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Thermolysis of 1,4-diphenyl-1,4-dioxa-2,3-benzopyrone (endoperoxide 1) in p-xylene solution generates chemiluminescence. Two intermediate products are formed from thermolysis of 1. The major product, trapped in 70% yield by added maleic anhydride is 1,4-diphenyl-2,3-benzodioxin (o-xylylene peroxide 2). This peroxide becomes eventually o-dibenzoylbenzene 3 which is isolated from the reaction in 85% yield. The second intermediate is unidentified. It is formed in ca. 3% yield and apparently becomes eventually the other isolated

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Chemiluminescence of Organic Peroxides.

Thermal Generation of an o-Xylylene Peroxide

by

Jimmie P. Smith, Alan K. Schrock and Gary B. Schuster

Prepared for Publication

in

Chemiluminescence of Organic Peroxides.   Thermal

Generation of an o-Xylylene Peroxide.[1]

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Abstract: Thermolysis of 1,4-diphenyl-1,4-dioxa-2,3-benzopyrone (endoperoxide

1) in p-xylene solution generates chemiluminescence. Two intermediate products

are formed from thermolysis of 1. The major product, trapped in 70% yield by

added maleic anhydride, is 1,4-diphenyl-2,3-benzodioxin (o-xylylene peroxide 2).

This peroxide becomes eventually o-dibenzoylbenzene 3 which is isolated from

the reaction in 85% yield. The second intermediate is unidentified. It is

formed in ca. 3% yield and apparently becomes eventually the other isolated

product of the reaction phenyl-(o-benzoyl) benzoate (4). The chemiluminescence

results from interaction of 2 with an added fluorescent activator or with the

minor intermediate according to the chemically initiated electron-exchange

luminescence (CIEEL) mechanism.

The molecules and mechanisms responsible for chemiluminescence and bio-luminescence have been of considerable interest to chemists since the dawn of the science.[2] Much recent interest in this topic has centered on the thermal chemistry of organic peroxides.[3] Our efforts to discover new chemiluminescent systems and to probe the mechanism of electronically excited state generation led to the synthesis and investigation of new heterocyclic examples of this functional group. In this report we describe the preparation, characterization and thermal reactions of endoperoxide $\underset{\sim}{1}$. The properties of this molecule provide further insight into the chemistry of organic peroxides and into the mechanistic details of chemiluminescence.

Results and Discussion

Synthesis. The preparation of endoperoxide $\underset{\sim}{1}$ proceeds straightforwardly by photooxygenation of the previously described lactone $\underset{\sim}{2}$.[4] Irradiation of an acetone solution of $\underset{\sim}{2}$ and methylene blue with visible light, filtered so that only the sensitizer is excited, at 0° under O_2 leads to the rapid consumption of the lactone. Removal of the sensitizer by filtration through silica gel, evaporation of the solvent, and recrystallization of the resulting residue gives a peroxidic white solid. The structure of this material was deduced from spectroscopic, osmometric, and microanalytic investigation to be endoperoxide 1, eq. 1. The details of the structural assignment are presented in the experimental section.

Scheme I

$$\text{2} \quad + \quad O_2 \quad \xrightarrow[\text{h}\nu]{\text{methylene blue}} \quad \text{1} \qquad (1)$$
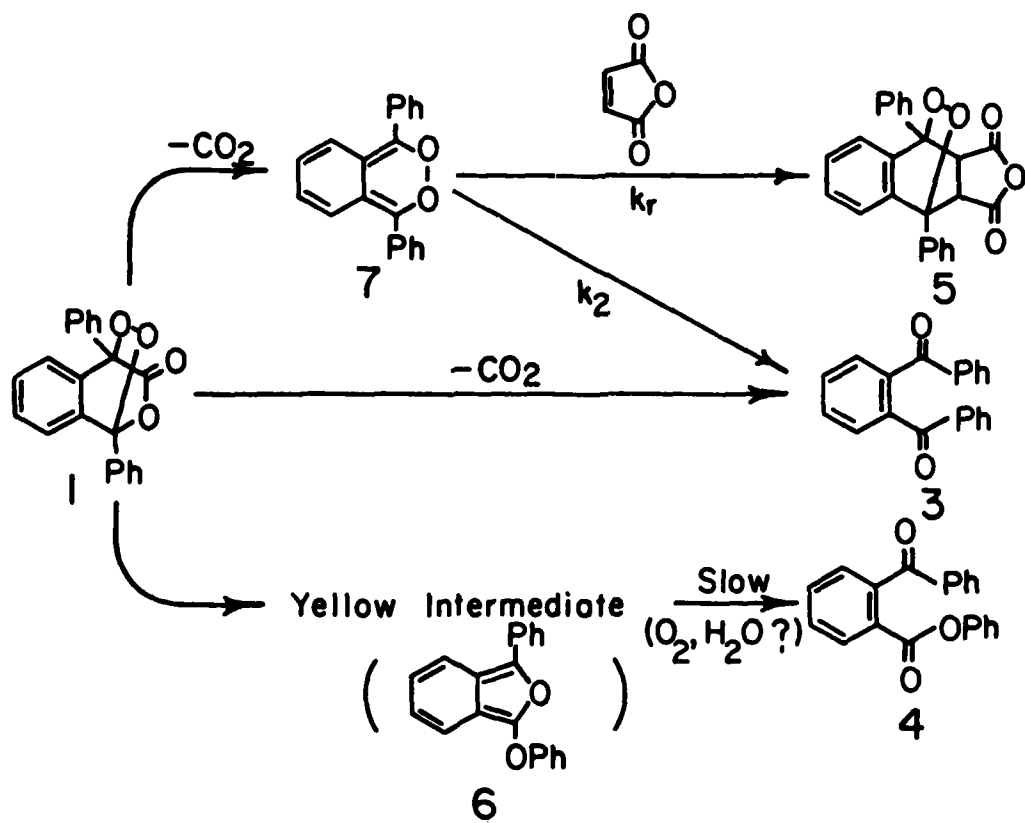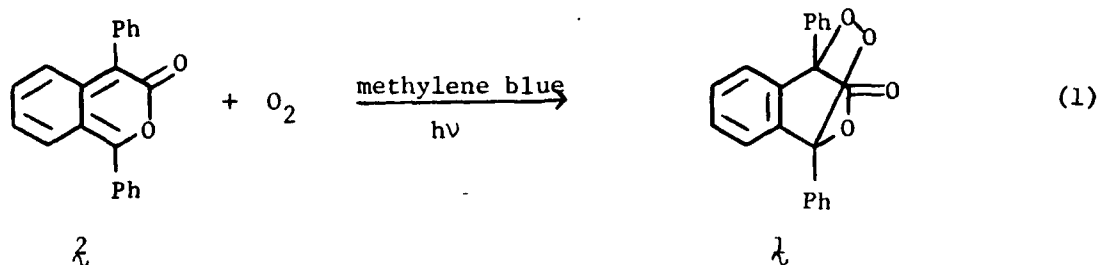
Thermolysis of endoperoxide 1. The thermal reactions of peroxide 1 are

on the surface quite simple, but, as we will describe below, there is a

hidden complexity that becomes apparent only on detailed investigation. When

a solution of 1 in benzene, or p-xylene, is heated to ca. 100° under nitrogen

the first change observed is that what was a clear, colorless solution has

become deep yellow. Continued heating causes the yellow to fade and the

resulting solution is again colorless. If oxygen is not rigorously excluded

from the thermolysis solution the yellow color never develops. The stable

products of the thermolysis reaction are isolated by evaporation of the

solvent, separated by gas chromatography, and identified by comparison with

authentic samples as o-dibenzoylbenzene (3) and phenyl(o-benzoyl)benzoate

(4) with yields of 85% and 5% respectively, Scheme 1. Presumably there are

gaseous products formed simultaneously with the identified solid products,

but we did not attempt to isolate or to detect them.

On the presumption that the observed yellow intermediate product is a

precursor to diketone 3 or ketoester 4 we carried out the thermolysis of 1

in the presence of maleic anhydride.   A 1.0×10^{-3} M p-xylene solution of 1 con-

taining 5.1×10^{-5} M maleic anhydride on thermolysis in the absence of oxygen

does not turn yellow, gives no ketoester 4, but gives a yield of diketone 3

that is essentially the same as in the absence of anhydride. Increasing the

maleic anhydride concentration to 1.5×10^{-2} $\underline{M}$ results in the reduction of the

diketone yield to 25%. However, further increases in the maleic anhydride

concentration beyond 1.5×10^{-2} $\underline{M}$ do not result in any further reduction of

the yield of diketone 3. The major product of the reaction in the presence

of a high concentration of maleic anhydride is the Diels-Alder trapping

product 5. This compound is isolated, by evaporation of the solvent, subli-

mation of the excess maleic anhydride, and then recrystallization, in 70%

yield. The details of the structural assignment are given in the experimental

section.[5]

The maleic anhydride trapping experiments show that there are at least

two intermediate products formed from thermolysis of 1. The first is a pre-

cursor to ketoester 4 and is completely trapped at low anhydride concentra-

tion. The second is a precursor to diketone 3 and is trapped at high anhy-

dride concentrations to give 5. Also, there is a direct, or at least untrap-

pable, path leading from endoperoxide 1 to diketone 3 that accounts for

about one third of this product. To confirm these assertions, and to define

further the reaction path and structures of the intermediates, we undertook

a detailed kinetic and spectroscopic investigation of this reaction.

The least ambiguous method to determine the rate of reaction of endo-

peroxide 1 is by infrared spectroscopy. Peroxide 1 has a strong absorption

due to the lactone carbonyl group at 1785 cm^{-1}. As the thermal reaction

proceeds the intensity of this absorption decreases while the intensity of

the carbonyl absorption at 1680 cm^{-1} due to diketone 3 increases. Monitoring

the extent of reaction of a 1.0×10^{-2} $\underline{M}$ solution of 1 in p-xylene at 112°

as a function of time by infrared spectroscopy shows that the reaction

obeys a first order kinetic law with a rate constant (k_1) of $4.72 \pm 0.06 \times 10^{-4}$ s^{-1}, Figure 1. This corresponds to a half-life for endoperoxide $\underset{\sim}{1}$ of about 20 min. under these conditions. Similarly, the rate of appearance of diketone $\underset{\sim}{3}$ can be analyzed by infrared spectroscopy. The half-time for appearance of this product is approximately the same as for the consumption of $\underset{\sim}{1}$. This observation indicates that whatever intermediate may be involved in the conversion of $\underset{\sim}{1}$ to $\underset{\sim}{3}$ is short-lived with respect to endoperoxide $\underset{\sim}{1}$.

