

602272

AD No. _____

DDC FILE COPY

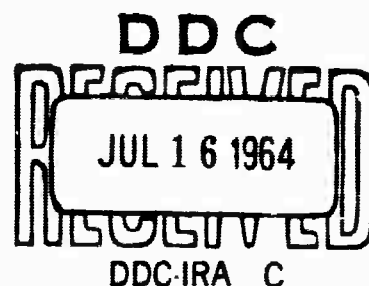
TECHNICAL REPORT NO. 4

TO THE
OFFICE OF NAVAL RESEARCH
AND
ADVANCED RESEARCH PROJECTS AGENCY
ARPA ORDER NO. 299, AMEND. 3
CONTRACT Nonr 4200 (00)
TASK NR 356-452

CHEMILUMINESCENT MATERIALS

AMERICAN CYANAMID COMPANY
CENTRAL RESEARCH DIVISION
STAMFORD, CONNECTICUT

MARCH 1 - MAY 31, 1964



REPRODUCTION IN WHOLE OR IN PART IS PERMITTED FOR ANY
PURPOSE OF THE UNITED STATES GOVERNMENT

DISCLAIMER NOTICE

THIS DOCUMENT IS THE BEST
QUALITY AVAILABLE.

COPY FURNISHED CONTAINED
A SIGNIFICANT NUMBER OF
PAGES WHICH DO NOT
REPRODUCE LEGIBLY.

70

The following persons made primary contributions to the technical effort:

CHEMISTRY

- M. M. Rauhut

L. J. Bollyky, D. Sheehan, R. A. Clarke,
A. M. Semsel, R. W. Whitman

ELECTROCHEMISTRY -

D. L. Maricle, J. P. Mohns

PHYSICS

- R. C. Hirt

B. G. Roberts, J. S. Brinen

TABLE OF CONTENTS

Summary	1
Introduction	3
Section I - Reaction Mechanisms in Chemiluminescence	5
A. Oxalyl Peroxide Chemiluminescence	5
B. Reductive Electrochemiluminescence of 3-Aminophthalhydrazide	14
C. Anthracene Photoperoxides	21
Experimental	26
Section II - Structural Criteria for Chemiluminescent Compounds	33
A. Relationship of Peroxides to Chemiluminescence	33
B. Ion Radical Chemiluminescence	41
Experimental	50
Section III - Spectroscopy and Energy Transfer	55
A. Recalibration of Spectroradiometer-Fluorimeter	55
B. Oxalyl Chloride-Hydrogen Peroxide Chemiluminescence	56
C. Energy Transfer in 3-Aminophthalhydrazide	61
Chemiluminescence	
Experimental	63
References	75
Distribution	77

SUMMARY

Progress in determining the processes fundamental to chemiluminescence is described with particular reference to (1) mechanism studies of oxalyl peroxide, 3-aminophthalhydrazide, and anthracene photoperoxide chemiluminescent reactions; (2) synthesis and exploratory studies of potentially new chemiluminescent materials; and (3) energy transfer studies in chemiluminescent systems.

The chemiluminescent reaction of oxalyl chloride with hydrogen peroxide is more efficient in polar than non-polar solvents, and use of rubrene as a fluorescer gives greater over-all efficiency than 9,10-diphenylanthracene. Experiments with pairs of fluorescers are discussed. Analyses of gaseous products from oxalyl chloride-hydrogen peroxide reaction show carbon monoxide and carbon dioxide as main products with some phosgene, but little oxygen formed. A new example of oxalyl peroxide chemiluminescence is reported.

Strong chemiluminescence from 3-aminophthalhydrazide was generated in neutral non-aqueous solvents at an electrolytic cathode in the presence of oxygen. Evidence suggests reaction of an oxygen dianion produced at the cathode with 3-aminophthalhydrazide, followed by previously studied reactions.

Collisional energy transfer was observed in the system: 3-aminophthalhydrazide-base-hydrogen peroxide-rubrene-dimethylsulfoxide as evidenced by a substantial quantum gain derived from the addition of rubrene. The system is not suitable, however, for quantitative energy transfer studies.

Synthesis of a series of anthracene photoperoxides is described. 9,10-Diphenylanthracene photoperoxide gives low level chemiluminescence, with 9,10-diphenylanthracene as the only observable product. 1,4-Dimethoxy-9,10-diphenylanthracene gives moderate chemiluminescence and more complex decomposition products.

Efforts are described to prepare potentially chemiluminescent acridine peroxides based on mechanistic hypotheses. None of the desired compounds have yet been obtained. Related studies have provided chemiluminescent reactions believed to involve electron transfer processes with ion radicals. Chemiluminescence is obtained in the absence of oxygen.

INTRODUCTION

Emission of light in chemiluminescence as in fluorescence results from the transition of an electron from an energetic antibonding orbital in an excited molecule to a stable bonding or non-bonding orbital (generally the former) corresponding to the ground state molecule. Thus a chemiluminescent process must accommodate the formation of excited molecules as a product of chemical reaction. Two requirements for chemiluminescence are immediately apparent: (1) the reaction must liberate an amount of chemical energy at least equivalent to the energy difference between a product molecule and its excited state (41 to 72 KCAL/mole for emission of visible light) and (2) the product either must be fluorescent itself or be capable of transferring its excitation energy to a fluorescent compound present in the system. Many, if not most, reactions meeting these requirements do, in fact, generate a low level, barely discernible chemiluminescent emission. Moderately bright emission, however, is limited to a very few reaction systems. Clearly a third requirement exists that an efficient mechanistic pathway must be available for the conversion of chemical energy to electronic excitation energy. It is also clear that this third requirement is rarely met.

Determination of this crucial mechanism for generating excited molecules is the primary goal of chemiluminescence research. Once this mechanism is understood, new chemiluminescent systems can be designed having the efficiency and other characteristics necessary for

practical lighting. Two approaches are being taken to achieve an understanding of the chemical chemiluminescence mechanism. The first approach (Section I) involves direct mechanism studies of several known chemiluminescent reactions. The second approach (Section II) involves exploratory studies of new, potentially chemiluminescent reactions designed to test working hypotheses regarding the chemiluminescence mechanism and to provide structural criteria for chemiluminescent compounds.

The third section of the report deals chiefly with the physical processes associated with chemiluminescence. Quantitative spectroscopic determination of quantum yields, spectra, reaction rates and related physical properties are described in this section. The third section also deals with quantitative energy transfer studies designed to clarify the role of energy transfer in chemiluminescence and to distinguish the source of yield loss in chemiluminescence between chemical and physical steps.

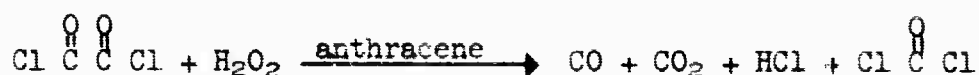
The reports in this series follow a consistent format so that the progress of a specific investigation can be followed conveniently over periods longer than a single quarter. To avoid excessive repetition, the objectives of a particular study are described in detail only in the report where the study is begun. Except for the discovery of ion radical chemiluminescence described in Section IIB, this report describes work introduced in earlier reports.

SECTION I

REACTION MECHANISMS IN CHEMILUMINESCENCE

A. Oxalyl Peroxide Chemiluminescence

Oxalyl peroxide chemiluminescence is illustrated by the reaction of oxalyl chloride with hydrogen peroxide in an organic solvent containing a fluorescent compound.



The emitted light is characteristic of the normal fluorescent emission of the fluorescent compound³. Under certain (anhydrous) conditions the over-all chemiluminescence efficiency is as high as 6%². The reaction is of substantial interest because of the implied energy transfer process whereby chemical energy released by the decomposition of peroxidic intermediates appears as singlet excitation energy in the fluorescent compound. Moreover, the simplicity of the starting materials and products offers opportunity for detailed mechanistic investigation in spite of the now evident complexity of the reaction.

An adequate description of the over-all mechanism requires answering fundamental questions dealing with: (1) the chemical mechanism of the process involving oxalyl chloride which leads to the generation of electronic excitation energy, and (2) the mechanism of the process by which the energy appears as the singlet excited state of the fluorescent acceptor. Our program is currently investigating both of these areas. The experimental work bearing on the second question is primarily spectroscopic and is discussed in Section III.

The previous report³ summarized results up to the end of the third quarter. Results bearing on the chemical process obtained during the fourth quarter are summarized below.

1. Effect of Reactant Ratios on Chemiluminescence Efficiency

Oxalyl chloride has been found to be a powerful quencher of hydrocarbon fluorescence (see Section III). Fluorescence quenching is thus a likely cause of decreasing efficiency with increasing oxalyl chloride-hydrogen peroxide ratios.

2. Free Radical Inhibitor Effects

The effects of the free radical inhibitor, 4-methyl-2,6-di-t-butylphenol, on the oxalyl chloride-hydrogen peroxide reaction have been found to vary markedly with solvent and other conditions. Moreover, recent qualitative experiments indicate that the induction period previously reported² is difficult to reproduce. A quantitative study of inhibitor effects will be undertaken to clarify the relationship of free radical chain processes to chemiluminescence.

3. Solvent Effects

Qualitative observations have been made of the oxalyl chloride-hydrogen peroxide reaction in various solvents. The results are summarized in Table I. In most of the solvents studied strong intensities and brief lifetimes were found. In several non-polar solvents, where hydrogen peroxide was poorly soluble, weak emission was observed at the peroxide-solvent interface. Acetophenone, however, offered a strong emission in spite of its low solvent capacity for hydrogen peroxide.

Table I

Solvent Effects on Oxalyl Chloride-Hydrogen Peroxide
Chemiluminescence^(a)

<u>Solvent</u>	<u>Chemiluminescence</u>	
	<u>Intensity</u>	<u>Duration</u>
Diethyl ether	strong	short
Di-n-butyl ether	strong	short
1,2-Dimethoxyethane	strong	short
Tetrahydrofuran	strong	short
Diphenyl ether ^(b)	weak	long
Anisole ^(b)	weak	-
Methyl isobutyl ketone	strong	short
Acetophenone ^(b)	strong	short
Ethyl acetate	strong	short
Dimethyl phthalate	strong	short
Triethyl phosphate	strong	short
Benzene ^(b)	weak	-

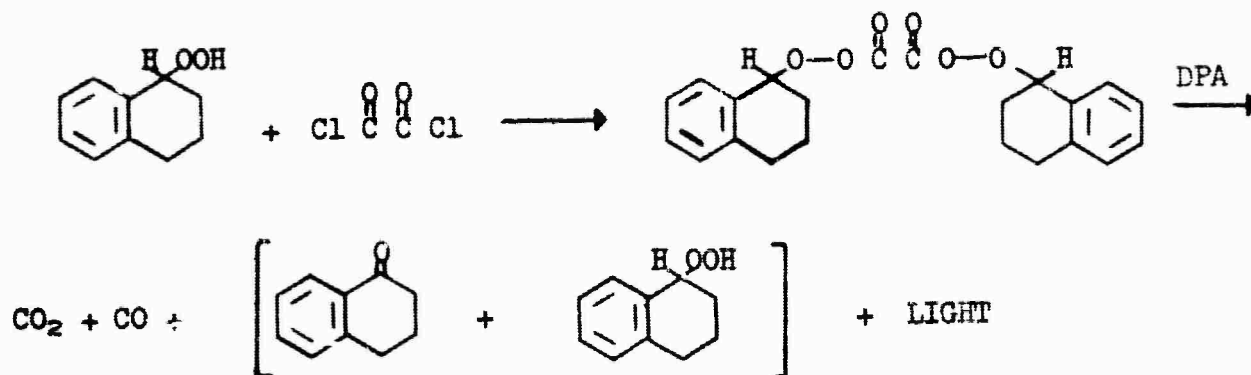
(a) One molar oxalyl chloride solutions were added to one molar hydrogen peroxide solutions (or mixtures) containing 6×10^{-4} molar 9,10-diphenylanthracene.

(b) Hydrogen peroxide was substantially insoluble in the solvent. Chemiluminescence was observed at the interface.

4. Scope of Chemiluminescence from Oxalyl and Related Peroxides

Five new chemiluminescent reactions based on oxalyl peroxide chemiluminescence have been reported in previous reports^{2,3}. To further define the essential structural features of the key peroxidic intermediate in the chemiluminescent reaction, the additional experiments summarized below were carried out.

Oxalyl Chloride and Tetralin Hydroperoxide



The reaction of t-butyl hydroperoxide with oxalyl chloride in ether containing 9,10-diphenylanthracene (DPA) is not chemiluminescent³ indicating that the decomposition of di-t-butyldiperoxyoxalate, $\text{Bu}^t-\text{OO}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{OO}-\text{Bu}^t$, does not produce excited molecules. We find, however, that the corresponding reaction with tetralin hydroperoxide produces a moderately strong, brief chemiluminescent emission. The reaction is somewhat similar to the previously reported chemiluminescent reaction of t-butylperoxyoxalyl chloride with isopropyl alcohol³. In each case chemiluminescence is evidently associated with the active tertiary hydrogen alpha to the peroxidic group. This in turn, as indicated previously, suggests a free radical chain process involving hydrogen abstraction as

a critical step. Such a process ~~cannot~~ occur with di-t-butyl-diperoxyoxalate.

Diisopropyl Diperoxycarbonate Decomposition

Decomposition of the peroxycarbonate in dilute ether or 1,2-dimethoxyethane solutions containing 9,10-diphenylanthracene generated weak chemiluminescence when warmed. Light was not obtained in the presence of methane sulfonic acid. A weak emission was obtained in the presence of oxalyl chloride.

