here (as distinguished from the measurements of the total amount of oxygen released) are not subject to systematic error arising from the estimate of the heated area.

The primary objective of the series of experiments reported here was to determine the fraction of oxygen released into the gas phase in the singlet delta state upon thermolysis of 2PVNE. To this purpose DMF or TME was

allowed to selectively react with singlet oxygen and the extent of this reaction was assayed by mass spectrometry. The results of this analysis were compared when TME and DMF were used as singlet oxygen titrants in the determination of fractional singlet oxygen yields derived from 19-nm-thick 2PVNE films. When TME was used, a fractional singlet oxygen yield of only 0.11 was measured, whereas a yield of 0.3-0.4 was measured with DMF. The substantially lower yield found for TME is not unexpected; the reaction rate constant of singlet oxygen with TME is a factor of 20 slower[5] than with DMF and a slower reaction rate provides more time for the quenching of oxygen by the buffer gas, by TME itself, and by the walls of the sample chamber. Even though the sample chamber was constructed of Teflon which is a very ineffective quencher of singlet delta oxygen, the endoperoxide coated Nesatron plate present in the sample chamber is probably a much more active quencher and could possibly have competed with the TME reaction for deexcitation of singlet oxygen.

The decay time of the singlet oxygen reaction is equal to the inverse of the density of DMF or TME (assuming that enough titrant is present so that its density remains approximately constant over the course of the reaction) multiplied by the reaction rate constant. The amount of titrant used in these experiments was about 2.5×10^{-9} mol/cm^3. Using a rate constant of 1.5×10^{10} cm^{3}mol^{-1}s^{-1} for DMF and 7.7×10^8 cm^{3}mol^{-1}s^{-1} for TME, an enfolding time for singlet oxygen of 0.03 and 0.5 seconds is calculated for DMF and TME, respectively. Since the yield of singlet oxygen as measured with TME is substantially less than that measured with DMF, it appears that quenching must be competing with the TME titration reaction and limiting the lifetime of singlet oxygen to less than 0.5 s.

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The extent of reaction of singlet oxygen with DMF was measured using two methods. The primary oxygen mass peak at m/e=32 and the primary DMF peak at m/e=96 were used to analyze the fraction of singlet oxygen produced by thermolysis of 2PVNE. Agreement between the two methods was not completely satisfactory; the fraction of singlet oxygen calculated from m/e=32 data is 0.4 which is substantially larger than 0.3 calculated from the m/e=96 data, though the standard deviation on the former, 0.08, is comparable to the extent of disagreement. The assumption made when calculating the fractional yield from m/e=32 data is that only O_2 contributes to the mass spectrometer ion current at this mass peak. It is possible that DMF fragments also contribute significantly to the ion current at m/e=32 and that consumption of DMF by singlet oxygen could result in a value for the fractional yield which is considerably larger than the true value. The primary DMF peak at m/e=96 is less subject to interference by fragmentation of other molecules. The only possible source of interference at this mass peak is the reaction product of DMF with singlet oxygen which was shown to contribute less than 5 per cent to the change in ion current at m/e=96.

The fraction of oxygen entering the gas phase in the singlet delta state which is measured by the decrease in ion current signal at the primary DMF mass peak depends markedly on the thickness of the 2PVNE film. A simple model for singlet oxygen diffusion and quenching in the polymer film is found to agree very well with the mass spectrometry results. The model employs a fitting parameter, k_q/D, which is the ratio of the pseudo-first-order rate constant for singlet oxygen quenching by the polymer to the diffusivity of singlet oxygen in the polymer. The value of this ratio when a good fit is achieved with the experimental data is determined by the values which are

assumed for two other parameters, the intrinsic yield of singlet oxygen, ϕ, and the probability that a singlet oxygen molecule will be quenched when it encounters the Nesatron surface - polymer interface, γ. The fractional singlet oxygen yield at the limit of zero film thickness is found to be close to 0.5 in the present series of experiments. This constrains ϕ to values between 0.5, when $\gamma = 0$, and 1 when $\gamma = 1$.

When both $\phi = 1$ and $\gamma = 1$, kq must be 2×10^{12} cm^{-2} for a good fit with the experimental data. From this value and an estimate of the diffusivity, the lifetime of singlet oxygen in the polymer can be calculated. The diffusivity of singlet oxygen in 2PVNE has not been measured but the diffusivity of ground state oxygen in polystyrene has been reported and will be assumed to provide an order of magnitude estimate of the diffusivity sought. In polystyrene at 88 C the diffusivity of oxygen is 1×10^{-6} cm^2/s. With this value for the diffusivity of singlet oxygen in 2PVNE a lifetime ($1/k_q$) of 0.5 microseconds is calculated.

An equally good fit of the model calculations with the data is found when $\phi = 0.5$ and $\gamma = 0$, however, inspection of equation 1S shows the k_q/D must be reduced by a factor of 4 in order to fit the experimental data. Therefore, the lifetime for singlet delta oxygen in the polymer film is increased by a factor 4 to 2 microseconds. The range of lifetimes consistent with the experimental results (0.5 to 2 microseconds) is about an order of magnitude below that expected from a comparison with the singlet delta oxygen lifetime in hydrocarbon solvents (approximately 20-30 microseconds at room temperature).[6]

In previous work the fractional yield of singlet oxygen released from 2PVNE films was calculated from photometric measurements of emission at

1.27 μm and examined as a function of 2PVNE film thickness. Agreement of the photometric results with model calculations and with the DMF titration results is quite good. The same values of k_q/D used to fit the titration data also furnish a good fit between model calculations and photometric results. The extent of agreement is somewhat surprising because the two sets of experimental results were not only determined by different methods but the data was collected at different thermolysis temperatures; 88 C in the case of the DMF titration results and 130 C in the case of the photometric results. However, the fractional yield of singlet oxygen is not expected to depend strongly on temperature if k_q/D does not and because k_q/D is a ratio of two quantities which are expected to increase weakly with temperature, the fractional yield may be relatively constant over the 42 C difference in temperature between the two sets of results.

From the agreement of model calculations with fractional singlet oxygen yield results, it is not possible to determine the extent of singlet oxygen quenching at the polymer - Nesatron interface since a good fit is obtained at both extremes of the range of this parameter. Overcoating the Nesatron surface with silicon monoxide was found to have no observable effect on the fractional singlet oxygen yield. From this we conclude that surface trapped or free charge carriers are not involved in the quenching of singlet oxygen at the Nesatron/2PVNE interface. It may be that the quenching probability of singlet oxygen at the Nesatron surface is unusually high as a result of hydroxyl groups attached to the metal oxide surface. If this is the case a silicon monoxide overcoating would not be expected to provide much protection from quenching since this surface also has surface hydroxyl groups which could participate in the quenching of singlet oxygen.

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