The course of the thermal reactions of $\underset{\sim}{1}$ can be followed also by ultra violet-visible spectroscopy. As noted above, the reaction mixture first turns yellow then clear as the thermolysis proceeds. The absorption, excitation, and fluorescence spectra of the yellow intermediate responsible for this color change are shown in Figure 2. Measuring the absorbance at 400 nm as a function of time during the thermolysis of the endoperoxide provides kinetic data on the formation and reaction of the yellow intermediate. Heating a 5.0×10^{-4} $\underline{M}$ $\underline{p}$-xylene solution of $\underset{\sim}{1}$ at 112° causes an increase in absorbance at 400 nm which grows to a maximum in $\underline{ca}$. 65 min and then slowly decreases. The data, shown in Figure 3, can be interpreted within a simple consecutive reaction model. The rate constant for formation of the yellow intermediate derived from these data is $4.84 \pm 0.0.1 \times 10^{-4}$ This value is the same, within experimental error, as that obtained for disappearance of endoperoxide $\underset{\sim}{1}$ by infrared spectroscopy (k_1). This finding indicates that the endoperoxide is the precursor of the yellow intermediate. The rate constant for decay of the absorbance at 400 nm is $1.97 \pm 0.0.1 \times 10^{-5}$ sec^{-1} which corresponds to a half-life of 587 min. Thus, the slowly-reacting yellow intermediate cannot be a major source of the rapidly appearing diketone product. These kinetic findings support the maleic anhydride trapping results that indicate at least two intermediate products are formed on thermolysis of $\underset{\sim}{1}$.

The yield of long-lived yellow intermediate can be estimated by titration with maleic anhydride. The kinetics of its formation and reaction reveal that the concentration of yellow intermediate reaches a maximum 65 min. after the thermolysis of $\underset{\sim}{1}$ has begun. Also, at this time 78 % of the intermediate that will be formed is present in solution. Addition of a maleic anhydride solution to the reaction at this point bleaches the yellow color. With the assumption that the stoichiometry of the trapping reaction is one to one, we estimate that the total yield of yellow intermediate is ca. 3 % based on the initial endoperoxide concentration. This product thus represents a minor reaction path for endoperoxide $\underset{\sim}{1}$, but as described below, it plays a critical role in the direct chemiluminescence[6] of this system.

The structure of the yellow intermediate remains uncertain. We have been unable to separate it, or its trapping product with maleic anhydride, from the major products of the reaction. However, based on its spectral properties (Figure 2) which are quite similar to 1,4-diphenylisobenzofuran,[7] the presumption that it is the precursor to ketoester $\underset{\sim}{4}$, and the observation that it reacts rapidly with maleic anhydride and with oxygen, we tentatively assign isobenzofuran derivative $\underset{\sim}{6}$ (Scheme 1) as this intermediate.

The major intermediate formed from thermolysis of endoperoxide $\underset{\sim}{1}$ is a precursor to diketone $\underset{\sim}{3}$ and can be trapped with maleic anhydride to give $\underset{\sim}{5}$ in 70% yield. It is important to note that maleic anhydride does not react with endoperoxide $\underset{\sim}{1}$ directly. Thus the measured rate of reaction of $\underset{\sim}{1}$ is independent of the maleic anhydride concentration. The structure of the major intermediate is revealed by the structure of its trapping product to be o-xylylene peroxide $\underset{\sim}{2}$. This compound is the first example of this class of conjugated cyclic unsaturated peroxide, and, therefore, we investigated is properties in some detail.[7]

Cleavage of the oxygen-oxygen bond of o-xylylene peroxide 7, in principle,
can lead directly to diketone 3. This reaction is exothermic by ca. 90 kcal/mole.
From this point of view it is surprising that 7 lives long enough under the
reaction conditions to be trapped by dieneophiles such as maleic anhydride. We
decided to use this trapping reaction to obtain an estimate of the lifetime of
peroxide 7. The thermal reaction of 7 with maleic anhydride is too fast to use
under thse conditions so we substituted dimethylmaleic anhydride. The thermal
conversion of 7 to 3 is in competition with the reaction of 7 with dimethylmaleic
anhydride. Thus, as the anhydride concentration increases the yield of diketone
decreases. After correction for the uninhibitable yield of 3, the double recipro-
cal plot of the yield of 3 against dimethylmaleic anhydride concentration, Figure 4,·
gives a straight line. The slope of this line is the ratio of the rate constant
for the unimolecular thermal reaction of 7 (k_2) to that of the bimolecular trapping
reaction with dimethylmaleic anhydride (k_r). Unfortunately, there is no way to
measure directly the latter value. However, if we assume that dimethylmaleic
anhydride reacts with 7 with a rate constant similar to that for its reaction
with 1,4-diphenylisobenzofuran (which 7 resembles closely) we can approximate
the lifetime of the o-xylylene peroxide. We determined the bimolecular rate
constant for the furan and the anhydride at 112° in xylene solution to be
$2.02 + 0.01 \times 10^{-1} M^{-1} s^{-1}$. From this value, and from the slope of the line shown in
Figure 4, we estimate the half-life of 7 to be ca. 20 seconds under these con-
ditions. Thus, though by no means easily isolable, the o-xylylene peroxide,
at least by this estimate, has modest thermal stability.

Chemiluminescence of endoperoxide 1. The chemiluminescence observed during
the thermolysis of endoperoxide 1 can be separated operationally into two

types. The first type, direct chemiluminescence, is the generation of light from solutions of 1 alone.   The second type, activated chemiluminescence,[6] is light formation by reaction of solutions of 1 and some added molecule (the activator). Although operationally different, as will be shown below, for endoperoxide 1 these two types are in fact conceptually identical.

Heating a 1×10^{-3} $\underline{M}$ solution of 1 in p-xylene at $112°$ results in a build-up of chemiluminescence intensity to a peak $\underline{ca}$. 20 min after the reaction begins followed by a decay of the light intensity to background levels, Figure 5. The total chemiluminescence intensity observed in this experiment is directly proportional to the square of the initial endoperoxide concentration, Figure 6. And the chemiluminescence spectrum is identical to the fluorescence spectrum of the yellow intermediate (Figure 2) described above. Non-linear least squares analysis of the kinetics of build-up and decay of the chemiluminescent emission provides two rate parameters. The first is $4.12 \pm 0.013 \times 10^{-4}$ sec^{-1}, which is identical to the rate constant (k_1) for reaction of 1 derived from the infrared and ultra violet kinetic analyses. This finding indicates that reaction of the endoperoxide is somehow responsible for light generation. The second rate parameter is $1.06 \pm 0.02 \times 10^{-3}$ s^{-1}. It is important to note that this rate parameter is, within experimental error, twice the size of the first.

When an additional fluorescent molecule is included with endoperoxide 1 in the reacting solution quite different results are obtained. For example, when 5×10^{-4} $\underline{M}$ perylene is included in the reaction mixture the chemiluminescent emission spectrum shifts to the fluorescence spectrum of perylene. The intensity of the perylene activated chemiluminescence does not rise to a maximum and then decay as it does in the absence of perylene, but starts at its maximum value and then decays exponentially with a rate constant at $112°$ in

p-xylene of $4.03\pm0.04\times10^{-4}$ s^{-1}, a value identical to that which we have assigned to the reaction of endoperoxide 1, (k_1) Figure 7. Finally, the total perylene activated chemiluminescence is much more intense than without activator, and is proportional to the first power of the endoperoxide concentration, not its square as it is in the absence of activator.

These findings seem to suggest that there may be two different mechanisms operating to produce chemiluminescence from endoperoxide 1. In fact that is not the case. The chemiluminescence observed in the presence and absence of activator is the result of the same fundamental processes.

The activated chemiluminescence could presumably result from the inter- action of activator with endoperoxide 1, with the intermediate o-xylylene peroxide 7, or with the long-lived yellow intermediate 6. We can rule out the latter based on the rate of decay of the activated chemiluminescence and the measured lifetime of the yellow intermediate. That is, the chemiluminescence decays faster than the intermediate, so the latter cannot be the precursor of the former. Since o-xylylene peroxide 7 is much shorter lived than endoperoxide 1 it is not possible to decide based on kinetics which peroxide reacts with the activator to generate excited states. However, it is possible to use the specific trapping of 7 by maleic anhydride to distinguish these possibilities.

Addition of increasing amounts of maleic anhydride to solutions of endoperoxide 1 and perylene result in a decrease in the activated chemilumin- escence intensity without changing the rate of decay of the chemiluminescent emission, Figure 7. Part of the decrease in chemiluminescence intensity is a result of the quenching of excited perylene by maleic anhydride.[8] The quenching constant for this process was determined by adding maleic anhydride to photo- excited perylene at 95° to be 115 ± 7 M^{-1}. The activated chemiluminescence

intensity when corrected for quenching of perylene fluorescence still decreases with increasing maleic anhydride concentration. Figure 8 is a plot of these data according the equation (2) where I^{corr} and I_o^{corr} are the corrected intensities in the presence and absence of maleic anhydride respectively, k_r is the

$$\frac{I_o^{corr}}{I^{corr}} = 1 + \frac{k_r}{k_2} \text{[ma'eic anhydride]} \tag{2}$$

rate constant for the bimolecular reaction of o-xylylene peroxide 7 with the anhydride, and k_2 is the rate constant for unimolecular thermolysis of 7. These findings indicate that the generation of excited states in this system is the result of an interaction between the activator and a species capable of reaction with maleic anhydride. The observation that the rate of reaction is independent of maleic anhydride concentration (Figure 7) confirms our conclusion that trapping product 5 comes from an intermediate, not directly from endoperoxide 1. These results indicate that it is the interaction between activator and o-xylylene peroxide 7 that is responsible for generation of the chemiluminescence, Scheme 2.