The weak emission observed in these experiments is evidently characteristic of the chemiluminescence observed from most peroxide decompositions. The result emphasizes the unique character of the oxalyl peroxide structure.

5. Gas Phase Products from Oxalyl Peroxide Decomposition

Reactions

The preceding report described preliminary analyses of the gaseous products evolved from a number of oxalyl chloride-hydrogen peroxide reactions. Those results were described as tentative, pending confirmation of the mass spectrometric analytical method by vapor phase chromatography. The results have now been confirmed with good agreement being found for the two analytical procedures. Additional experiments have also been carried out to extend the range of conditions studied, and several analyses have been performed on related systems.

Yields of gaseous products are summarized in Table II. Reasonable account (generally within $\pm 10\%$) of the oxalyl chloride carbon from hydrogen peroxide reactions was obtained as carbon monoxide,

Table II

Gaseous Products from Oxalyl Peroxide Decomposition Reactions

Oxalyl Chloride (millimoles)	Hydrogen Peroxide (millimoles)	Solvent	Solution Volume (ml)	Conversions Based on Oxalyl Chloride				
				CO ₂ ^a	CO ₂ ^a	O ₂ ^b	COCl ₂ ^a	VPC CO ₂ ^a O ₂ ^b
4.93	4.90	ether	15	38.2	47.0	1.8	0	- -
5.00 ^c	5.00	ether	15	46.5	46.8	7.0	0	- -
4.93 ^d	4.90	ether	15	37.3	45.8	2.0	0	- -
10.00	10.00	ether	20	35.2	41.7	0	0	- 0
5.35	4.90	DMP	15	25.0	71.2	0.13	11.8	- -
5.35 ^d	4.90	DMP	15	25.9	69.5	0.05	11.4	- -
5.35	9.80	DMP	20	30.7	69.3	0.05	12.9	- -
5.35 ^d	9.80	DMP	20	44.0	57.1	0.33	0	- -
10.00	10.00	DMP	15	31.6	64.4	0.78	9.1	28.8 0
10.00	50.00	DMP	35	29.0	59.8	0.60	12.4	25.7 0.24
10.00	Tetralin Hydroperoxide 10.00	benzene	35	39.3	34.5	0.34	0	41.0 0
t-Butylperoxy- oxalyl chloride 7.60	Water 5 ml.	hexane	20	5.7	85.6	0	0	5.0 0
Phosgene 9.98	Hydrogen Peroxide 10.00	benzene DMF	10 5	0 ^e	42.8	5.2	1.61	0.06 5.6

See following page for footnotes.

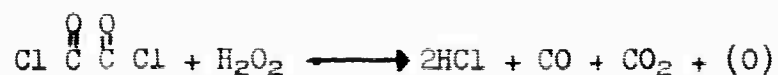
Footnotes for Table II

- a Per cent conversion of oxalate carbon.
- b Moles of oxygen as a percentage of acid chloride charged.
- c This reaction was allowed to age 36 min. following the end of light emission before sampling the evolved gases. All other experiments were sampled within two minutes after chemiluminescence had ceased.
- d One mole per cent based on oxalyl chloride of 4-methyl-2,6-ditertiarybutylphenol was present as a radical inhibitor.
- e Relative yields. Absolute yields were not determined.

carbon dioxide and (in dimethyl phthalate experiments) as phosgene. Ratios of CO to CO₂ were somewhat variable even within a set of experimental conditions, but lower CO:CO₂ ratios were obtained in dimethyl phthalate than in ether. Results in ether suggest tentatively that additional CO is liberated following the end of chemiluminescence so that a higher CO:CO₂ ratio is obtained when the reaction mixture is allowed to age before sampling. This effect as well as the relationship of gas evolution rate to chemiluminescence intensity will be studied further. The free radical inhibitor, 4-methyl-2,6-di-t-butylphenol had little effect on products except in a 1:2 oxalyl chloride-hydrogen peroxide experiment in dimethyl phthalate where the CO:CO₂ ratio was increased.

Substantial yields of phosgene were found in dimethyl phthalate experiments but not from experiments run in ether. The rapid gas evolution in these experiments is evidently able to remove phosgene from the liquid phase in spite of its reactivity toward hydrogen peroxide. It is likely, however, that a portion of the CO₂ found resulted from a phosgene-hydrogen peroxide reaction. Phosgene reacts with hydrogen peroxide to give CO₂ exclusive of CO as indicated in the table.

Only insignificant amounts of oxygen were found in the experiments. Reabsorption by autooxidation of liberated oxygen would be expected in ether under the conditions used, but this is unlikely in dimethyl phthalate. It is clear from the 1:1 oxalyl chloride-hydrogen peroxide stoichiometry previously reported that one atom of hydrogen peroxide oxygen remains unaccounted for by the gas phase analysis.



Liquid phase products will be determined.

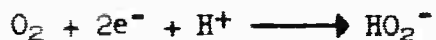
The chemiluminescent reaction of tetralin hydroperoxide with oxalyl chloride provided approximately equal amounts of CO and CO₂ but little oxygen.

t-Butylperoxyoxalic acid decomposes in hexane to provide carbon dioxide as the major product with only 6% of the oxalic carbon appearing as carbon monoxide. This small yield of CO may derive from oxalyl chloride as an impurity, but its possible relationship to chemiluminescence must be considered.

B. Reductive Electrochemiluminescence of 3-Aminophthalhydrazide

It has been observed that electrolytic reduction of air saturated, aqueous alkaline solutions of 3-aminophthalhydrazide generates a weak light at the cathode⁵. This electrochemiluminescence is distinct from anodic emission and has been attributed to the reduction of O_2 to HO_2^- , followed by the usual chemiluminescent reaction of HO_2^- with 3-aminophthalhydrazide⁵ monoanion (LH^-). It had also been noticed during the course of studies on the electrochemical oxidation of LH^- in non-aqueous systems² that the auxiliary electrode (a cathode) was exhibiting rather intense electrochemiluminescence. An investigation was begun to determine the reaction sequence responsible for the cathodic generation of light in these non-aqueous systems.

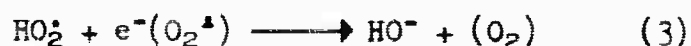
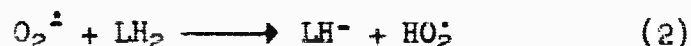
The system investigated most extensively was dimethylsulfoxide (DMSO), 0.1 M in tetrabutylammonium perchlorate. The reduction of oxygen in the absence of LH^- was examined first. Figure I shows the cyclic voltammogram of an air saturated solution obtained on a platinum micro-electrode. The existence of a reoxidation peak, and the quasi-reversible appearance of the peaks indicates that the reduction is quite different from the process observed in aqueous solutions. The aqueous reduction is described by the following equation:



Reductions involving proton transfer, however, are generally very irreversible in a solvent such as DMSO, in which the availability of protons is very low. This suggests that the oxygen simply picks up one electron and exists as the superoxide anion:



This supposition is substantiated by Figure II which shows the same system after the addition of 10^{-3} M 3-aminophthalhydrazide (LH_2). The scan was started at -0.4 volts vs. the saturated calomel electrode (SCE) and scanned anodically over the phthalhydrazide oxidation peak to +1.1 volts, cathodically to -2.1 volts, anodically to +0.4 volts and finally back to -0.4 volts. Three conclusions can be drawn from this experiment: 1) The oxidation peak at +0.1 V is identical in potential and product lifetime to that observed² for LH^- but it only occurs after the oxygen reduction peak has been scanned. 2) The height of the oxygen reduction peak is more than double that observed in the absence of LH_2 , indicating the up-take of more electrons. 3) The oxygen reoxidation peak has decreased considerably in size indicating a reduced lifetime of the product. These observations indicate that the following reactions are occurring when oxygen is reduced in the presence of LH_2 .

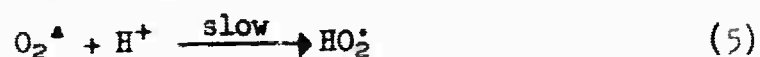
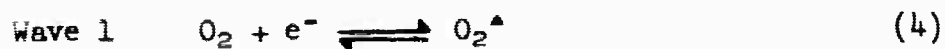


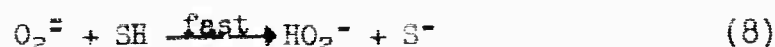
The LH_2 apparently supplies protons rapidly enough to convert the oxygen reduction process largely to the normal two-electron reduction to peroxide observed in aqueous systems, thus increasing the reduction peak height, decreasing the $O_2^{\cdot -}$ oxidation peak height and generating LH^- .

However, when the same platinum electrode was visually observed

in a darkroom as the potential was scanned or held at suitable fixed values, only barely detectable light was emitted in the potential region between the O_2 reduction peak and background discharge (~ -2 V.). Therefore, equations (1)-(3) do not generate significant concentrations of species responsible for light emission.

Intense electrochemiluminescence is observed, however, when the electrode potential is shifted to the -2.3 to -2.5 V. region. The reason for this was found by examining the polarography of oxygen in DMSO on a DME (dropping mercury electrode) in the absence of any LiH_2 . The over voltage for solvent reduction on mercury is greater and hence the useful range on this electrode extends to -2.7 volts. Figure III shows two oxygen reduction waves. The first observed at $E_{1/2} = -0.73$ V. vs. the SCE corresponds to the peak previously observed on platinum. The second wave, not seen on platinum, appeared at $E_{1/2} = 2.40$. The currents corrected for the changes in drop time for waves 1 and 2 are $3.2 \mu a$ and $2.1 \mu a$, respectively. This indicates that two one-electron processes are involved. The reduction of oxygen in non-aqueous solvents then appears analogous to the reduction of aromatic hydrocarbons in similar systems. Slow protonation of $O_2^{\cdot -}$ by the solvent (or impurities) may be responsible for the lack of a 1:1 ratio of diffusion currents for wave 1:wave 2. The equations may be written:

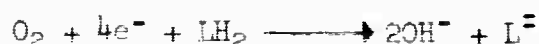


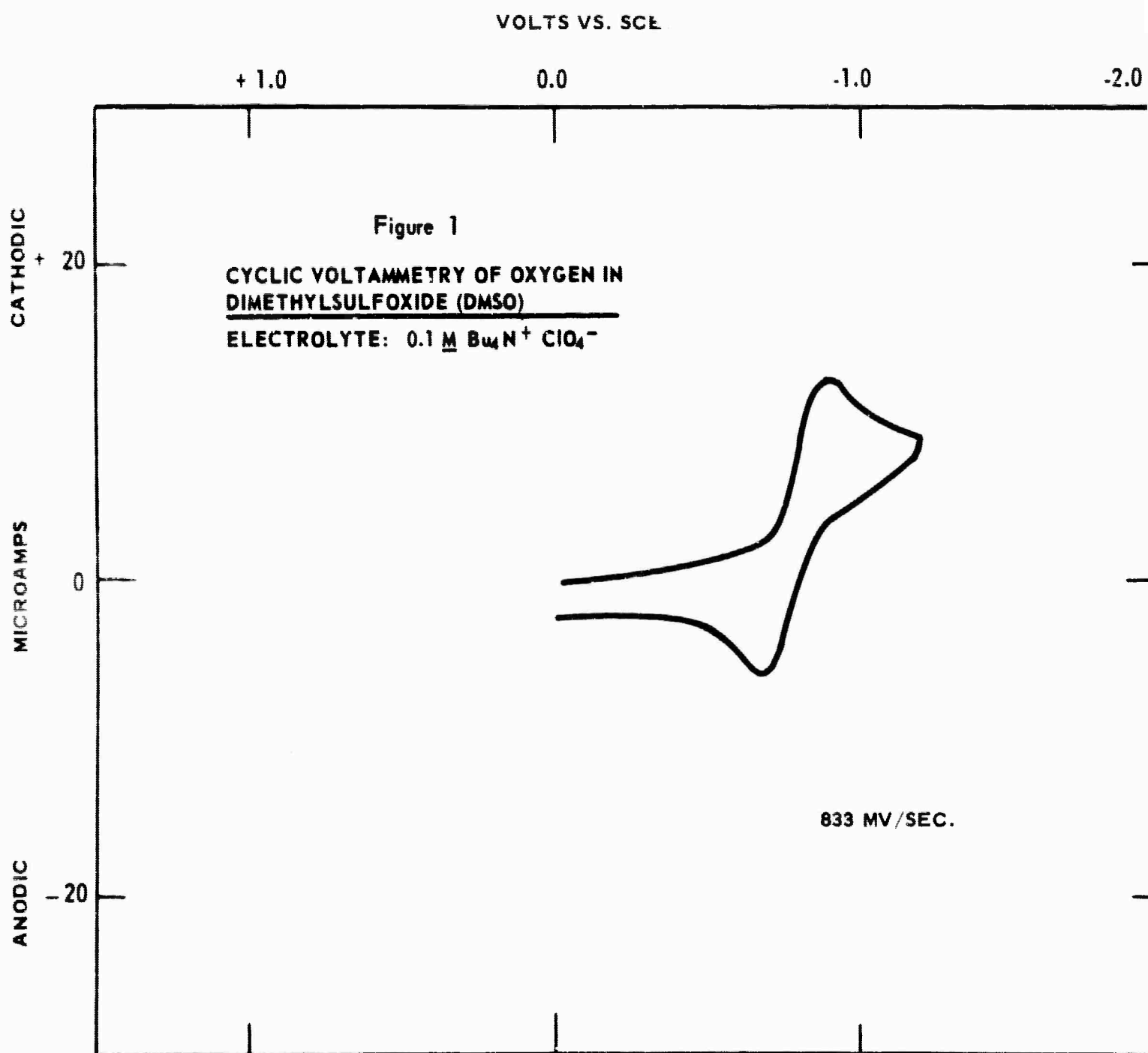


Thus to the extent that $\text{O}_2^{\cdot -}$ is protonated by traces of impurities in the solvent, wave 1 will increase at the expense of wave 2.