We examined the nature of the interaction of the o-xylylene peroxide with the fluorescent activators that leads to electronically excited states. The structure of the activator greatly affects the intensity of the observed chemiluminescence. For example, comparison of 9,10-diphenylanthracene with acridine orange reveals that at equal concentrations the latter generates three hundred times more light than the former. However, neither the anthracene nor the acridine orange affect the overall rate of reaction. Similarly, we examined the light generating efficiency of eight other activators choosen from amines, conjugated furans, and aromatic hydrocarbons. The chemiluminescence intensity, corrected

Scheme 2

Scheme 3

Encounter Complex

Chemiluminescence
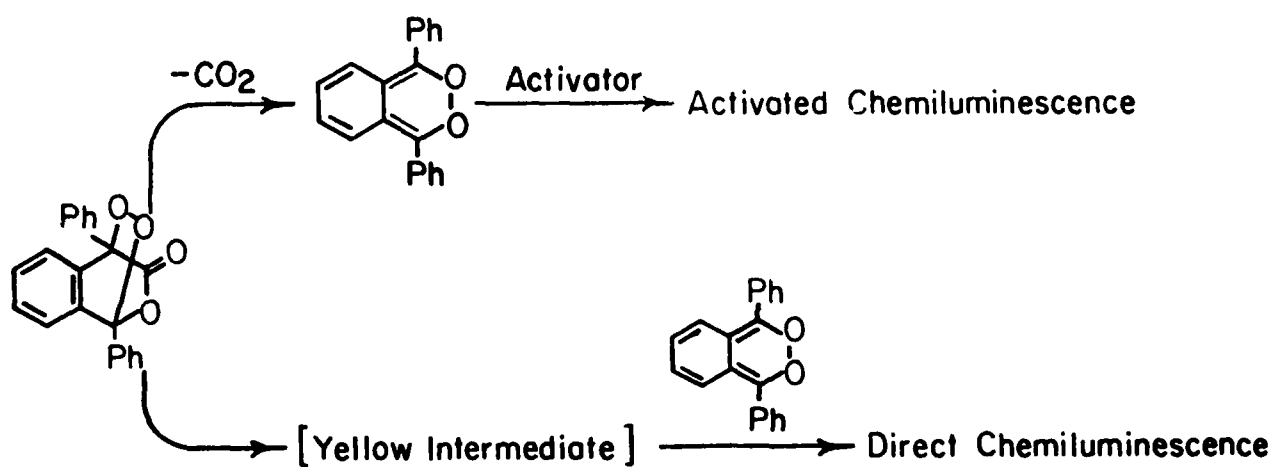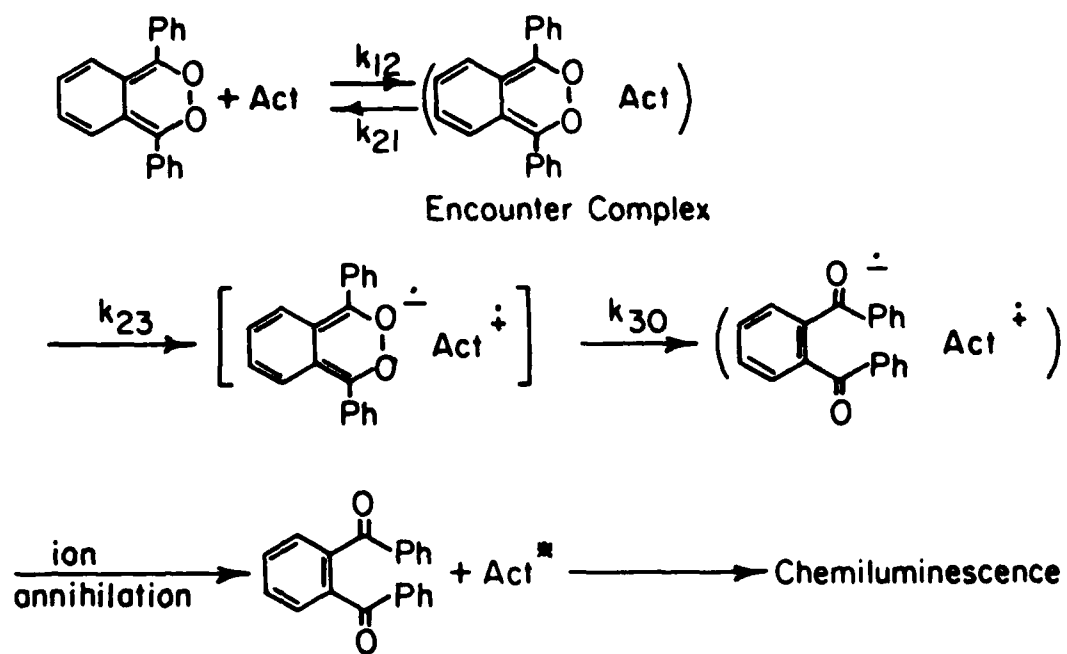
for activator fluorescence efficic... at 112°, (essentially a yield of excited singlet states), for 5×10^{-4} M activator varies linearly with the one electron oxidation potential (E_{ox}) of the activator, Figure 9. This observation is prime evidence for the operation of the chemically initiated electron-exchange luminescence (CIEEL) mechanism.[9] This con... ... a has recently been challanged,[10] but the objection has been shown by us t... ... unfounded.[11] Further support for the operation of the CIEEL mechanism comes from the observation that dimethyl-dihydrodibenzo[b,i]phenazine (DMBI) as activator fails to generate the expected amount of light.

The CIEEL mechanism applied to o-xylylene peroxide 7 is shown in Scheme 3. The first step is formation of an encounter complex. For most of the peroxides we have studied no evidence of this complex has been obtained[12] except for those cases where the activators are certain metalloporphyrins.[13] Thus we assume that there is little if any stabilization of the complex of activator with o-xylylene peroxide 7. Electron transfer from the activator to the peroxide generates, as an intermediate or, more likely, a transition state, the peroxide radical anion. Cleavage of the oxygen-oxygen bond forms o-dibenzoylbenzene radical anion in the same solvent cage as activator radical cation. Annihilation of these oppositely charged ions, if sufficiently energetic, forms the excited singlet state of the activator which we detect by its emission. This mechanism explains the observed intensity dependence on activator oxidation potential and the failure of DMBI to generate the expected amount of light. This is because the annihilation of DMBI·[+] and 8·[-] is not sufficiently energetic to form the excited singlet state of DMBI.[14] Thus, this annihilation must produce either ground-states or non-emissive triplets which we do not detect.

The direct chemiluminescence in the absence of added activator can also be understood within the CIEEI mechanism. In this case, however, the activator is the yellow intermediate formed as a side product by the reaction, Scheme 2. Thus at the initiation of the reaction there is no activator and therefore no light As the reaction proceeds yellow intermediate is formed and the chemiluminescence intensity grows. Finally as endoperoxide $\underset{\sim}{1}$ is consumed the steady-state concentration of $\underline{o}$-xylylene peroxide declines and the light intensity decreases. Quantitatively, this mechanism leads to the prediction that the light intensity profile should be of the form:

$$I = e^{-k_1 t} - e^{-2k_1 t} \tag{3}$$

which is precisely what is observed, where k_1 is the previously defined rate constant for consumption of endoperoxide. Also, this scheme accounts for the unusual dependency of the direct chemiluminescence on the square of the initial concentration of endoperoxide $\underline{1}$. In essence, it takes two molecules of $\underset{\sim}{1}$ to product a photon, one to generate the yellow intermediate (internal activator) the second to form $\underline{o}$-xylylene peroxide $\underline{7}$. Although we don't know with certainty the structure of the yellow intermediate, its key role in the direct chemiluminescence of $\underset{\sim}{1}$ is clear.

Conclusions: This investigation has revealed several interesting facets of the thermal chemistry of endoperoxide $\underline{1}$ and intermediates derived therefrom. Among these is the finding that thermolysis of $\underline{1}$ leads to three reactions; decarboxylation to $\underline{o}$-xylylene peroxide $\underline{7}$ (70"), decarboxylation and ring cleavage directly to diketone $\underset{\sim}{3}$ (25"), and rearrangement apparently through a thermally stable intermediate, to form eventually ketoester 4 (5").

The chemiluminescence that accompanies thermolysis of $\underline{1}$ is a result of the interaction of $\underline{o}$-xylylene peroxide $\underline{7}$ either with the internal activator (direct chemiluminescence) or an added activator (activated chemiluminescence) accord-

ing to the CIEEL mechanism. The yield of electronically excited states from thermolysis of $\underset{\sim}{1}$ is only 0.8%. This result is due in part to the relatively rapid, non-light producing thermal conversion of $\underset{\sim}{7}$ to $\underset{\sim}{3}$ that is in competition with excited state formation.

The chemiluminescence of $\underset{\sim}{1}$ may serve as a model for the excitation step of luminol chemiluminescence.[15] Unfortunately, there is very little direct evidence for the structure of the ground-state intermediate immediately preceding excited state formation in this system. Early spectulation, and recent experimental evidence,[16] has placed azoendoperoxide $\underset{\sim}{8}$ on the reaction path. By analogy with endoperoxide $\underset{\sim}{1}$, loss of nitrogen from $\underset{\sim}{8}$ would generate o-xylylene peroxide $\underset{\sim}{9}$. Conversion of $\underset{\sim}{9}$ to excited aminophthalic acid, the observed emitting species in luminol chemiluminescence, may occur by intramolecular electron transfer in analogy to some amino substituted dioxetanes.[17] Our findings described above provide some support for this reaction path which is outlined in equation 4.

$$\xrightarrow{-N_2} \qquad \xrightarrow{-2H^+} \qquad (4)$$
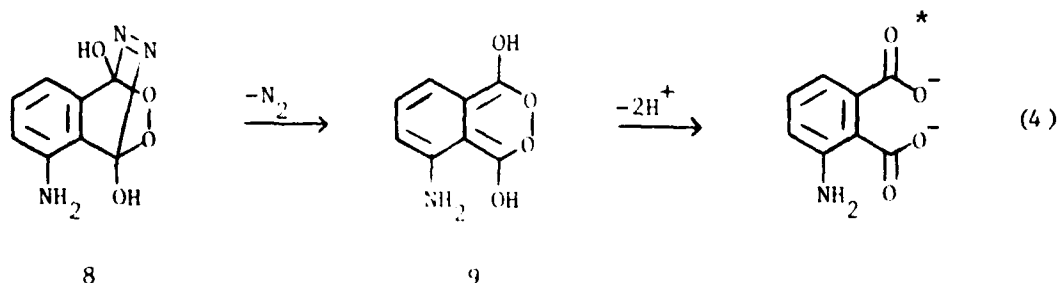
Finally, we were surprised by the stability of o-xylylene peroxide $\underset{\sim}{7}$. Our estimate of a 20 sec half-life at 112° should be considered as no more than a rough guide to the actual thermal properties of this molecule. However, that measurement in conjunction with the efficient trapping with relatively low maleic anhydride concentrations indicates that $\underset{\sim}{7}$ has more than a fleeting existence. This unusual "stability" may be traced to the electronic properties of this structure. Figure 10 shows a schematic state correlation diagram for the thermal reaction of $\underset{\sim}{7}$ according to the formalism proposed by Michl[18] and applied to the reaction of luminol.[19]

The key point is that if a rigid separation between π and σ symmetry is main-
tained throughout the conversion of 1 to 3, the ground-state of the o-xylylene
peroxide correlates with a very high energy doubly $n\pi^*$ excited state of diketone
3. Similarly, a high energy doubly excited $\pi\sigma^*$ state of 1 correlates with the
ground state of 3. The avoided crossing of these two states provides a path
for the thermal conversion of 1 to 3. This analysis suggests that the thermal
stability of 1 results from the fact that its conversion to 3 is "forbidden".
A second prediction resulting from analysis of Figure 10 is that excitation of
1 to its lowest $\pi\pi^*$ state should not result in its spontaneous conversion to
either ground or excited state 3. Conversion of $\pi\pi^*$ excited 1 to 3 is also a
forbidden reaction and, as such, is an exception to the commonly observed
alternation between ground and excited state reactivity. Our investigation of
this prediction, and the other properties of o-xylylene peroxides, is continuing.

Experimental

General. Proton magnetic resonance spectra were recorded on a Varian A-60A, A-56-60, EM-390 and HR-220 spectrometers. [13]C magnetic resonance spectra were recorded on a JEOL FX-60 spectrometer. Chemical shifts are relative to tetramethylsilane used as an internal standard. IR spectra were obtained with a Perkin-Elmer 137 sodium chloride instrument, a Perkin-Elmer 237B grating infrared spectrophotometer, or a Beckman IR 12 spectrophotometer. UV-VIS absorption spectra were recorded on a Beckman Acta MVI, a Carey 14, or a Perkin-Elmer 552 spectrophotometer. Mass spectra were obtained with a Varian MAT CH-5 and 731 mass spectrometers. Gas chromatographic analyses were carried out using a Varian Aerograph Model Series 2700 chromatograph equipped with flame ionization detectors. A six foot glass column packet with SE-30 (3%) on Chromosorb Q was used unless otherwise noted. Photoexcitation emission spectra were recorded on a Farrad Mark I spectrofluorometer, or by photon counting to permit direct comparison with chemiluminescence emission spectra. Elemental analysis, active oxygen and molecular weight determinations were performed by J. Nemeth and Associates, Department of Chemistry, University of Illinois, Urbana, Illinois. All melting points are uncorrected.

Chemiluminescence Measurements. The photon-counting technique was used, employing an EMI 9813B or 9816B photomultiplier tube. Spectral resolution was achieved with a Jarrel-Ash 0.25 M monochromator, equipped with a grating with 1180 grooves/mm. The band pass under high resolution conditions is calculated to be 5 nm. Under low resolution conditions the band pass is calculated to be 26 nm. The data were collected in a 128 channel digital input buffer with a variable time per channel of 1 to 800 seconds. The buffer was interfaced with a Wang series 2000 computer which was used for all data analysis. Sample

temperature was regulated to within $\pm 0.1°C$ by means of an electrically heated cell holder. A National Bureau of Standards thermometer was used to calibrate sample temperatures. Pyrex cuvettes equipped with Teflon stopcocks, were used for all chemiluminescence experiments. In all cases the solvent was p-xylene. It was purified by washing with sulfuric acid, drying over calcium chloride, passed through basic alumina and distilled.

Activators. Rubrene, tetracene, 1,3-diphenylisobenzofuran, and 9,10-diphenylanthracene (Aldrich) were chromatographed on alumina with benzene as eluent, and were recrystallized from benzene. 9,10-(Phenylethynyl)anthracene (DPEA), 5,12-bis-(phenylethynyl)tetracene (DPET) were prepared by published procedures,[13] and were purified by chromatography.

1,4-Diphenyl-1,4-dioxa-2,3-benzopyrone (endoperoxide 1). A solution of 100 mg (3 mmol) of 1,4-diphenyl-2-benzopyron-3-one (lactone 2),[4] and 10 mg of methylene blue in 20 ml of acetone was prepared and cooled in an ice-water bath. The solution was saturated with oxygen and then maintained under an oxygen atmosphere while being irradiated with the output of a 250 W Tungsten-Halogen lamp filtered through a corning CS2-59 glass plate (only the methylene blue absorbs) for 4 h. The reaction solution was filtered through ca. 2 cm of silica gel to remove the methylene blue, the solvent was removed under reduced pressure, and the residue was recrystallized from pentane-CH_2Cl_2 to give 1 36 mg (32%) as a white solid, m.p. 109° (with decomposition). ^{1}HNMR ($CDCl_3$): 7.0-6.8 (d, 2H); 7.9-7.2 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 166, 136, 133.5 130.3, 130.2, 129.6, 129.3, 128.8, 128.2, 126.9, 126.5, 124.7, 123.2, 123.0, 105.9 82.4, Ir ($CHCl_3$) 2950, 1735, 1525, 1460, 1330 cm^{-1}. MS (field desorption, low resolution) m/e (rel abundance) 298 (2.38), 287 (13), 286 (61), 271 (2), 270 (10), 210 (9), 209 (61), 105 (15); 44 (base peak); Mol. wt. (osmometry) required 330, found 328$\pm$4; active oxygen content, 87$\pm$10% of theoretical.

Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.36; H, 4.24. Found: C, 76.34; H, 4.27.

Thermolysis of Endoperoxide 1. A solution of 21 mg (0.06 mmol) of 1 in 5 mL of benzene was refluxed under nitrogen for 6 h. As the reaction progresses the initially colorless solution first turns yellow then colorless. The products of the reaction were identified and quantitated using gas chromatography by comparison with authentic o-dibenzoylbenzene (Aldrich) 85% and phenyl-(o-benzoyl)benzoate[5] 5%.

Thermolysis of 1 with maleic anhydride. A solution of 102 mg (6.3 mmol) of endoperoxide 1 and 30.2 mg (3.0 mmol) of maleic anhydride was prepared in 100 mL of benzene. The solution was refluxed under nitrogen for 6 h. and then the solvent was evaporated under reduced pressure leaving a solid white residue. The residue was transferred to a vacuum sublimator and evacuated (0.01 mm) at room temperature for 24 h to remove the excess unreacted maleic anhydride. The remaining product, a white solid, (100 mg) was recrystallized from pentane-CH_2Cl_2 to give adduct 5, m.p. 145° (with decomposition). ^{1}H NMR ($CDCl_3$): δ 7.85-7.0 (m, 14H), 4.1 (s, 2H); mol. wt. (osmometry) required 384; found 381±5; active oxygen content 94.4±6% of theoretical; Ir ($CHCl_3$) 2980, 1870, 1690, 1600, 1490 cm^{-1}.

Anal. Calcd for $C_{24}H_{16}O_5$: C, 74.99; H, 4.20. Found: C, 74.65; H, 4.28. The stereochemistry of the adduct is not revealed by these results.

Rate of reaction of 1 determined by infra-red spectroscopy. A 0.1 $\underline{M}$ solution of 1 in p-xylene was prepared and deoxygenated by purging with dry Ar. The solution was heated to 112° and six 400 ul. aliquots were removed over a 1 h period and stored at 0° for later analysis. The infrared spectra of the aliquots was determined on a Beckman IR-12 spectrophotometer. The optical density at 1785 cm^{-1}, which earlier had been shown to be directly proportional to the concentration of 1, was analyzed (Figure 1) to give the rate constant for reaction of 1.

Rate of appearance and consumption of the yellow intermediate by uv-vis spectroscopy. A 1×10^{-3} M solution of 1 in p-xylene was prepared and deoxygenated by purging with dry Ar. The sample was placed in a cell holder heated to 112° in the sample compartment of a Perkin-Elmer 552 spectrometer. The optical density at 400 nm was recorded at 256 equally spaced points over a period of 10 h. to give the results shown in Figure 3. Non-linear least squares analysis of these data[23] gives two rate parameters (see text).

Chemiluminescence from 1 with and without added activators. The intensity of chemiluminescence from 1 in the presence and absence of added activator was monitored at 112° by photon counting. Figure 5 shows the results for a 1×10^{-3} M solution of 1 in deoxygenated p-xylene with no activator. The total chemiluminescent intensity at 450 nm was computed by determining the area under this curve. Similarly, the total chemiluminescent intensity for starting endoperoxide 1 concentrations from 2.2×10^{-3} M to 2.5×10^{-4} M was determined. This intensity was shown, Figure 6, to be proportional to the square of the concentration of 1. The chemiluminescence of solutions containing added activators corresponds to the fluorescence of the activator. For example, solutions of 1 (1×10^{-3} M) and rubrene (1×10^{-5} to 8×10^{-4} M) in deoxygenated p-xylene exhibit chemiluminescence that decays, independent of the initial concentration of 1 or rubrene, with a first order rate constant at 112° of 3.9×10^{-4} s^{-1}. Moreover, the rubrene concentration does not change, as indicated by its optical absorption, during the course of the experiment. The total chemiluminescent intensities in the presence of various activators (1×10^{-4} M) and 1×10^{-3} M in p-xylene were obtained by integrating the intensity at the fluorescence maximum under low resolution conditions and then correcting for the spectral response of the photomultiplier tube and monochromator according to data supplied by the manufacturer. These data, as well as the oxidation potentials and fluorescence efficiencies of the activators are shown in Table 1.