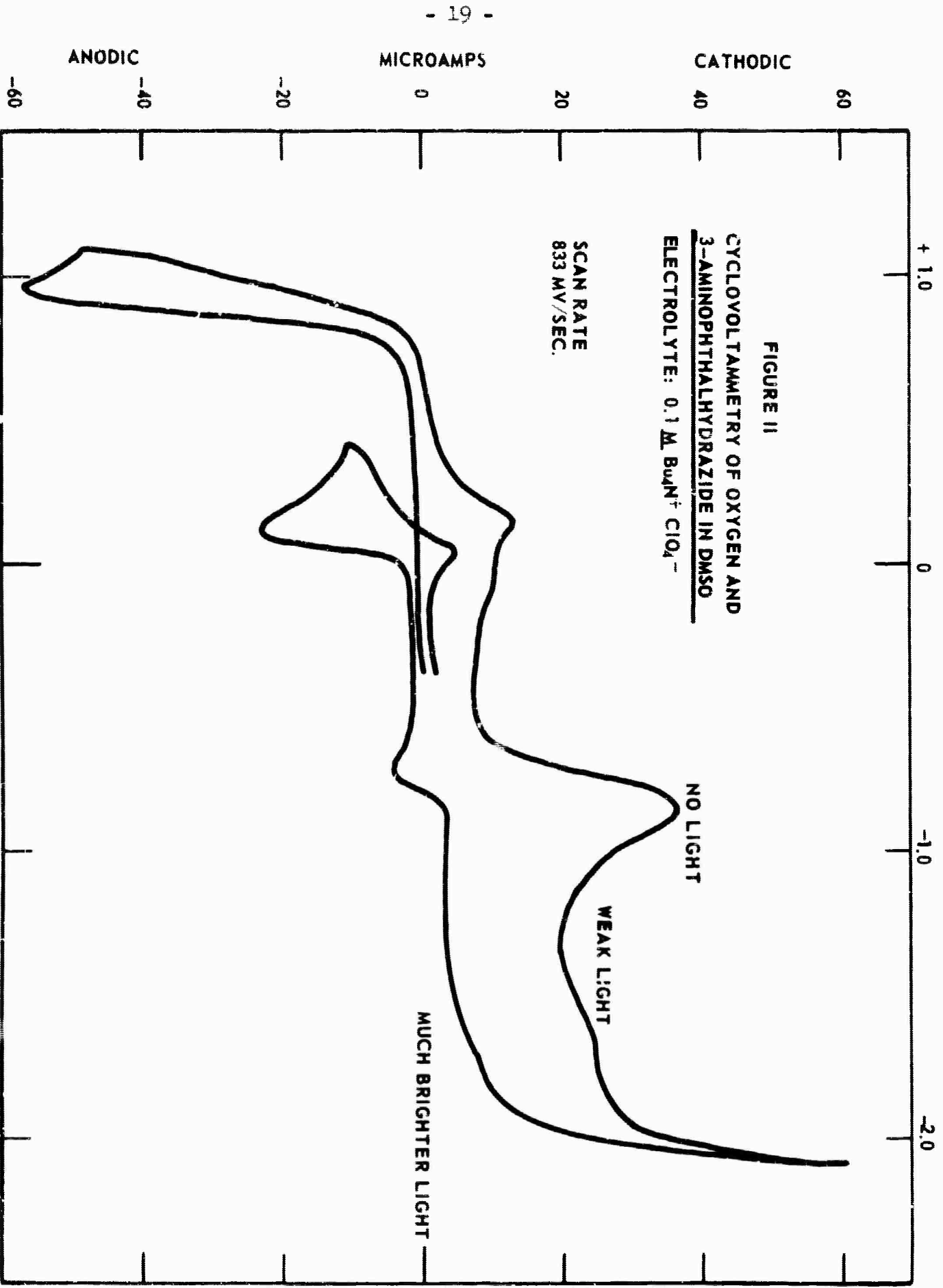
Further evidence for the existence of essentially two one-electron waves was obtained by analyzing the slope of the rising portion of the first wave in the usual manner.²⁵ A slope of 0.070 was obtained and is considered consistent with a one-electron wave. Also a paramagnetic species was detected by means of electron spin resonance spectroscopy in a solution in which prolonged oxygen reduction had been carried out. The spectrum was very similar to that reported⁶ for $\text{HO}_2^{\cdot}$.

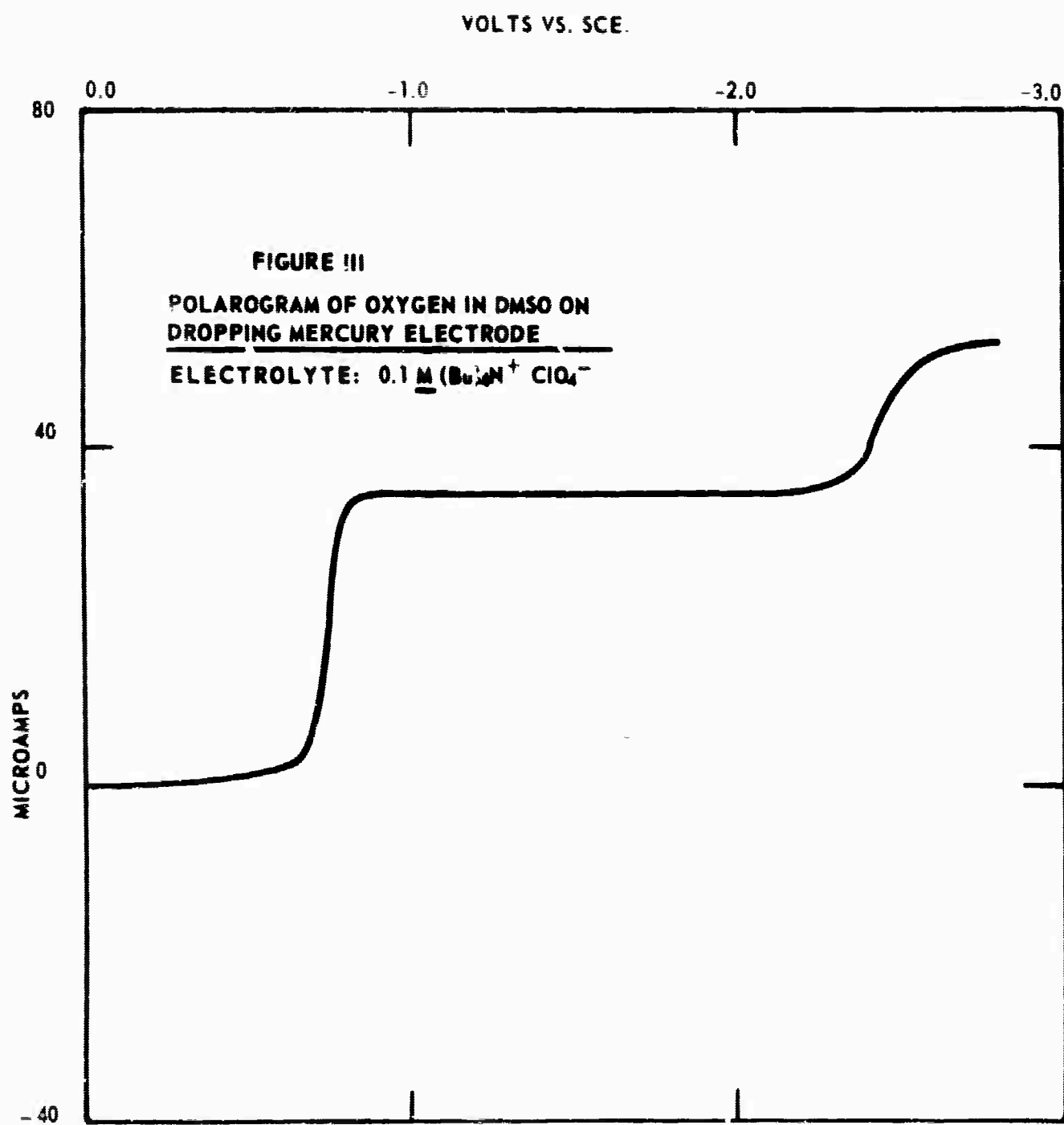
The intense electrochemiluminescence observed in the -2.3 to -2.5 volt region evidently involves a simple acid-base reaction between LH_2 and the bases produced by the second oxygen reduction process, resulting in the generation of substantial quantities of $\text{L}^{\cdot -}$. $\text{L}^{\cdot -}$ is known to react chemically directly with oxygen, producing light^{7,8,9,10}. The oxygen ion radical, $\text{O}_2^{\cdot -}$, while able to monoionize LH_2 , is apparently not a strong enough base to form significant quantities of $\text{L}^{\cdot -}$, hence the rate of the light producing reaction is very low when the potential is such that only the first oxygen reduction process is occurring. When the potential is sufficiently negative to carry out the second oxygen reduction, the concentration of $\text{L}^{\cdot -}$ is much higher and, consequently, the rate of light generation is much greater. The reaction occurring during the second oxygen reduction process in the presence of an acid (LH_2) are presumably:





VOLTS VS. SCE.



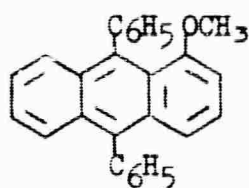


C. Anthracene Photoperoxides

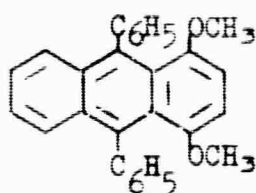
As discussed in Technical Report No. 3³, thermal decompositions of certain 9,10-diphenylanthracene photoperoxides are chemiluminescent and are reported to proceed cleanly to give the parent anthracene and oxygen as sole products^{11,12,13}. The reaction thus appears to provide an opportunity to investigate directly a one-step process producing an excited product. A number of photoperoxides are being prepared for an initial survey of chemiluminescence efficiencies and reaction products.

Photoperoxide Synthesis

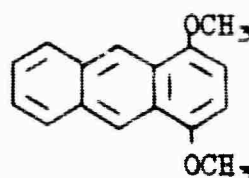
Anthracenes I through VI have been or are being prepared for conversion to the corresponding photoperoxides. Preparations of I and III were described in the previous report³.



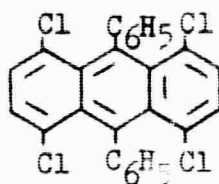
I



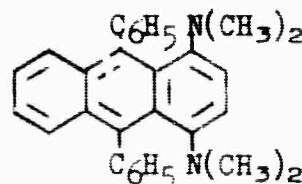
II



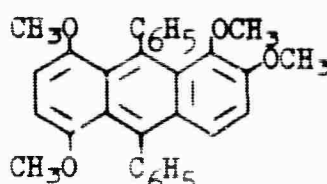
III



IV



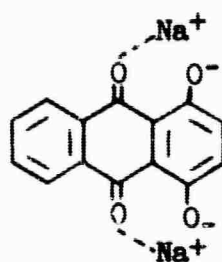
V



VI

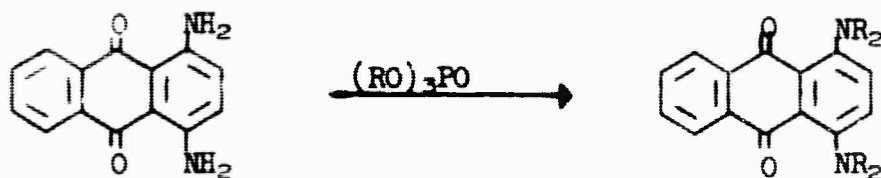
The synthesis of anthracene II, described in the previous report, has been substantially improved by carrying out the sodium hydride-dimethyl sulfate methylation of 1,4-dihydroxyanthraquinone in

1,2-dimethoxyethane instead of the more usual solvent, dimethylformamide. The yield of 1,4-dimethoxyanthraquinone was 55% in contrast to the 11% yield previously obtained. This marked improvement may be related to the known cation solvating power of 1,2-dimethoxyethane¹⁴ which could increase the reactivity of the alkoxide groups.



The over-all yield of anthracene II in the three-step synthesis³ is now 35%.

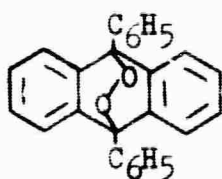
Compound IV was prepared from tetrachloro-anthraquinone by addition of phenyllithium and subsequent reduction of the diol with titanium trichloride. Zinc-acetic acid failed to effect the reduction even in the presence of small amounts of potassium iodide. Methylation of 1,4-diaminoanthraquinone to 1,4-bis(dimethylamino)anthraquinone required for the preparation of V failed with dimethyl sulfate in triethanolamine¹⁵ or in pyridine¹⁶. However, the alkylation was effected in a small



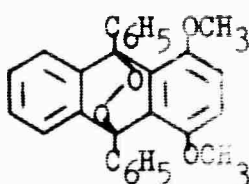
(3%) yield with triethyl phosphate. Further steps will involve addition of phenyllithium and reduction to Compound V.

A number of attempts were made to prepare 1,2,5,8-tetramethoxy-anthraquinone needed for preparation of VI. The complete methylation of 1,2,5,8-tetrahydroxyanthraquinone failed with potassium hydroxide-dimethyl sulfate. Very small yields (2-3%) were obtained with sodium hydride-dimethyl sulfate in 1,2-dimethoxyethane or in dimethylformamide. Another attempt will be made under other conditions.

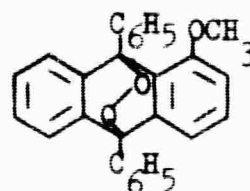
Three of the required photoperoxides have been prepared to date.



VII



VIII



IX

The photoperoxides were prepared by irradiating oxygen saturated solutions of the anthracenes with ultraviolet light. These reactions are tedious on a preparative scale, since quite dilute (0.5%) anthracene solutions are required to avoid concentration quenching and in some cases dimerization. Moreover, precautions must be taken to avoid light and thermal decomposition of the products. Photodecomposition can be avoided by using a pyrex filter to remove light below about 350 mμ. Thermal decomposition becomes serious on a preparative scale for compounds decomposing below room temperature, since the immersion lamp used as the ultraviolet source generates much heat. Adequate cooling of the lamp is necessary but is difficult for temperatures much below 0°.

Compound VII formed readily on irradiation of the parent anthracene in carbon disulfide saturated with oxygen. The carbon disulfide was dried over molecular sieves to remove water, a known inhibitor. Rapid agitation of the solution was also essential to assure a reasonable rate. Because of the strong absorption of carbon disulfide at wavelengths shorter than 375 m μ , agitation is required to renew the surface film of the solution that is effectively irradiated.

The methoxy-substituted anthracenes VIII and IX were converted to unidentified carbonyl containing products on photooxidation in carbon disulfide or in chloroform. The desired peroxides could be obtained, however, from reactions in diethyl ether or in ethyl acetate. Ether, however, presents a potential danger due to its tendency for peroxide formation, its high volatility, and its low autoignition point. Ethyl acetate is preferred.

Decomposition Studies

The chemiluminescence, reported in the literature, of peroxides VII and VIII has been confirmed. Peroxide VIII emits light above 30° in solution, but the chemiluminescence is readily observed only at 70-80° C. The quantum yield is estimated to be lower than that of the luminol system by visual observation. Compound VII is also chemiluminescent at temperatures above 230° C., but is substantially less efficient than VIII.

Decompositions of peroxides VII and VIII were followed in tetrachloroethylene solution by infrared analysis. The reactions were carried out in heated salt cells. An observable decomposition of VII

took place at 100° C. 9,10-Diphenylanthracene was the sole product up to 130° C. Peroxide VIII, however, decomposed at 100° C. to products exhibiting carbonyl and carboxyl bands. The expected anthracene was not detected. Decomposition of peroxide VIII in 2-methoxyethanol at 60° yielded at least some 1,4-dimethoxy-9,10-diphenylanthracene, however, as indicated by ultraviolet analysis. Although these observations indicate that the chemistry of the decomposition of some photoperoxides may be complex, a careful study of the decomposition will be required prior to a final conclusion.

SECTION I

EXPERIMENTAL

Reaction of Oxalyl Chloride with Tetralin Hydroperoxide - Addition of 5 ml. (5 millimoles) of 1 M oxalyl chloride in benzene to 25 ml. (10 millimoles) of 0.4 M tetralin hydroperoxide¹⁷ in benzene containing 5 mg. of 9,10-diphenylanthracene produced a brief blue chemiluminescence. When a similar reaction in ether containing 5 mg. rubrene was maintained at -78° C. for 10 minutes, then allowed to warm to room temperature, a weak long-lived yellow chemiluminescence was observed. Addition of hydrogen peroxide had no effect on the intensity, while the addition of water increased the intensity slightly.

Diisopropyl Diperoxycarbonate Decomposition - To 25 ml. of a 10^{-3} molar solution of 9,10-diphenylanthracene in ether was added 0.2 g. (1.1×10^{-3} mole) of diisopropyl diperoxycarbonate¹⁸. When the resulting solution was warmed on the steam bath a very weak light emission was observed. In a similar reaction with anhydrous 1,2-dimethoxyethane as the solvent, again a very weak chemiluminescence was observed on warming.

Reaction of Diisopropyl Diperoxycarbonate with Methane Sulfonic Acid in Glyme - The addition of 0.2 g. (1.1×10^{-3} mole) of diisopropyl diperoxycarbonate to 25 ml. of 0.5 molar methane sulfonic acid in glyme containing 10^{-3} moles per liter of 9,10-diphenylanthracene failed to produce light at room temperature. On heating to 60° the reaction still produced no light.

Reaction of Diisopropyl Diperoxycarbonate with Oxalyl Chloride - To 25 ml. of 0.5 M (12.5 millimoles) oxalyl chloride in anhydrous 1,2-dimethoxyethane containing 10^{-3} moles per liter of 9,10-diphenylanthracene was added 1.8 g. (10 millimoles) of diisopropyl diperoxy carbonate. Gas was evolved, but the reaction was dark. On warming to 60° a weak blue chemiluminescence was observed. In a similar reaction with ether as the solvent, no light was obtained at reflux. However, when water was added to the ether solution after refluxing, a weak blue chemiluminescence was observed.

Tertiary Butyl Peroxy Oxalyl Chloride¹⁹ - The procedure of the last report³ was followed up to the removal of the solvent at reduced pressure. An addition funnel in the apparatus was used to add 40 ml. of hexane to the distillation flask, and this fresh solvent was removed under reduced pressure. The process was repeated several times until the distillate no longer gave chemiluminescence when reacted with hydrogen peroxide solution containing 9,10-diphenylanthracene. The distillate also did not chemiluminesce when reacted with water in the presence of 9,10-diphenylanthracene indicating that no tertiary butyl

peroxy oxalyl chloride had distilled over. A known weight of hexane was then added to the distillation flask and the resulting solution was weighed to determine a crude yield; 6.1 g. (~68%) of material was obtained. The product was stored at -78°.

Dehydration of Ether-Hydrogen Peroxide Solutions - A one molar solution of hydrogen peroxide in ether was prepared by cautiously adding 37.8 g. (1.0 mole) of 90% hydrogen peroxide in water to ether and diluting to one liter in a volumetric flask. Aliquots of this solution were then allowed to stand over the dehydrating agents listed below for a 24-hour period. The absorbance of each solution at 1640 cm^{-1} was then measured and compared to that of the untreated solution.

<u>Dehydrating Agent</u>	<u>Absorbance</u>	<u>Moles/l. H_2O</u>
none	0.42	0.21
anhydrous MgSO_4	0.11	0.06
anhydrous Na_2SO_4	0.38	0.19
molecular sieve Type 5A	0.52	peroxide decomposed

Gaseous Products from Oxalyl Chloride-Hydrogen Peroxide Reactions - The reactions in Table II were carried out in an apparatus consisting of a 500 ml. round bottom flask equipped with a magnetic stirrer and fitted with two evacuated gas sample bulbs, a 10 ml. dropping funnel and a three-way stopcock leading to a helium tank, a differential manometer, and a vacuum pump. The total volume of the system was 620 ml. A solution of hydrogen peroxide in ether or dimethyl phthalate containing 10 mg. of 9,10-diphenylanthracene was placed in the flask, cooled to -78° C. and the system evacuated. The system was tested for leaks by observing changes in pressure with the manometer after isolating the vacuum pump by means of the stopcock. The cooling bath was removed and oxalyl chloride added from the dropping funnel. When chemiluminescence had ceased, the pressure of the system was observed and a sample of gas taken for analysis by mass spectroscopy. The system was then raised to atmospheric pressure with helium and a sample of gas taken for analysis by vapor phase chromatography (VPC). Mass spectroscopic analysis provided the mole fractions of ether, CO , CO_2 , O_2 , phosgene and nitrogen (to guard against leakage) present and thus allowed the calculation of the yields of the various products from the observed pressure, temperature and volume of the reaction system. Since only the CO_2 determination was free from possible interference by peaks from other components of the system, the reliability of oxygen and carbon monoxide analyses was considered uncertain. To double check these results, the VPC analysis was used to obtain the ratios of the various components to CO_2 . These ratios were compared with the unambiguous CO_2 analysis obtained by mass spectroscopy to determine the reported VPC yields. In experiments with inhibitor present, the inhibitor was added to the peroxide solution at the start. The experiments with reactants other than oxalyl chloride and hydrogen peroxide were conducted in a similar manner with the acid chloride being added from the dropping funnel to the oxidant in vacuo.

- 20 -

1,4-Dimethoxyanthraquinone - Fifty grams of 1,4-dihydroxyanthraquinone (Eastman) was extracted with three 1000-ml. portions of boiling acetone, and the combined extracts were decolorized with activated charcoal. Evaporation of the solvent provided material of satisfactory purity. Twenty grams (0.08 mole) of the purified anthraquinone were dissolved in 1.5 liters of hot 1,2-dimethoxyethane [previously dried over molecular sieve (Linde 4A)], and the solution was filtered, dried over element 1 sodium and decanted.

Sodium hydride dispersion (10 g. of 50% disp. in mineral oil, 0.2 mole) was washed three times with anhydrous 1,2-dimethoxyethane, centrifuged and decanted, (Caution: dry NaH is pyrophoric), then added in a slurry with dry 1,2-dimethoxyethane to the stirred solution of 1,4-dihydroxyanthraquinone.

The dark brown mixture was stirred one hr. at reflux temperature in a 3-necked flask equipped with water-cooled condenser, calcium chloride drying tube and mechanical stirrer. Freshly distilled dimethyl sulfate was added slowly to the stirred mixture. The reaction mixture was refluxed 2 hrs., then 6.3 g. (0.05 mole) of dimethyl sulfate was added. The reaction mixture was refluxed for one additional hr., and diluted with 3 volumes of water.

The quenched reaction mixture was saturated with sodium chloride, stirred for 1 hr., and filtered. The precipitate was collected on a filter, washed with water, dried on the filter under rubber dam, and digested in 2 liters of hot benzene. The benzene solution was treated with activated charcoal, filtered, evaporated to 1/3 its volume, then allowed to stand at 5° to obtain the crystalline product. The yellow needles were collected on a filter, washed with petroleum ether, and dried on the filter under rubber dam to obtain 10.2 g. of product. The benzene filtrate was diluted with 5 volumes of heptane to obtain an additional 2.1 g. of product. Total yield of product, (m.p. 170-171°), was 55.2%.

1,4,5,8-Tetrachloro-9,10-diphenyl-9,10-dihydroxy-9,10-dihydroanthracene - 1,4,5,8-Tetrachloroanthraquinone (25 g., 0.07 mole) was added slowly to a stirred solution of 175 ml. of 2.4 M phenyllithium in ether-benzene (Lithium Corp. of America) and 200 ml. tetrahydrofuran. The solution was stirred for 15 min. and allowed to stand for 2 hrs. Dilute acetic acid (200 ml., 10%) was added slowly to the stirred reaction mixture. The organic phase was separated, and the aqueous phase extracted with two 250 ml. portions of ether. The combined organic phase was washed with two 250 ml. portions of water, dried with MgSO₄, and evaporated to dryness to obtain 15 g. (42%) of red oil as product.

1,4,5,8-Tetrachloro-9,10-diphenylanthracene - 1,4,5,8-tetrachloro-9,10-diphenyl-9,10-dihydroxy-9,10-dihydroanthracene (1 g., 0.002 mole) was dissolved in 400 ml. anhydrous methanol. Titanium trichloride (10 g.) was added to the solution, and the reaction mixture was refluxed 10 hrs., filtered while hot, and the filtrate was cooled in an ice bath for 1 hr. The yellow-orange precipitate which separated was collected, chromatographed on neutral alumina in benzene, and recovered from the eluent by evaporation to obtain 0.2 g. (22%) of non-crystalline yellow product, whose infrared spectrum is in agreement with that expected for the desired product. Further identification will be carried out after the preparation of the compound on a larger scale.

1,4-(Diethylamino)anthraquinone - A mixture of 2.4 g. (0.01 mole) of 1,4-diaminoanthraquinone and 25 ml. of triethyl phosphate was refluxed 4 hrs. Then 75 ml. of 20% sodium hydroxide was added and the reaction mixture refluxed an additional hour.

The reaction mixture was diluted with 250 ml. of water, then extracted with two 500 ml. portions of benzene. The combined benzene solutions were washed with three 250 ml. portions of water, dried over magnesium sulfate, then evaporated to dryness. The semi-solid residue was taken up in benzene and chromatographed on a neutral alumina column prepared in hexane. The eluent was collected and evaporated to dryness to obtain 0.1 g. (13%) of brown product, whose infrared spectrum is in agreement with that expected for the desired product. Further characterization is planned when a larger sample is available.

Purification of Anthracenes - After repeated recrystallization from methanol, the samples described in the previous report³ were dried under vacuum at 80° and were submitted for elementary analysis.

9,10-Diphenylanthracene

Calcd. for $C_{26}H_{18}$: C, 94.51; H, 5.49.

Found: C, 94.68; H, 5.49.

m.p. 250-51°, Lit. m.p. 250-51°²⁰

1,4-Dimethoxyanthracene

Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92; O, 13.43.