Quenching of perylene activated chemiluminescence of 1 with maleic anhydride.
The integrated chemiluminescence intensity at 475 nm (low resolution) from a
deoxygenated p-xylene solution of 1 ($5x10^{-4}$ $\underline{M}$) and perylene ($5x10^{-4}$ $\underline{M}$) at 112°
was measured as described above. Similarly, the integrated intensity was
determined for eight solutions containing between $1x10^{-4}$ and $1x10^{-2}$ $\underline{M}$ maleic
anhydride. The total intensity in the presence of maleic anhydride was cor-
rected for quenching of perylene fluorescence measured at 98° using the Stern-
Volmer equation. The ratio of intensity in the absence of anhydride to the
corrected intensity in its presence is plotted in Figure 8. The decay of the
chemiluminescence is shown in Figure 7.

Quenching of diketone formation from 1 with dimethylmaleic anhydride.
Solutions of endoperoxide 1 ($1.5x10^{-3}$ $\underline{M}$) and dimethylmaleic anhydride
($3.0x10^{-3}$ to $1.5x10^{-2}$ $\underline{M}$) and eicosane (internal standard for gas chromato-
graphic analysis) in p-xylene were degassed by freeze-pump-thaw techniques
and sealed in individual glass ampules. The ampules were heated at 112° for
12 h. The yield of diketone 3 was determined by gas chromatography (see
above). The data are shown on Figure 4.

TABLE 1. TOTAL INTENSITIES FOR ACTIVATORS USED IN
CHEMILUMINESCENCE STUDY

activator	ϕ_{fl}[a]	λ_{nm}[b]	Ox.Pot.(V)[c]	corrected total intensities[d]
acridine orange	1.0	515	0.72	1.05×10^8
9-dimethylamino[b]benzophenazine	0.14	515	0.73	1.06×10^8
7-dimethylamino-2-methylphenazine	0.22	528	0.74	1.01×10^8
1,3-diphenylisobenzofuran	0.96	475	0.79	3.40×10^7
rubrene	0.56	585	0.82	2.28×10^7
tetracene	0.21	486	0.87	1.59×10^7
DPET	0.66	583	0.97	8.08×10^6
perylene	0.84	475	1.06	3.20×10^6
DPEA	0.96	490	1.165	9.25×10^5
DPA	0.85	420	1.20	3.77×10^5

a) Determined at 98^c in deoxygenated p-xylene.

b) Wavelength monitored to determine chemiluminescence intensity.

c) Determined by cyclic voltammetry relative to SCE.

d) Corrected for fluorescence efficiency of the activator and the spectral response

of the chemiluminometer.

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Captions for Figures

<u>Figure 1</u> Rate of reaction of endoperoxide $\underline{1}$ in p-xylene at 112° determined by infrared spectroscopy.

<u>Figure 2</u> Absorption, fluorescence, and fluorescence excitation spectra of the yellow intermediate formed by thermolysis of endoperoxide $\underline{1}$.

<u>Figure 3</u> The time dependency of the build-up and decay of the absorption at 400 nm due to the yellow intermediate formed from thermolysis of endoperoxide $\underline{1}$ at 112° in p-xylene.

<u>Figure 4</u> Double reciprocal plot of the trapped product yield from thermolysis of endoperoxide $\underline{1}$ in the presence of dimethylmaleic anhydride against the concentration of anhydride.

<u>Figure 5</u> The time dependency of the build-up and decay of the direct chemiluminescence from thermolysis of a 1×10^{-3} M solution of $\underline{1}$ in p-xylene at 112°.

<u>Figure 6</u> Dependence of the integrated direct chemiluminescence intensity from $\underline{1}$ on the square of the peroxide concentration in p-xylene at 112°.

<u>Figure 7</u> Log of the perylene activated chemiluminescence from $\underline{1}$ in p-xylene at 112° against time at various concentrations of maleic anhydride.

<u>Figure 8</u> Quenching of perylene activated chemiluminescence of $\underline{1}$ by maleic anhydride.

<u>Figure 9</u> Response of the chemiluminescent intensity to the oxidation potential of the activator (1×10^{-4} <u>M</u>) in p-xylene at 112°. The points correspond to: (1) 9,10-diphenylanthracene (DPA); (2) 9,10-diphenylethynylanthracene (DPEA); (3) perylene; (4) 5,12-diphenylethynyltetracene (DPET); (5) tetracene; (6) rubrene; (7) 1,3-diphenylisobenzofuran; (8) 7-dimethylamino-2-methylphenazine; (9) 9-dimethylaminobenzo[b]phenazine; (10) acridine orange free base.