Found: C, 80.62; H, 6.02; O, 13.31.

m.p. 136-37°, Lit. m.p. 137°²¹

1-Methoxy-9,10-diphenylanthracene

Calcd. for $C_{27}H_{20}O$: C, 89.97; H, 5.60; O, 4.44.

Found: C, 89.69; H, 5.76; O, 4.61.

m.p. 179-180°, Lit. m.p. 176-177°²²

1,4-Dimethoxy-9,10-diphenylanthracene

Calcd. for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68; O, 8.19.

Found: C, 85.88; H, 6.01; O, 7.89.

m.p. 199-200°, Lit. m.p. 202-203°²³

9,10-Diphenylanthracene Photoperoxide - A three-neck flask (1000 ml.) was provided with a capillary oxygen inlet tube, and with a dry ice condenser protected by a drying tube. A solution of 7.79 g. of 9,10-diphenylanthracene (Aldrich Chemical Co.) in 800 ml. of carbon-disulfide (Baker Analyzed Reagent, dried over molecular sieves, Linde 4A) was added to the flask and was agitated vigorously with a magnetic stirrer. The solution was irradiated with a 140 Watt Hanovia "utility" mercury lamp through a pyrex filter for 32 hours. At that time a sample of the solution evaporated to dryness showed no fluorescence when it was redissolved in benzene.

The mixture was evaporated to dryness and was twice recrystallized from carbon disulfide to obtain 7.4 g. (87%) of peroxide, m.p. 184° dec. (melting point depends on rate of heating).

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.18; H, 5.00; O, 8.83;
mol. wt., 362.14.

Found: C, 86.19; H, 5.16; O, 8.14;
mol. wt., 390 (vapor pressure thermister method in chloroform²⁴).

1-Methoxy-9,10-diphenylanthracene Photoperoxide - A solution of 0.5 g. of 1-methoxy-9,10-diphenylanthracene (Aldrich Chem. Co.) in 1800 ml. of ethyl acetate was placed in a photoreactor, which consisted of a cylindrical pyrex vessel (diameter: 100 mm; length: 300 mm) equipped with three tapered glass joints (60/50, 19/38, 24/40) to accommodate, respectively, a Hanovia immersion well (19433, Vycor) containing a 450 Watt mercury lamp (67QA-36) with pyrex filter, a capillary for oxygen addition and a dry ice condenser protected by a mercury bubbler valve to exclude air and moisture. An ice bath was used to cool the solution and ice water was circulated via a pump in the jacket of the immersion well. The solution was vigorously agitated by a large magnetic stirrer.

The irradiation was carried out in three 15-min. intervals interrupted by 15-min. cooling periods. At this point ultraviolet analysis showed essentially no unreacted anthracene present.

The reaction mixture was evaporated to dryness under vacuum and the residue was recrystallized from ether to obtain 0.25 g. (46%) of photoperoxide, m.p. 173° dec. Infrared and ultraviolet spectra were in agreement with the assigned structure.

Analysis is pending.

1,4-Dimethoxy-9,10-diphenylanthracene Photoperoxide - A solution of 1,4-dimethoxy-9,10-diphenylanthracene in 650 ml. of anhydrous ether (Mallinckrodt Chem. Works) was placed in a photoreactor. The reactor was a small version (length: 250 mm, diameter: 80 mm) of the one described above for the preparation of 1-methoxy-9,10-diphenylanthracene photoperoxide. Cooling was provided by a dry ice-alcohol bath. The immersion well of the lamp was cooled by passing nitrogen gas through the jacket. (Ether as solvent creates a potentially hazardous condition by its tendency for peroxide formation and due to the possible overheating of the lamp coupled with the low auto-ignition temperature of ether. Ethyl acetate will be used for future experiments.)

The irradiation lasted for two 15-min. intervals interrupted by a 15-min. cooling period. Ultraviolet analysis showed no significant amount of unreacted anthracene.

The product (0.15 g., 70%) was recrystallized from ether. Infrared and ultraviolet spectra agreed with the assigned structure.

Chemiluminescence of Photoperoxides

Household Wax (Esso) was melted in a ceramic casserole and heated to the desired temperature with an electric immersion heater. This molten paraffin wax was vigorously agitated via a magnetic stirrer. The experiment was carried out in a dark room. After the lights were turned off, a small sample (~0.01 g.) of the photoperoxide was added to the hot paraffin bath. The chemiluminescence was observed visually.

9,10-diphenylanthracene photooxide: Short lived (1-2 seconds), weak intensity, blue light observable only over 230°.

1,4-dimethoxy-9,10-diphenylanthracene: Blue light readily observed at 60-70° with a life time of 0.5-1 minute. The light is much more intense and has a shorter duration (4-5 seconds) at 120°.

Decomposition Study of 9,10-Diphenylanthracene Photoperoxide VII -

A Perkin-Elmer 521 infrared spectrophotometer was used for the study. Sodium chloride solution cells provided with electric heater and thermocouple were employed for the measurement. A solution (~20%) of VII in tetrachloroethylene (Eastman Spectro Grade) was placed into the cell and was heated in 20° steps accompanied with periodic scanning. The decomposition of the photoperoxide was monitored at the wave numbers: 1455, 671 and 633 cm^{-1} . The appearance of anthracene was followed at the wave numbers: 1381, 660, and 607 cm^{-1} . Detection of other compounds was feasible at regions where the solvent tetrachloroethylene did not absorb (4000-1360, 1330-1200, 1100-1000, 725-600 cm^{-1}).

No decomposition of the photoperoxide occurred below 100°. Above this temperature sole product of the decomposition was 9,10-diphenylanthracene. Neither intermediates nor by-products were detected.

Decomposition Study of 1,4-Dimethoxy-9,10-diphenylanthracene Photoperoxide VIII - A study of the decomposition was carried out using an infrared technique identical to that described above for VII.

The decomposition of VIII in tetrachloroethylene up to 100° resulted in products showing carbonyl and carboxyl absorption bands at 1603, 1667, and 1735 cm^{-1} . Bands corresponding to the expected anthracene were not observed under these conditions.

Because photoperoxide VIII is insufficiently soluble in non-polar solvents (e.g. 1-octane), 2-methoxyethanol was chosen as solvent for the study of the decomposition by ultraviolet analysis. The solution was maintained at 60° in a constant temperature bath. Samples were withdrawn periodically and analyzed by Cary 14 spectrometer. The photoperoxide was monitored at λ 260-320 $\text{m}\mu$ and the anthracene was followed at λ 360-420 $\text{m}\mu$. Bands corresponding to the anthracene appeared gradually during the decomposition. However, the final decomposition product contained less than 50% of the theoretical anthracene yield.

SECTION II

STRUCTURAL CRITERIA FOR CHEMILUMINESCENT COMPOUNDS

A. Relationship of Peroxides to Chemiluminescence

While chemiluminescence is observed during oxidations of a variety of apparently unrelated organic compounds, with few exceptions appreciable chemiluminescence is observed only from oxidations by oxygen or hydrogen peroxide. This almost general oxygen requirement has been interpreted by others^{4,10} in terms of oxygen promoted triplet-singlet intersystem crossing. However, the relatively high efficiencies of the 3-aminophthalhydrazide^{2,8,10} and oxalyl chloride chemiluminescent⁴ systems are not consistent with a process involving triplet intermediates. In a triplet process the maximum efficiency would necessarily be that observed in slow fluorescence and be less than about 10^{-3} ²⁶. Moreover, we have demonstrated (Section IIB) that oxygen is not essential to oxidative organic chemiluminescence.

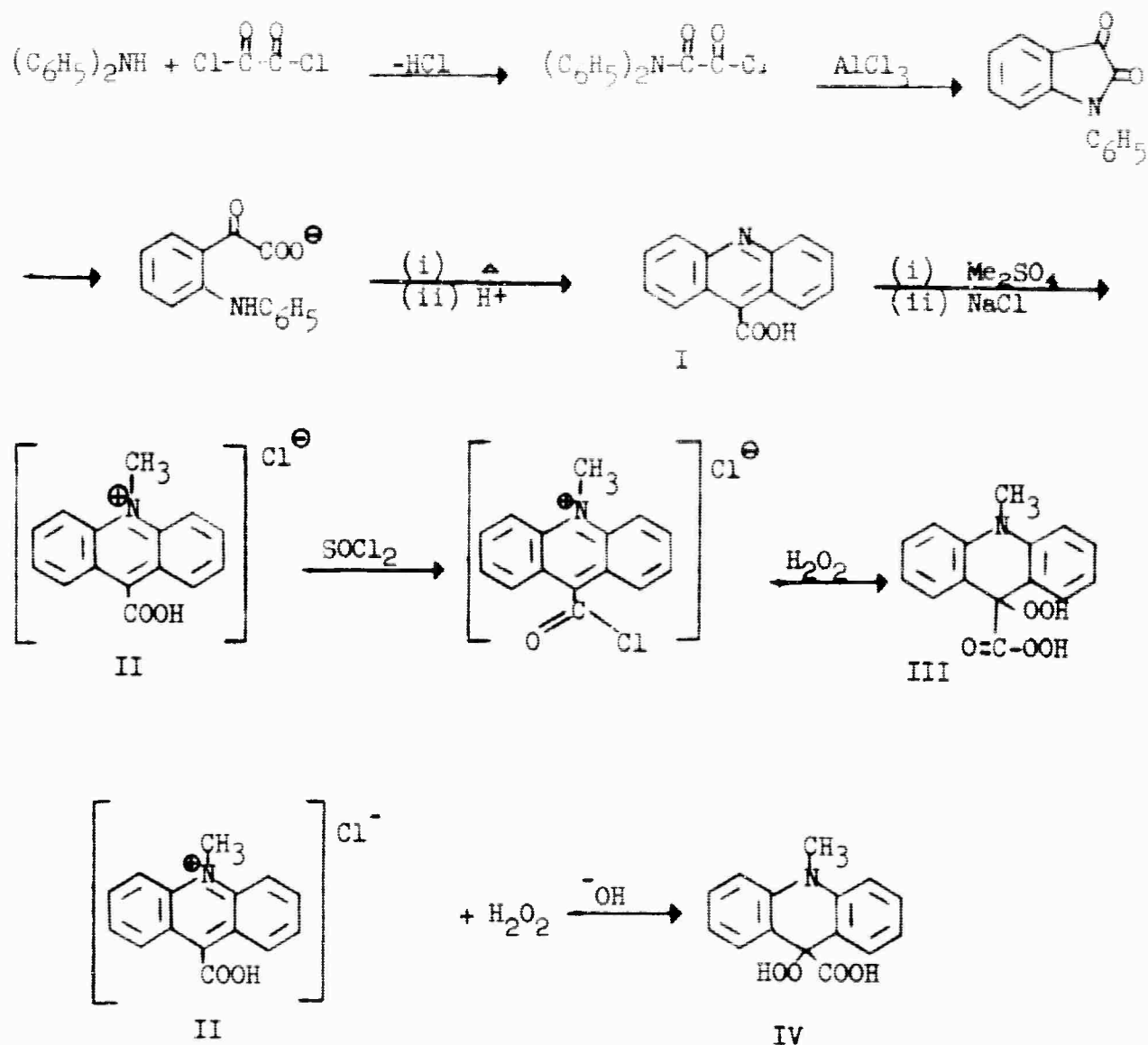
The action of oxygen or hydrogen peroxide in chemiluminescence is better explained in terms of the formation of essential peroxidic intermediates¹. Thus while a variety of oxidizing agents will oxidize 3-aminophthalhydrazide, only oxygen or hydrogen peroxide would accommodate the formation of a hydroperoxide intermediate. Moreover, several unambiguous hydroperoxide decompositions are, in fact, chemiluminescent. Prominent examples include the tetralin hydroperoxide-porphyrin reaction²⁷, the oxalyl chloride-hydrogen peroxide system (Section IA), and the anthracene photoperoxide decomposition reaction (Section IE).

The generality of the relationship between peroxide decomposition and chemiluminescence is being examined by the design and synthesis of new compounds. The potential chemiluminescent compounds described below have been selected to meet three criteria: (1) Formation of fluorescent decomposition products; (2) Ease of preparation (although synthesis in this area is inherently difficult); (3) Structural variation to provide a correlation between structure and chemiluminescence efficiency.

1. Peroxides Based on the Acridine System

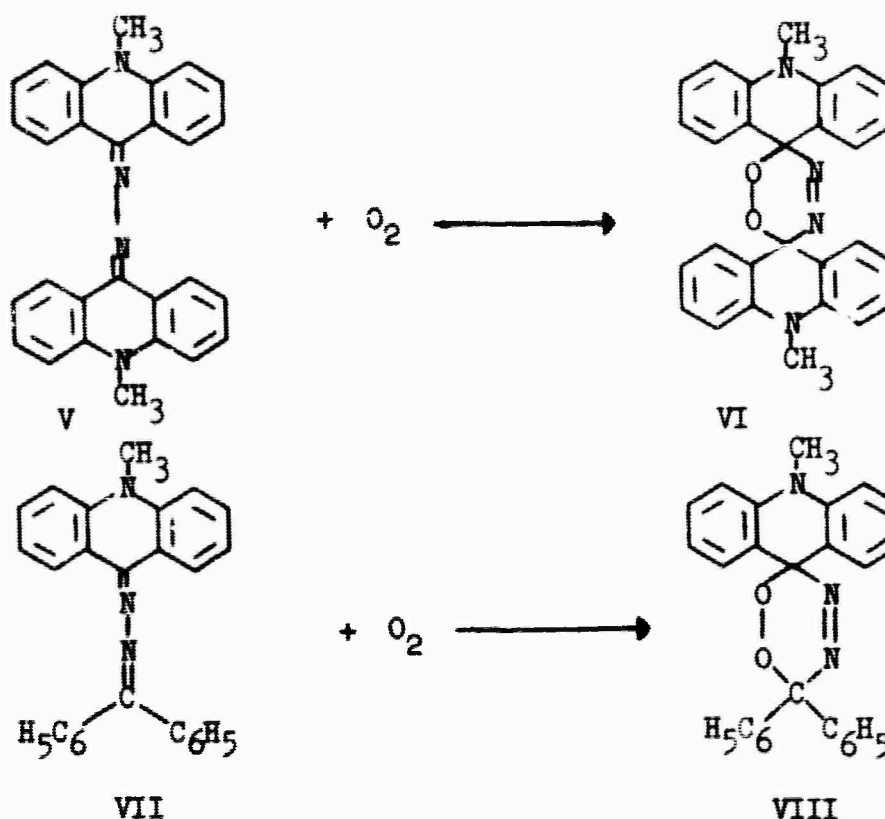
The acridines represent a particularly attractive compound group upon which to base the design of new chemiluminescent materials. Many members of the class have the high fluorescence efficiency required for an efficient emitting species in chemiluminescence. Moreover, several reactive acridine derivatives can be readily prepared to serve as versatile starting materials for synthesis. Some approaches and attempts to synthesize potentially chemiluminescent compounds based on acridine chemistry were described in Technical Report Nos. 1¹ and 3³.

In Technical Report No. 3 we reported progress toward the synthesis of acridine peroxides III and IV by the following route:



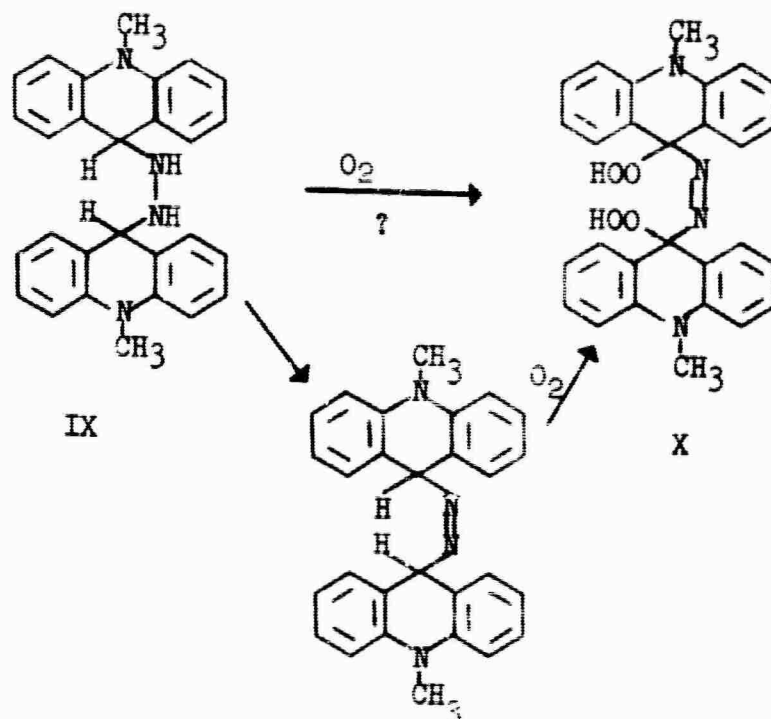
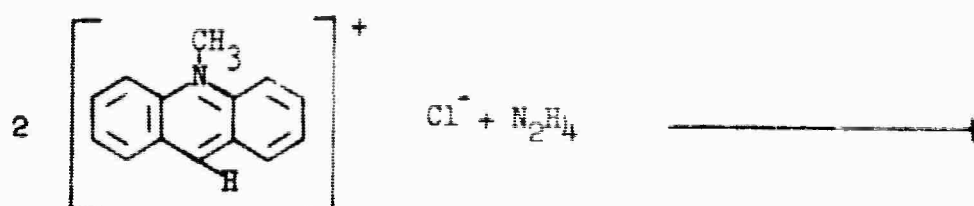
9-Carboxyacridine, I, had been satisfactorily prepared, and we indicated tentatively that its methylation had provided 9-carboxy-10-methylacridinium chloride, II. Closer examination of the methylation product, however, has demonstrated that the product obtained was actually the isomeric 9-carbomethoxyacridine hydrochloride. Methylation of I under more vigorous conditions is expected to provide 9-carbomethoxy-10-methylacridinium chloride, and acid hydrolysis of the ester is expected to provide the desired acid II.

Efforts to prepare the azo peroxides VI and VIII by autooxidations of azines V³ and VII³ have been unsuccessful.



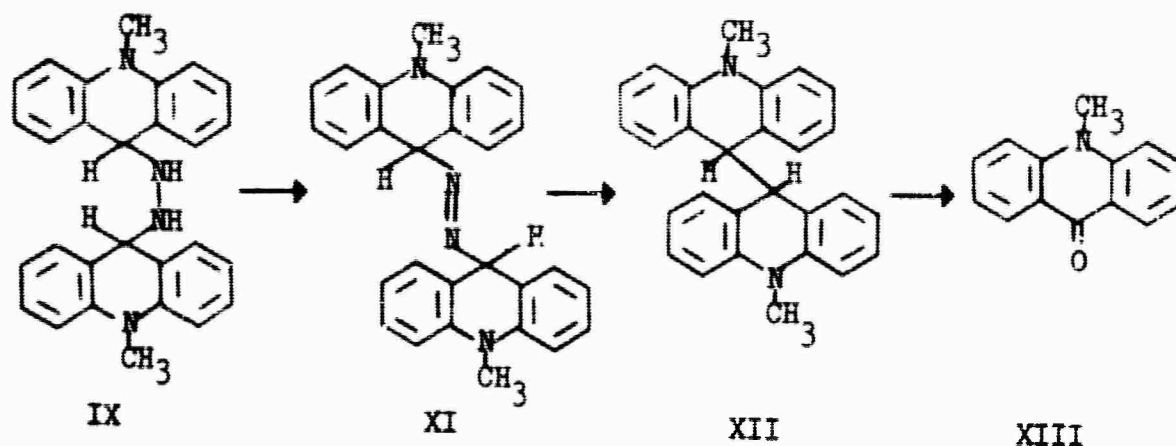
Attempted reactions of V or VII with oxygen in the presence of cobalt naphthenate under ultraviolet irradiation in chloroform for extended reaction periods resulted only in unchanged starting materials. An additional attempt will be made under more vigorous conditions.

Preparation of the hydrazine bis acridan, IX, wanted as a possible precursor for peroxide X, has been achieved in moderate yields by reaction of 10-methylacridinium chloride with hydrazine under mild conditions under an inert atmosphere.



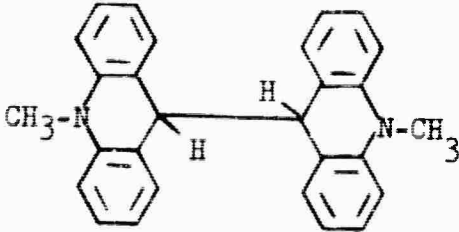
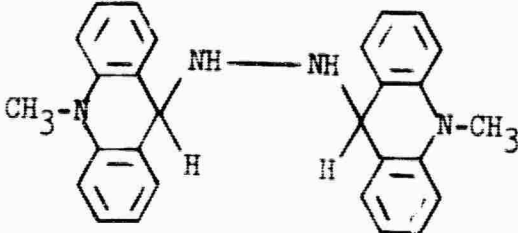
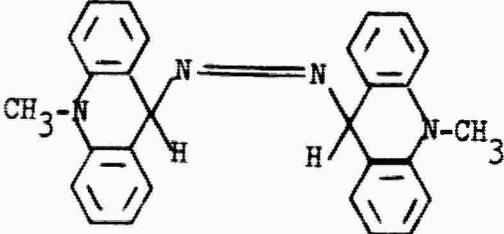
Hydrazine IX was found to be highly sensitive toward oxygen and was contaminated with its oxidation products even when moderate precautions were taken to exclude oxygen during its preparation and isolation.

Autooxidation of IX is complex, and it is now uncertain that X can be prepared by this route. Addition of oxygen to a solution of IX in methylene chloride at -60° has been indicated by n.m.r. analysis to proceed by the following course:



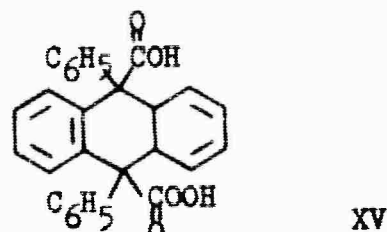
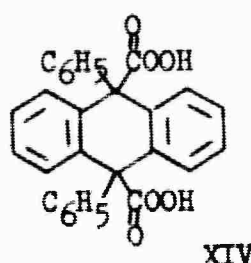
Compounds IX and XII exhibit distinct pairs of absorption peaks in their n.m.r. spectra for the N-methyl groups and 9,9' protons. Another distinct pair of similar peaks (all pairs show the anticipated 3:1 ratio on integration) in the spectrum of crude IX correlate well with the predicted chemical shifts of XI (a summary of τ -scale chemical shifts for these derivatives in chloroform-d is given in Table I). This latter pair of peaks increases during oxidation at -60° C. with concurrent diminution of those due to IX. At room temperature, however, peaks due to XII also increase, suggesting thermal loss of nitrogen from XI. Compound XII was also the only isolable product when IX was oxidized by mercuric oxide in chloroform at room temperature. The transformation of XII to XIII was demonstrated independently by infrared analysis of a chloroform solution of XII on exposure to air. A more detailed n.m.r. study of the low temperature oxidation of IX is planned in order to confirm the transformations outlined above and to determine whether the azo compound XI can be oxidized to X.

Table I

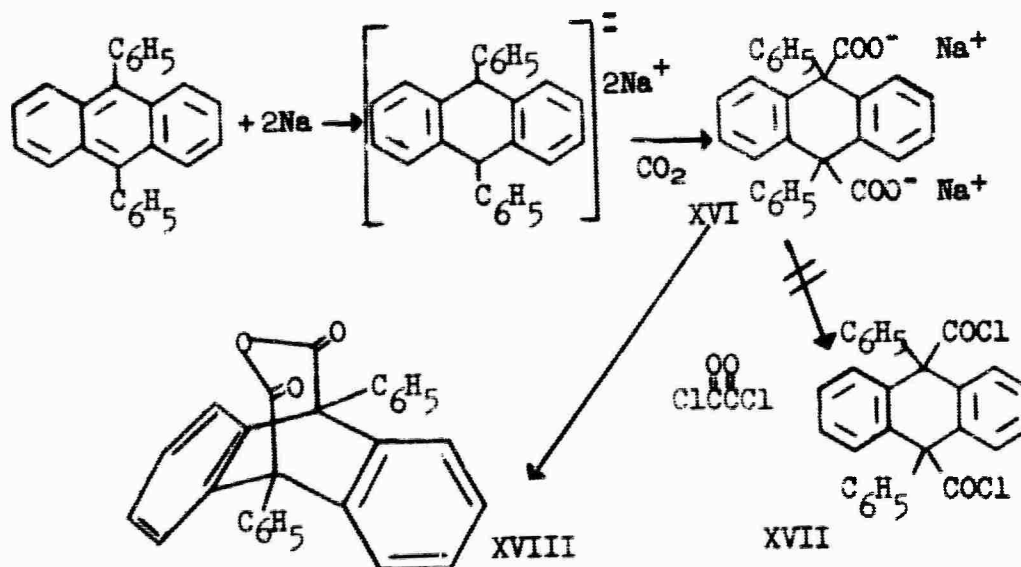
Compound	Linking Group	N-CH ₃	9,9' C-H
XII		7.03	6.08
IX		6.62	5.50
XI		6.54	4.43

2. Peroxycarboxylic Acid Chemiluminescence

Mechanism studies in progress (see Section I of this and preceding reports), while incomplete, suggest that peroxyacids XIV and XV will provide chemiluminescence on decomposition.



Carbonation of the dianion produced by the action of sodium metal on 9,10-diphenylanthracene afforded the disodium dicarboxylate (XVI). Treatment of this dicarboxylate with oxalyl chloride resulted in a



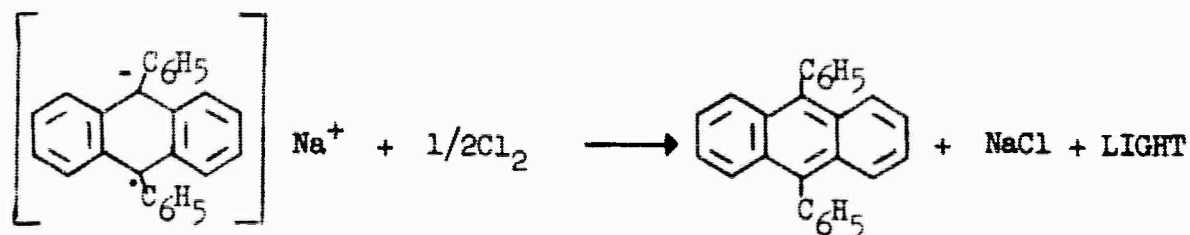
vigorous reaction. The product, however, was not XVII but the bridged anhydride, XVIII. Evidently, as the acid chloride is formed in the 9-position, immediate cyclisation occurs by displacement via the carboxylate anion in the 10-position. The anhydride is expected to be useful for the synthesis of XV.