Figure 10   State correlation diagram for the thermal conversion of o-xylylene
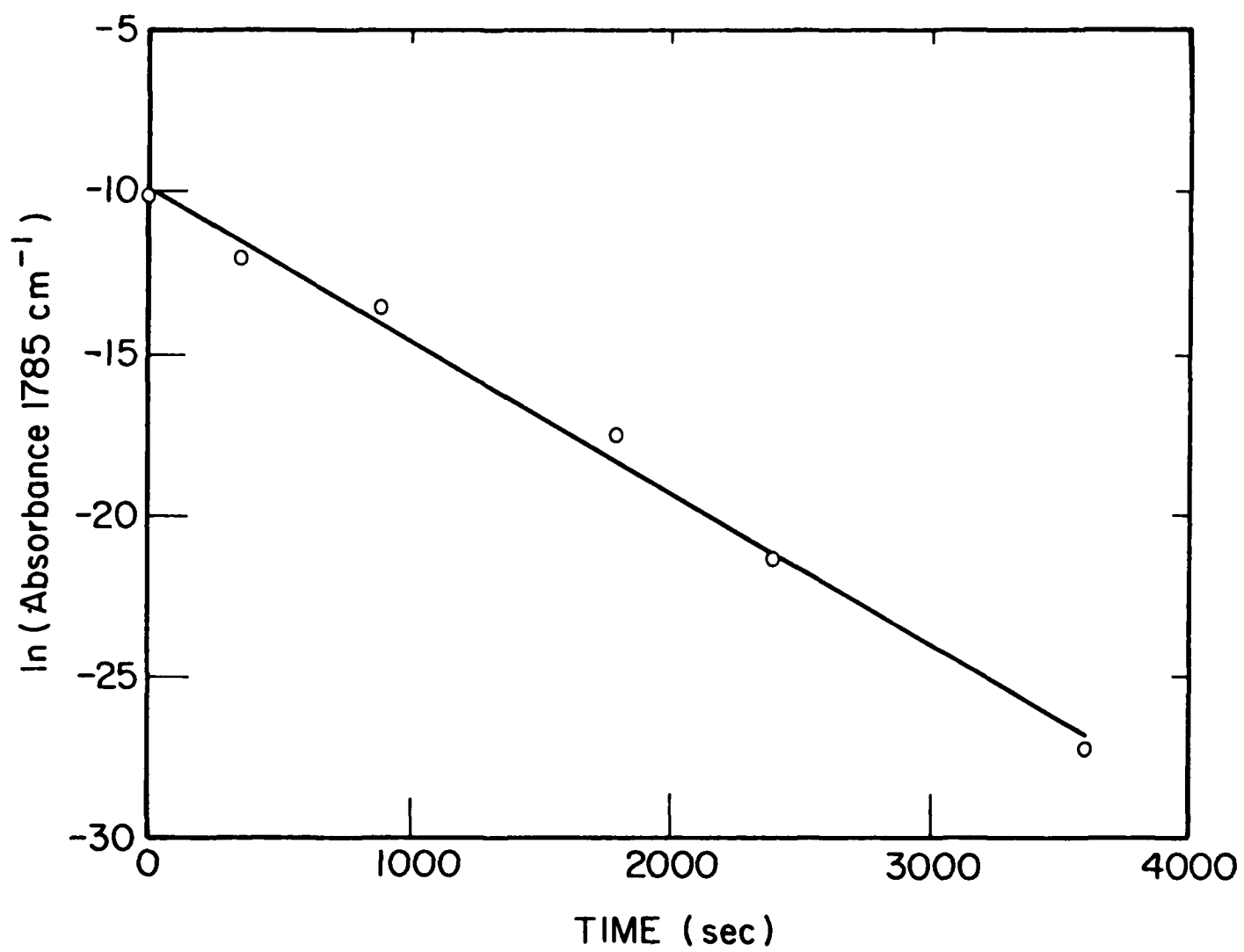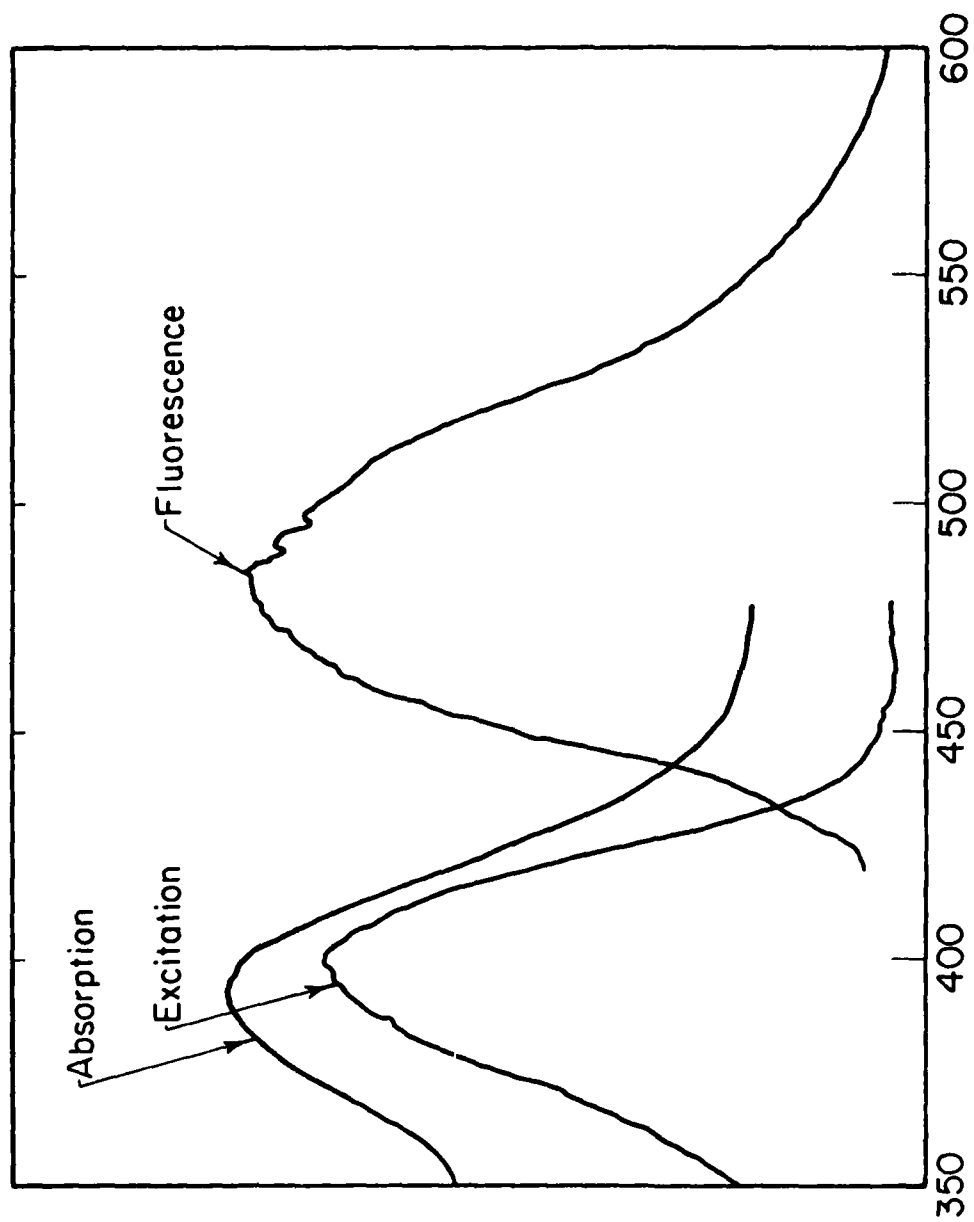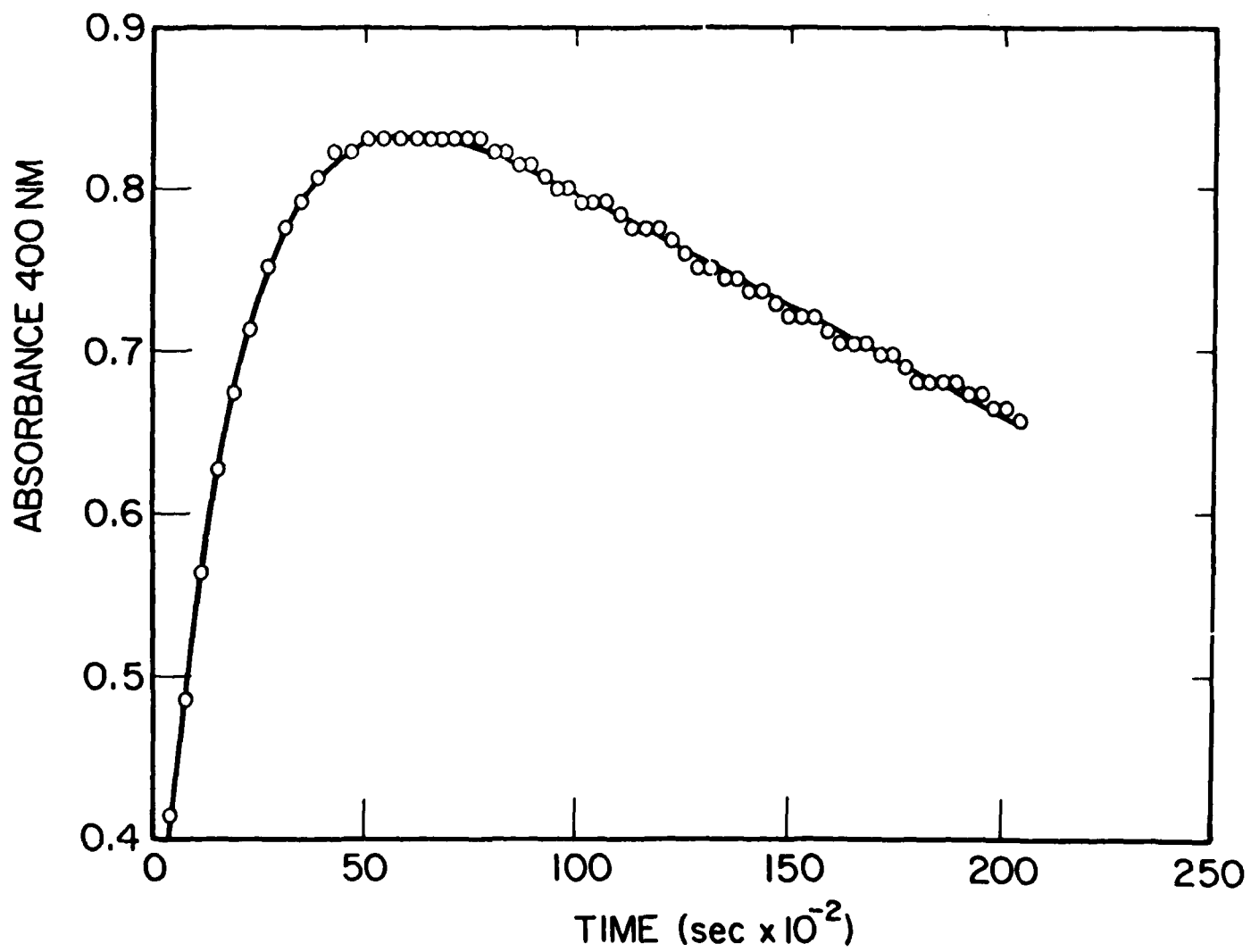