B. Ion Radical Chemiluminescence

During the fourth quarter two new classes of chemiluminescent reactions were discovered involving oxidations and reductions of certain aromatic hydrocarbon derivatives. In the first, chemiluminescence was found to accompany certain oxidations of anion radicals to corresponding fluorescent hydrocarbons or heterocycles. The second new process may involve the reduction of a cation radical to a fluorescent compound.



Anion radical chemiluminescence is illustrated by the oxidation of sodium 9,10-diphenylanthracenide by chlorine in tetrahydrofuran.



The reaction is essentially instantaneous, generating a bright blue flash. The color of the emission is typical of 9,10-diphenylanthracene fluorescence. During the reaction the solution loses the dark opacity characteristic of the radical ion and becomes transparent. The blue fluorescence of 9,10-diphenylanthracene is clearly evident.

Results obtained by oxidizing sodium 9,10-diphenylanthracenide with other oxidants are summarized in Table II. Chemiluminescence was observed in oxidations of chlorine and bromine but not iodine. Similarly, chemiluminescence was generated by benzoyl peroxide but not oxygen.

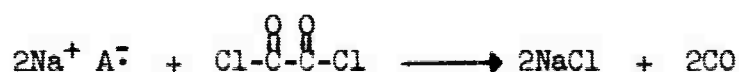
Table II

Effect of Various Oxidants on Sodium
9,10-Diphenylanthracenide in Tetrahydrofuran

<u>Oxidant</u>	<u>Chemiluminescence Intensity</u>	<u>Color</u>
Chlorine	strong	blue
Bromine	strong	blue
Iodine	none	-
<u>t</u> -Butylhypochlorite	medium	blue
Oxalyl chloride	medium	-
Oxygen	none	-
Benzoyl peroxide	strong	blue
Hydrogen peroxide	none	-
Potassium superoxide	none	-
Benzil	none	-
Benzophenone	none	-
7,7,8,8-Tetracyanoquinonodimethane	none	-
Diphenyldisulfide	none	-
Potassium persulfate	weak	-
Potassium permanganate	none	-
Potassium ferricyanide	none	-

Since each of these five oxidants convert the ion radical to the anthracene, iodine and oxygen evidently release insufficient energy to produce an excited intermediate. Other explanations are possible, however, and are being investigated.

Tertiarybutyl hypochlorite produced a medium intensity chemiluminescence as did oxalyl chloride. The latter reaction presumably occurs as indicated in the equation below.



Similarity is evident between this reaction and the chemiluminescent reaction between oxalyl chloride and hydrogen peroxide in the presence of 9,10-diphenylanthracene (Section IA), and a possible mechanistic correspondence is being investigated.

Other organic electron acceptors such as benzoquinone and 7,7,8,8-tetracyanoquinonedimethane failed to produce chemiluminescence. While the latter is a strong oxidant, it may quench anthracene fluorescence. Oxidants containing active hydrogen, such as hydrogen peroxide, were ineffective, as expected. The reaction mechanism with such materials follows an entirely different course²⁸. Inorganic oxidants insoluble in tetrahydrofuran were also ineffective with the exception of potassium persulfate, which produced a weak emission. Oxidation at an electrolytic anode was also observed to produce luminescence.

Results obtained from oxidizing a series of anion radicals are summarized in Table III. The required anion radical was generally prepared by reaction of sodium naphthalenide with the corresponding aromatic hydrocarbon or heterocycle²⁹, but in some cases the anion

Table III
Anion Radical Chemiluminescence

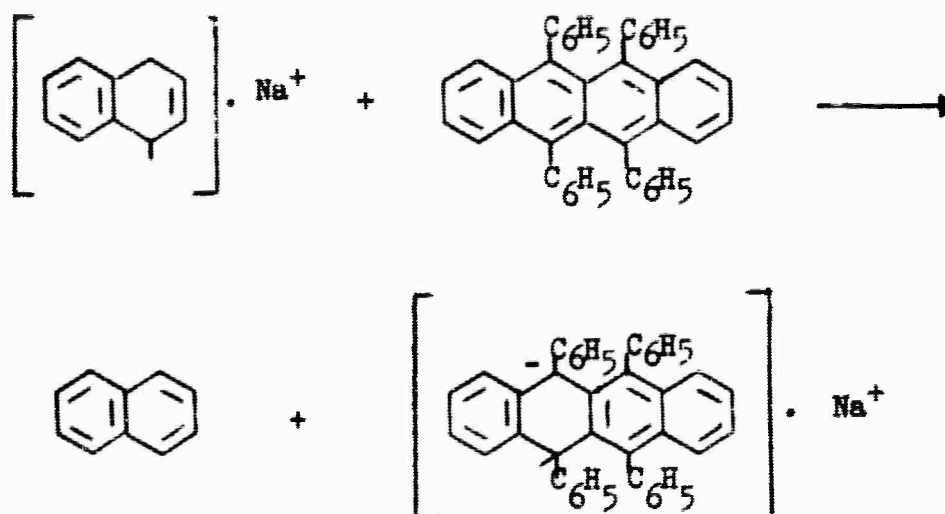
<u>Substrate</u>	<u>Reducing Agent</u>	<u>Solvent</u>	<u>Oxidant</u>	<u>Intensity</u>	<u>Color</u>
Anthracene	Na NAP	THF	Cl ₂	Very weak	Blue
Anthracene	Na ₂ STILB	THF	Bz. perox.	None	-
1,4-Dimethoxy-anthracene	Na NAP	THF	Cl ₂	Weak	Blue
9,10-Diphenyl-anthracene	Na	THF	Cl ₂	Strong	Blue
9,10-Diphenyl-anthracene	Na	THF	Bz. perox.	Strong	Blue
9,10-Diphenyl-anthracene	Na NAP	THF	Bz. perox.	Strong	Blue
9,10-Diphenyl-anthracene	Na ₂ STILB	THF	Bz. perox.	Strong	Blue
1-Methoxy-9,10-diphenylanthracene	Na NAP	THF	Bz. perox.	Medium	Blue
1,4-Dimethoxy-9,10-diphenylanthracene	Na NAP	THF	Bz. perox.	Medium strong	Green
1,4-Dimethoxy-9,10-diphenylanthracene	Na ₂ STILB	THF	Bz. perox.	None	-
Rubrene	Na NAP	THF	Bz. perox.	Strong	Yellow
Rubrene	Na ₂ STILB	THF	Bz. perox.	Strong	Yellow
Pyrene	Na NAP	THF	Bz. perox.	Weak	Blue
Pyrene	Na ₂ STILB	THF	Bz. perox.	None	-
Coronene	Na NAP	THF	Bz. perox.	Medium	Blue
Decacyclene	Na NAP	THF	Bz. perox.	Very weak	Green
2,3-Benzofluor-anthene	Na NAP	THF	Bz. perox.	Medium	Blue

Table III (Continued)

Substrate	Reducing Agent	Solvent	Oxidant	Intensity	Color
Dinaphthalene oxide	Na NAP	THF	Bz. perox.	Medium	Blue
1,3-Diphenyl-isobenzofuran	Na NAP	THF	Cl ₂	Very weak	Blue
1,7-Phenanthrolene	Na NAP	THF	Bz. perox.	Very weak	-
1,10-Phenanthrolene	Na NAP	THF	Bz. perox.	Very weak	-
Benzodiphen-anthridine	Na NAP	THF	Bz. perox.	Medium	Blue
N-methyl-paenothiazine	Na NAP	THF	Bz. perox.	Medium	Blue
<u>Trans</u> -stilbene	Na	THF	Cl ₂	None	-
<u>Trans</u> -stilbene	Na NAP	THF	Cl ₂	None	-
<u>Trans</u> -stilbene	Na ₂ STILB	THF	Bz. perox.	None	-

Negative chemiluminescence results were obtained by benzoyl peroxide oxidations of mixtures of sodium naphthalenide with acridine, dimethyldibenzisoquinoline, pentaphenylphosphole, anthraquinone, 1,4-dimethoxyanthraquinone, 7-H-benz(d,e)-anthracen-7-one, and disodium fluorescein.

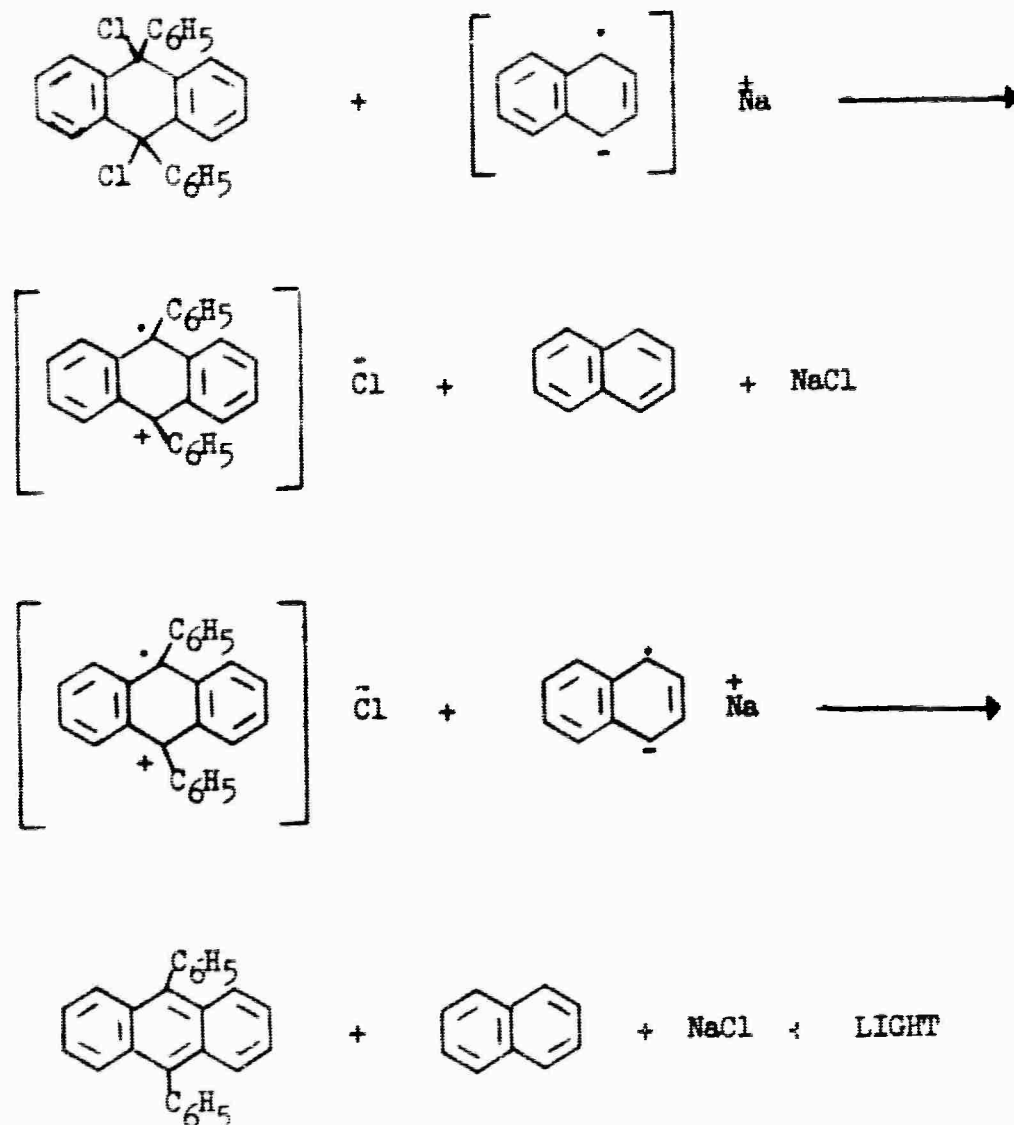
radical was prepared from reaction with disodium stilbene dianion or by direct reaction with sodium²⁸.



The ability of sodium naphthalenide to transfer an electron to higher polycyclic aromatic hydrocarbons has been well documented in the literature²⁹. However, the formation of some of the heterocyclic anion radicals by this reaction is less secure and will require additional proof.

All of the fluorescent polycyclic aromatic hydrocarbon anion radicals studied generated chemiluminescence on oxidation. Some of the fluorescent heterocycles were effective, while others were not, as indicated in Table III. Side reactions may be important where negative results were obtained; this will be studied further. Chemiluminescence was not obtained by oxidation of the stilbene anion radical or disodium stilbene. Evidently the reaction fails to produce a singlet excited state of trans-stilbene. Oxidation of several ion radicals derived from fluorescent ketones also failed to produce light.

Cation radical chemiluminescence may be involved in the reaction of 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene with sodium naphthalenide.



The over-all reaction is essentially instantaneous and provides a bright blue flash of light. Blue fluorescence apparently corresponding to 9,10-diphenylanthracene is evident in the reaction product. The validity of the hypothetical cation radical intermediate will require further evidence. Chemiluminescence is also observed when 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene is reduced with sodium metal, disodium

stilbene dianion, sodium stilbene anion radical, or sodium 9,10-diphenylanthracenide. The latter reaction may be a combination of anion radical and cation radical chemiluminescence. Attempted reactions of the chloroanthracene with zinc, magnesium, aluminum, lithium dicyclohexylphosphide, sodium hydride and sodium borohydride were not chemiluminescent, although with the metal hydrides chemical reaction was observed to occur. Reaction with lithium aluminum hydride in the presence of oxygen produced a weak yellow chemiluminescence entirely different from 9,10-diphenylanthracene fluorescence. In contrast to the chemiluminescent reactions described above, emission was not observed in the absence of oxygen.