peroxide to o-dibenzoylbenzene.
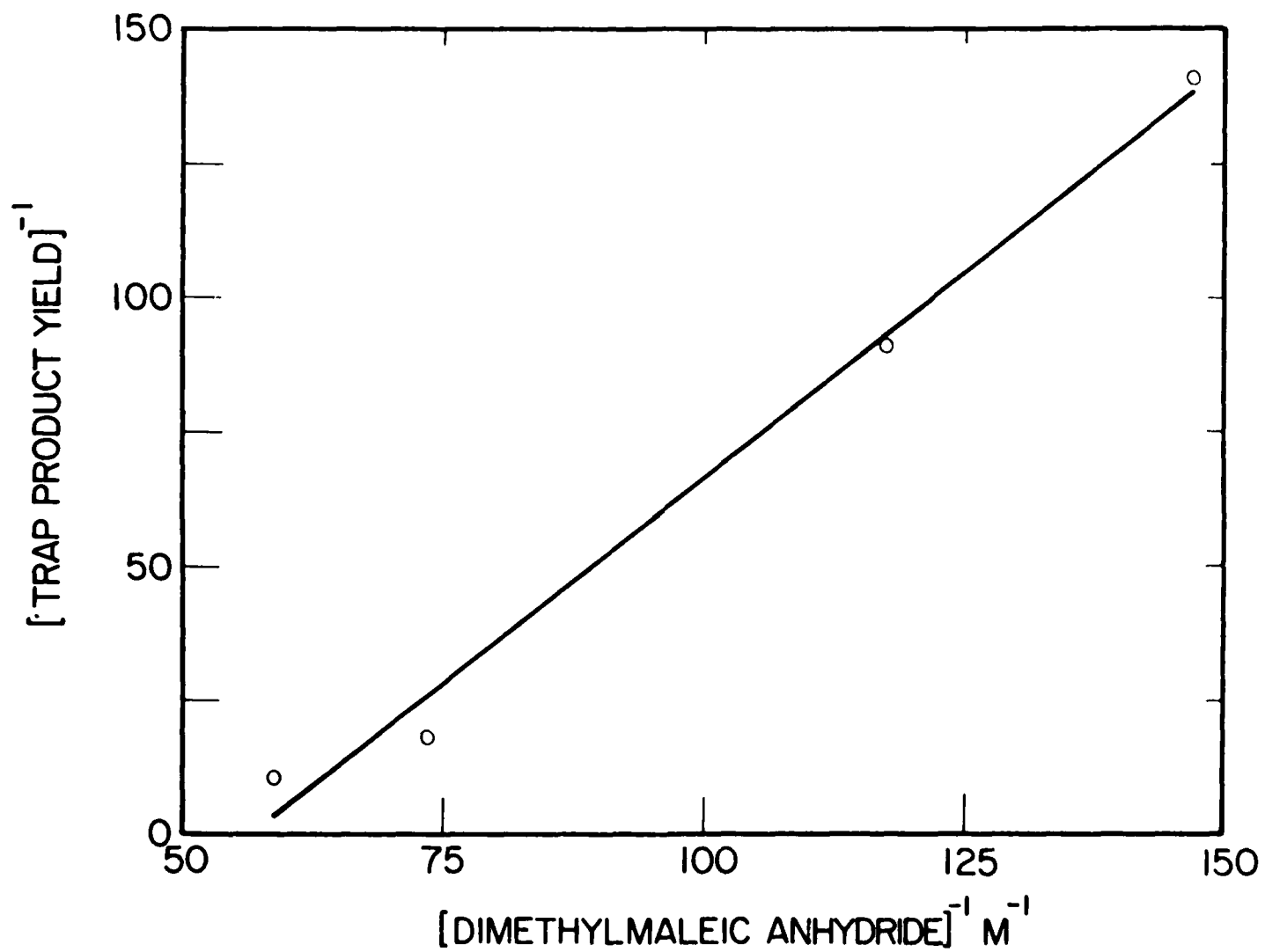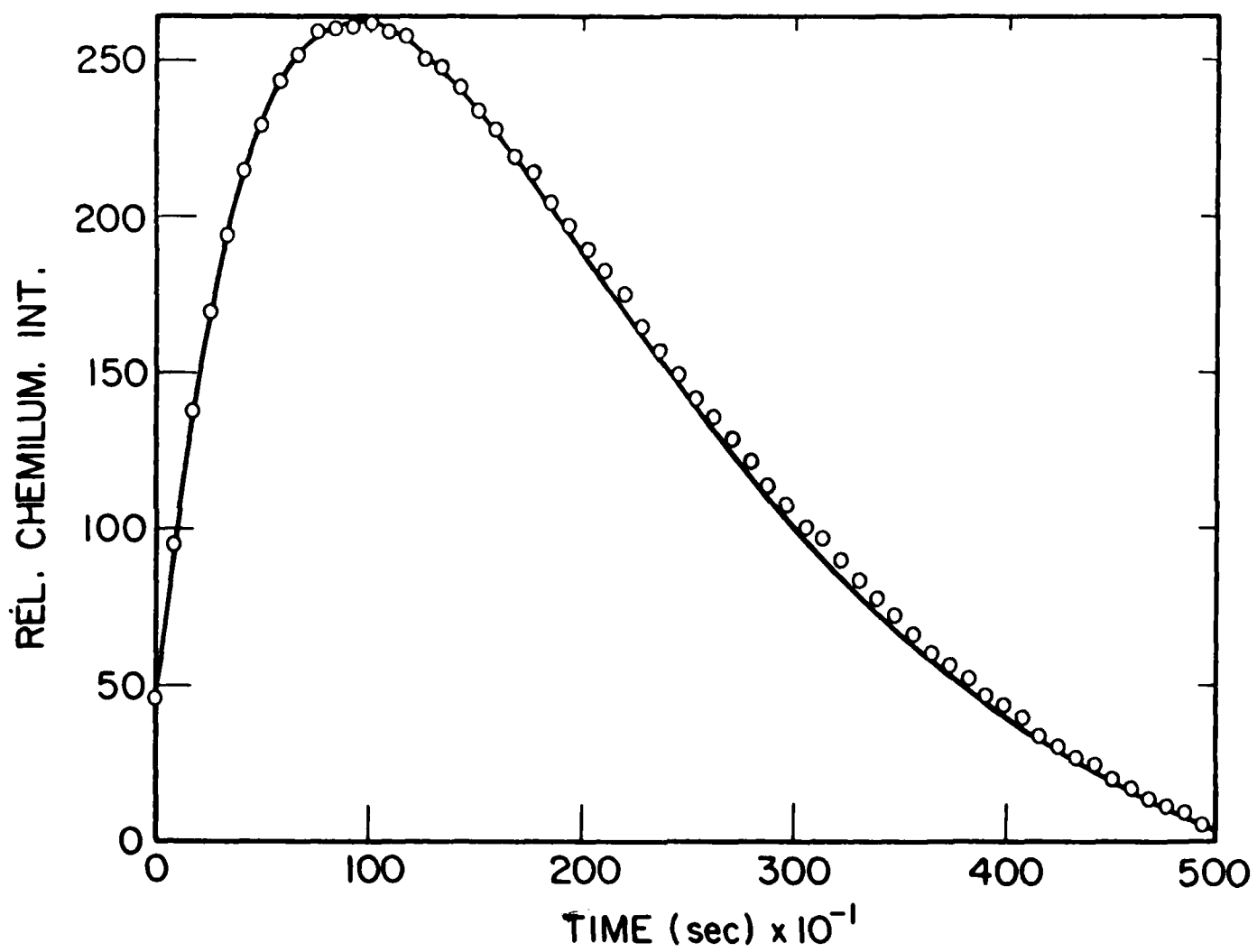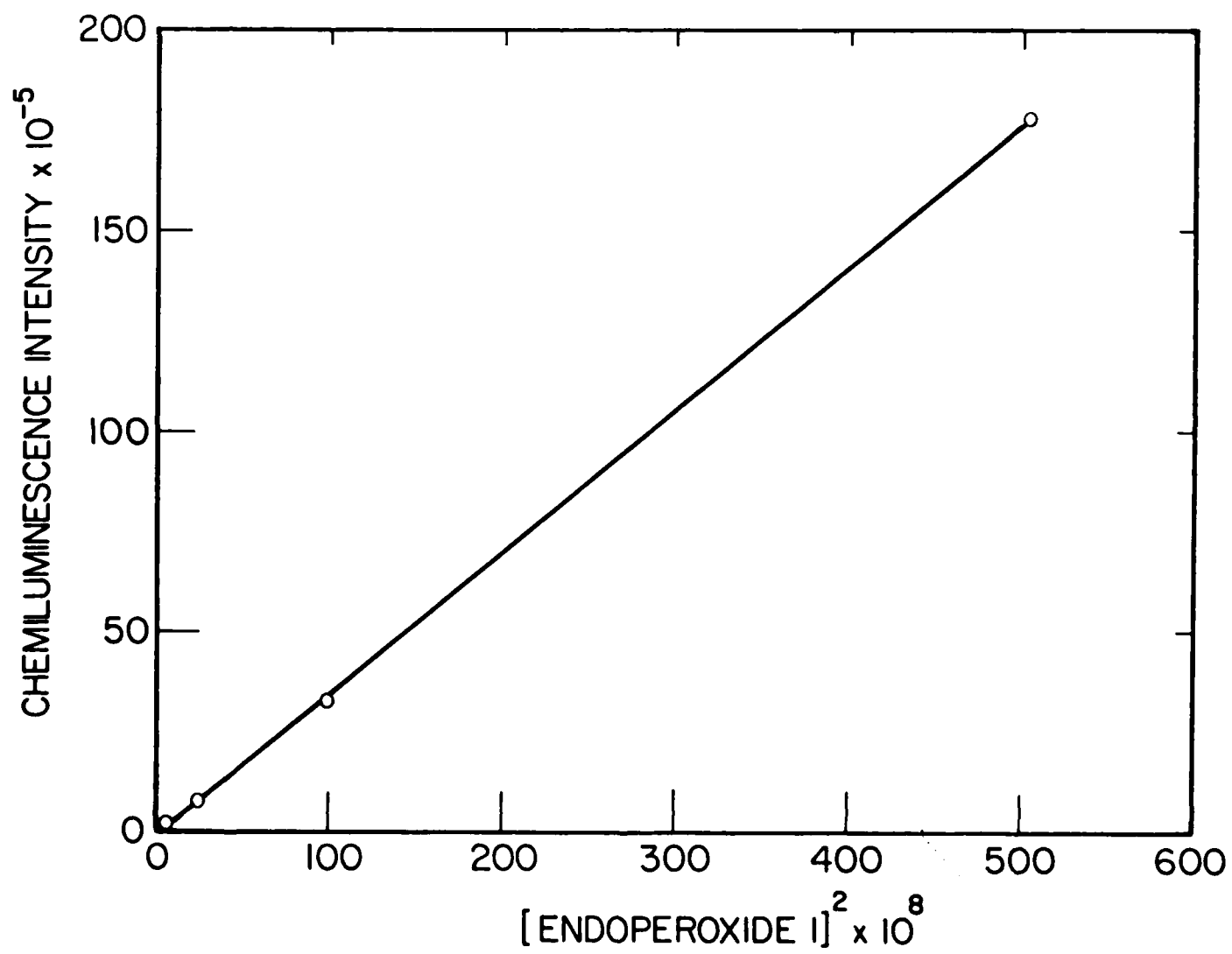
FIGURE 1

FIGURE 2

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 7

FIGURE 8

$I_0^{corr}/I^{corr} \times 10^2$ (y-axis)
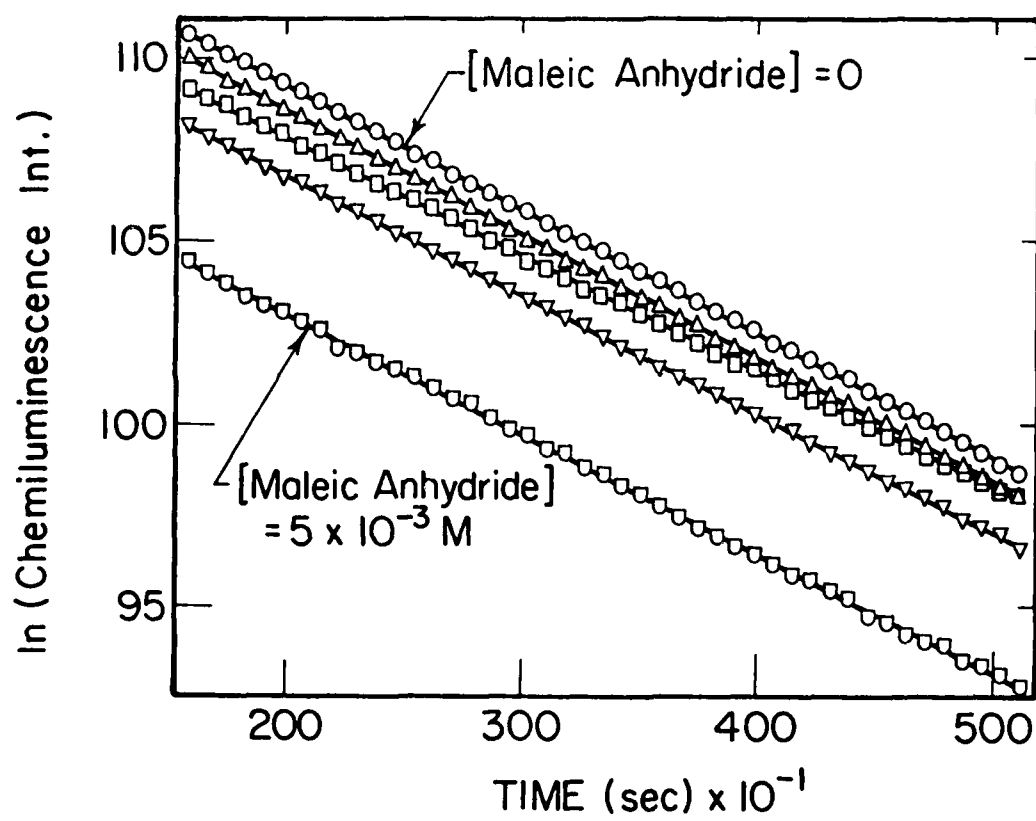
$(MALEIC \, ANH.) \times 10^4$ (x-axis)
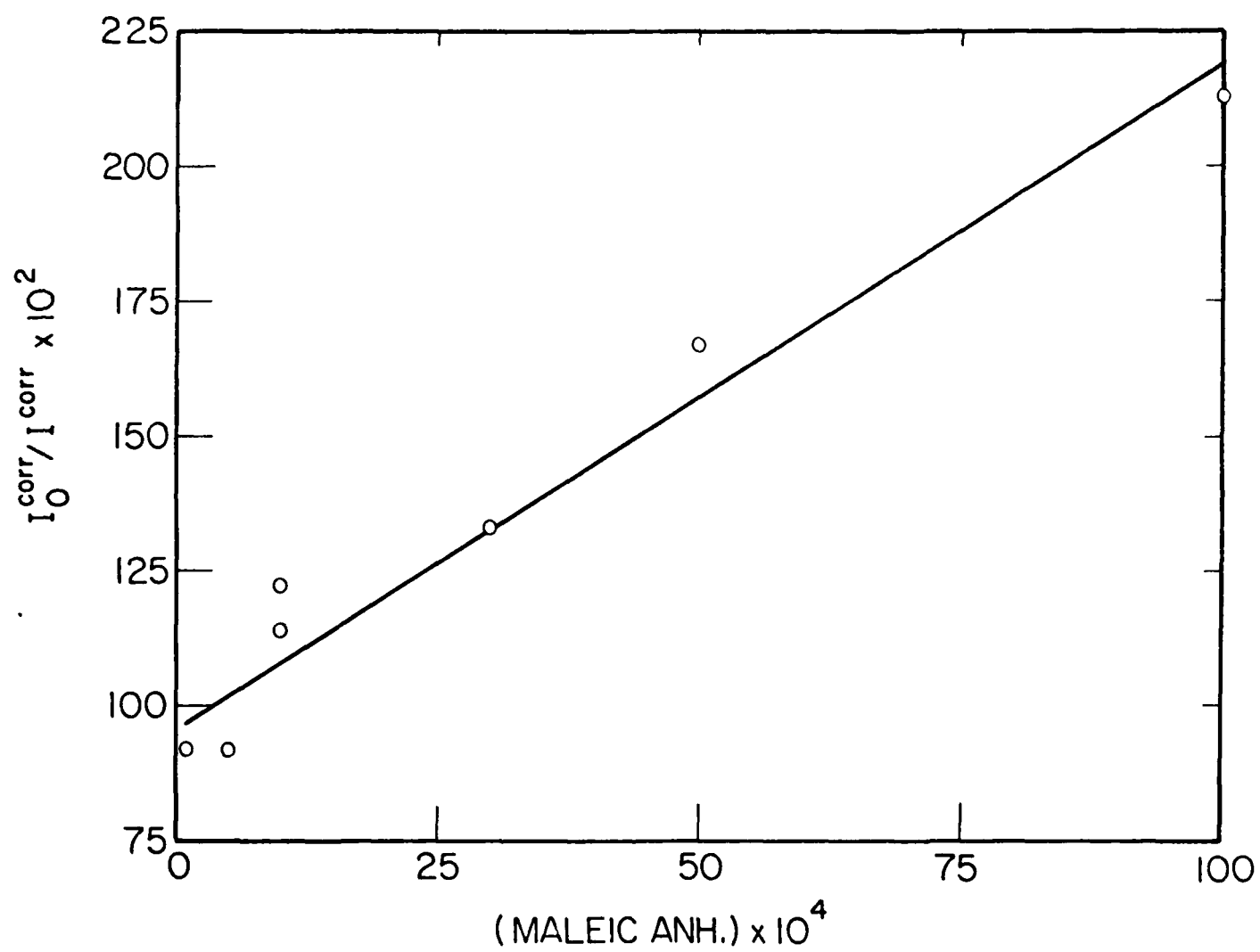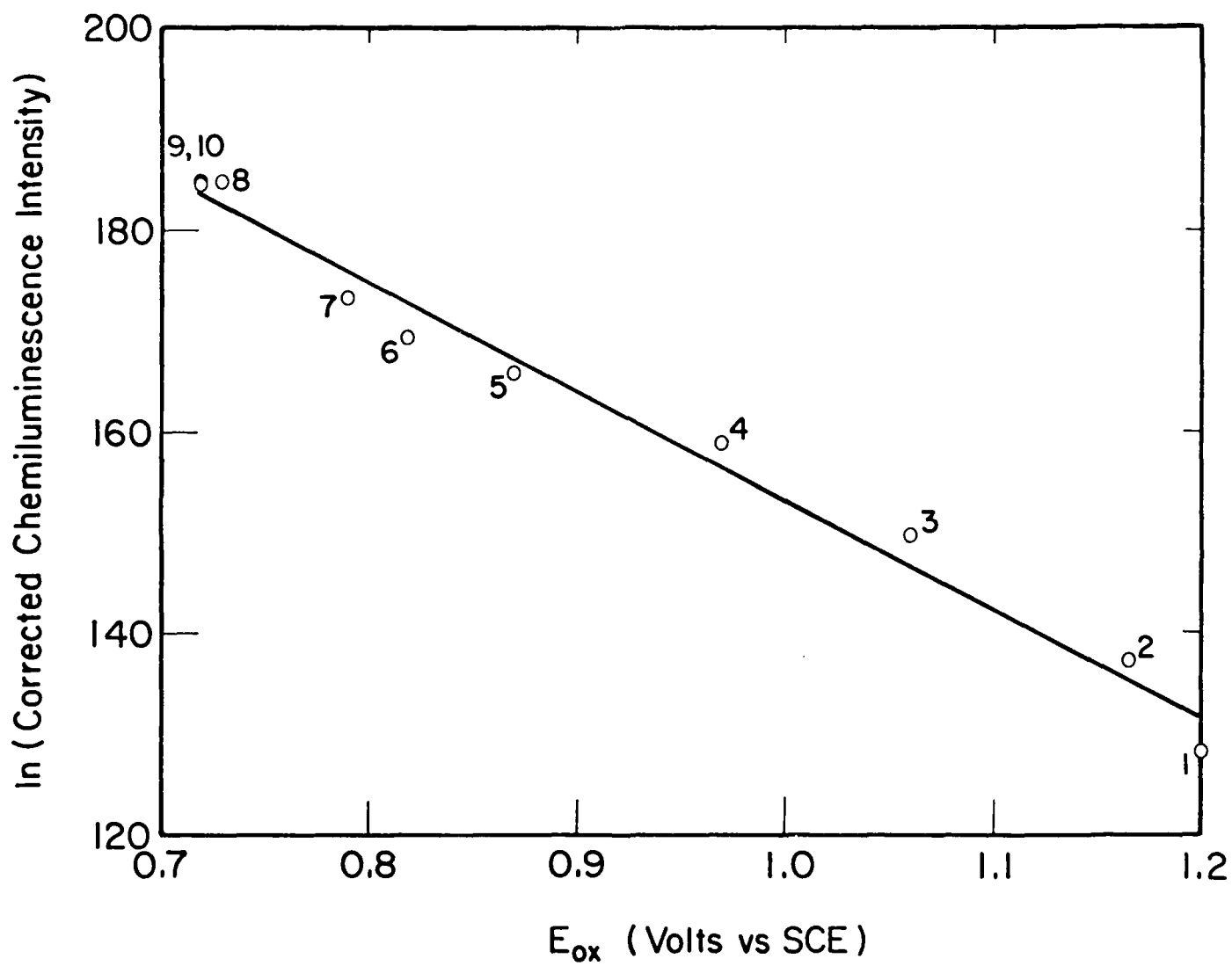
FIGURE 9

FIGURE 10
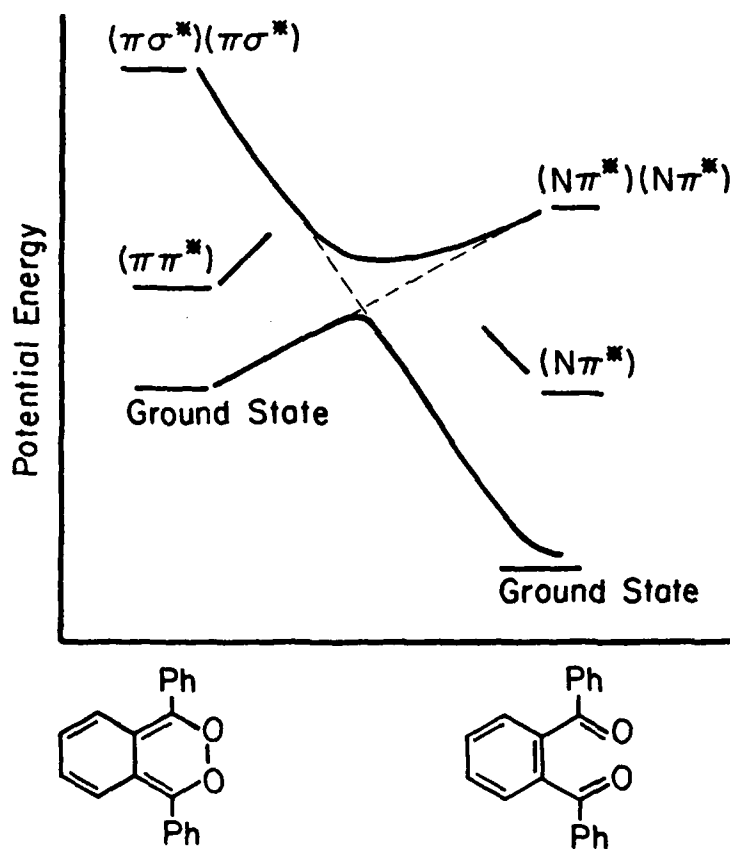
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