These demonstrations of bright (although brief) chemiluminescence under oxygen-free conditions indicate that oxygen does not play an essential and general role in the chemiluminescent process. The requirement of oxygen (or hydrogen peroxide) in other liquid phase chemiluminescent reactions such as 3-aminophthalhydrazide or oxalyl chloride oxidations seems best explained in terms of essential hydroperoxide intermediates which cannot be generated by other oxidants. (See Section IIA)

The chemistry of anion radicals and, to a lesser extent, cation radicals has been described in some detail in the literature³⁰. Ion radical chemiluminescence, however, has not been reported, to our knowledge. The reactions reported here appear to involve electron transfer processes. It is possible that electron transfer may be directly involved in some of the known solution chemiluminescent reactions. Luminescence apparently

related to electron transfer has been observed previously in both the gas and solid phases, as illustrated by the reactions of chlorine with sodium vapor³¹ and by cation-electron recombination following irradiation of certain solid glasses and crystals³². The present work seems to be the first authentic example of electron transfer luminescence in solution.

Additional work will be carried out to define the scope, conditions, and mechanism of solution ion radical chemiluminescence and related processes.

SECTION II

EXPERIMENTAL

Methyl 9-acridine Carboxylate - The product previously reported in Technical Report No. 33 to be 9-carboxy-10-methylacridinium chloride was shown to be methyl 9-acridine carboxylate hydrochloride by treatment of a suspension of the material (150 mg.) in 30 ml. of water with 5 ml. of saturated aqueous sodium bicarbonate. The yellow color was immediately discharged and the white precipitate was extracted with methylene chloride. The extract was evaporated and dried with sodium sulfate to afford almost pure off-white crystals of methyl-9-acridine carboxylate, m.p. 127.5-128.5° (lit³³ 128-130°).

Anal: Calcd. for $C_{15}H_{11}NO_2$: C, 75.9; H, 4.67; N, 5.9.

Found: C, 75.5; H, 4.50; N, 6.2.

Attempted Air Oxidation of 10-Methylacridan-9-one Azine (V) - A solution of 1 g. of V3 in 500 ml. of chloroform was treated with 1 ml. of a commercial 6% solution of cobalt naphthenate (Nuodex). Oxygen was passed through the solution via a capillary for fourteen hours, an aliquot was withdrawn and evaporated. The recovered red solid exhibited an infrared spectrum identical to that of V. The solution was then irradiated with a Hanovia lamp for eight hours while oxygen was bubbled through the solution, but again no change was observed in the infrared spectrum of recovered solid material.

Preparation of 9,9'-Hydrazobis(10-methylacridan) (IX) - To a solution of 20 ml. of hydrazine hydrate in 200 ml. of water in a 2-l. Erlenmeyer flask equipped with a magnetic stirrer and flushed with nitrogen, a freshly prepared solution of 10 g. of N-methylacridinium chloride in 500 ml. of water was added. A white solid immediately precipitated, and the mixture was stirred for 1 hour. The white solid dissolved on addition of 500 ml. of chloroform. The organic layer was separated, extracted with 500 ml. of water, separated, dried over magnesium sulfate and filtered to obtain a clear pale yellow chloroform solution of product (a nitrogen stream was maintained through all flasks and funnels during these operations). The chloroform was evaporated to ca. 50 ml. at the aspirator using a nitrogen capillary bleed. Some solid had separated from the cold dark brown solution but redissolved on brief warming. The flask was swirled as 200 ml. of methanol was added. Almost immediately after the addition rapid crystallization occurred and the mixture was stored overnight in an icebox. The product was filtered and dried in vacuo to afford 6.05 g. (66.5%) of off-white crystals. The m.p. was indeterminate; slow decomposition occurred between 170-250°. The n.m.r. spectrum indicated the presence of impurities corresponding to oxidation products of IX. (See Table L)

Anal: Calcd. for $C_{28}H_{26}N_4$: C, 80.3; H, 6.22; N, 13.4.

Found: C, 80.4; H, 6.09; N, 12.9.

Oxidation of 9,9'-Hydrazobis(10-methylacridan) (IX) with Mercuric Oxide - In a 100-ml. flask bearing a drying tube and nitrogen inlet, 2 g. of hydrazo compound (IX) was dissolved in 50 ml. of chloroform and 1.6 g. of mercuric oxide was added. The mixture was surrounded by an ice bath and magnetically stirred under nitrogen for three hours. Sodium sulfate (ca. 5 g.) was added together with 25 ml. of chloroform, the mixture stirred a further two hours and then filtered. Chloroform was evaporated in a nitrogen stream at the aspirator until the volume was ca. 25 ml. The addition of 50 ml. of methanol produced crystallization. The solid was collected and dried in vacuo to afford 1 g. of material, m.p. $\sim 240-260^\circ$ dec. (Lit.³⁴ ca. 280° dec.), which was shown by infrared and n.m.r. spectra to be 9,9'-bis(10-methylacridan).

Oxidation of 9,9'-Hydrazobis(10-methylacridan) (IX) at -60° - A boiling tube containing 1 g. of the crude hydrazo compound (IX) dissolved in 50 ml. of methylene chloride was immersed in a dry ice bath. Air was bubbled through the solution, which was maintained below -60° , for five hours via a capillary. Some crystallization occurred, but on warming to room temperature, a clear solution was obtained contaminated with a small upper layer of water. The solution was dried briefly over magnesium sulfate, filtered and the filtrate evaporated at the aspirator using a nitrogen capillary bleed. The brown solid thus obtained was analyzed by n.m.r. and though the major component was that assigned the azo structure (XI), the presence of the starting hydrazo compound (IX), the bis(acridan) (XII) and the acridone (XIII) was noted. The approximate molar ratio of these compounds appeared to be: XI:IX:XII:XIII = 5:3:3:1.

Preparation of 9,10-Dihydro-9,10-diphenylanthracene-9,10-dicarboxylic Anhydride - A solution of 3.3 g. of 9,10-diphenylanthracene (Aldrich Chem. Co.) in 100 ml. of tetrahydrofuran was treated with approx. 1 g. of freshly cut sodium pieces. The mixture was stirred magnetically for 72 hours in a nitrogen atmosphere in a stoppered flask. The solution became violet-black. The flask was opened under nitrogen pressure and carbon dioxide gas was rapidly swept over the surface of the solution. The mixture became pink. The mixture was diluted with excess water and a solid crystallized. Fractional crystallization from acetic acid afforded only mixtures. The various fractions were then combined and dissolved in 150 ml. of ethanol. The addition of approx. 40 ml. of 2N aqueous sodium hydroxide caused rapid crystallization of a product, m.p. $272-4^\circ$, (1.25 g.) which was shown by infrared analysis to be the disodium salt of the dicarboxylic acid. The salt was treated with 5 ml. of oxalyl chloride. A vigorous reaction occurred, and an orange, semi-solid mixture was obtained. After briefly heating on a steam bath, excess oxalyl chloride was removed at an aspirator and the residue dissolved in 50 ml. benzene. Evaporation to ca. 30 ml. and addition of hot heptane caused a solid to crystallize, which

was collected and dried to afford 300 mg. of material, m.p. 237° dec. Infrared analysis indicated that the product was the bridged anhydride of 9,10-dihydro-9,10-diphenylanthracene dicarboxylic acid.

Anal: Calcd. for $C_{26}H_{18}O_3$: C, 83.5; H, 4.50.

Found: C, 83.25; H, 4.62.

Sodium Naphthalenide²⁸ - A nitrogen filled 250-ml. round bottom flask was charged with 1.28 g. (0.1 mole) naphthalene in 100 ml. of freshly distilled anhydrous tetrahydrofuran and 2.3 g. (0.1 g. at.) of sodium metal was added. The system was allowed to stir under nitrogen for three hours. A green color appeared almost instantly and was very intense at the conclusion of the preparation.

9,10-Diphenylanthracene Radical Anion - A 125-ml. flask was carefully swept with nitrogen and then charged with 3.3 g. (0.01 mole) 9,10-diphenylanthracene in 50 ml. of anhydrous tetrahydrofuran. Sodium metal (0.23 g., 0.01 g. at) was added to the flask and the mixture was stirred under nitrogen for 14 hours. A deep purple solution was obtained indicating that the radical anion had formed.

In several experiments the anthracene radical ion was produced at a mercury or platinum electrode maintained at -2 to -2.2 volts vs. the saturated calomel electrode in a 2 millimolar solution of 9,10-diphenylanthracene in 2-methoxyethane containing 0.1 molar tetrabutylammonium perchlorate.

Radical Anions from Sodium Naphthalenide²⁹ - A solution of 0.33 g. (1 millimole) of 9,10-diphenylanthracene was dissolved in 10 ml. of anhydrous tetrahydrofuran and placed in a nitrogen filled 50-ml. Erlenmeyer flask. Without disturbing the nitrogen atmosphere of the flask, 1.0 ml. of 1 M sodium naphthalenide in tetrahydrofuran was added to the anthracene solution. An intense purple color developed immediately indicating the formation of the anthracenide.

The same technique was used to form radical anions from trans-stilbene radical ion. See Table III for a list of the anions prepared.

Chemiluminescence from Reaction of Sodium 9,10-Diphenylanthracenide with Chlorine - A solution of 3.5 g. (0.1 mole) of sodium 9,10-diphenylanthracenide in 50 ml. of anhydrous tetrahydrofuran contained in a glass-stoppered 125 ml. Erlenmeyer flask under nitrogen was briefly exposed to chlorine gas at the liquid surface. A brief, bright chemiluminescence was observed and the color of the purple anthracenide was discharged. Other reactions of radical anions with chlorine were conducted in a similar manner and are recorded in Table III.

Chemiluminescence from Reaction of Sodium 9,10-Diphenylanthracenide with Benzoyl Peroxide - To a solution of sodium 9,10-diphenylanthracenide prepared by combining 0.33 g. (1 millimole) of 9,10-diphenylanthracene in 10 ml. of anhydrous tetrahydrofuran with 1 ml. (1 millimole) of 1 M sodium naphthalenide in tetrahydrofuran under nitrogen, was rapidly added 0.24 g. (1 millimole) of benzoyl peroxide. A brief bright blue chemiluminescence was observed and the purple color of the anthracenide immediately changed to yellow. Other reactions of benzoyl peroxide and radical anions, recorded in Table III, were carried out by a similar procedure.

Effect of Various Oxidants on Sodium 9,10-Diphenylanthracenide in Anhydrous Tetrahydrofuran - For the experiments summarized in Table II a 10-ml. aliquot of sodium 9,10-diphenylanthracenide solution, which had been prepared by adding 16 ml. (16 millimoles) of 1 M sodium naphthalenide in anhydrous tetrahydrofuran to 5.28 g. (16 millimoles) of 9,10-diphenylanthracene in 144 ml. of anhydrous tetrahydrofuran, was placed in a nitrogen filled flask. One millimole of the oxidant was then added to the solution in the dark and the intensity of the chemiluminescence observed. Even in cases where no light was observed, the addition of oxidant destroyed the anthracenide as was evident from the discharge of the strong deep purple color of the anthracenide.

In experiments with anodic oxidation, 2-methoxyethane solutions, 10^{-3} to 10^{-2} molar in sodium or ammonium 9,10-diphenylanthracenide and 0.1 molar in ammonium perchlorate, were electrolyzed using mercury or platinum electrodes. Luminescence was observed at the anode in these experiments with an anode voltage of about -1.5 volts vs. the saturated calomel electrode and a current of 0.5 ma.

Chemiluminescence of Radical Anions - In the experiments summarized in Table III, one millimole of test compound was dissolved in 10 ml. of anhydrous tetrahydrofuran in a nitrogen filled 50-ml. flask and 1 ml. of 1 M sodium naphthalenide in anhydrous tetrahydrofuran was added to the solution. A color change indicated the formation of the radical anion. Chlorine gas was then passed over the surface of the solution in the dark and the color and intensity of the emitted light was observed. Alternatively, 0.1 g. of solid benzoyl peroxide was added under nitrogen to the radical anion solution instead of chlorine gas. A change of color was an indication that a reaction had taken place.

Reduction of 9,10-Dichloro-9,10-diphenyl-9,10-dihydroanthracene with Sodium Naphthalenide - A dark green solution of sodium naphthalenide (5 ml.) prepared from 6.4 g. of naphthalene (0.05 mole) and excess sodium metal in 100 ml. of tetrahydrofuran was added under nitrogen dropwise to a solution of 1 g. of 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene (2.5 mmole) in 100 ml. of tetrahydrofuran. A bright blue light emission occurred with the addition of each drop of naphthalenide solution. The final reaction mixture exhibited the fluorescence typical of 9,10-diphenylanthracene.

Reaction of Sodium with 9,10-Dichloro-9,10-diphenyl-9,10-dihydroanthracene - Addition of 0.25 g. of freshly cut sodium metal (0.11 g. atom) to a solution of 1 g. of 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene (2.5 mmole) in 100 ml. of tetrahydrofuran produced a weak blue light emission from the surface of the sodium.

Reactions of 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene with sodium stilbene ion radical, stilbene dianion and sodium 9,10-diphenylanthracenide were carried out by essentially the same procedure.

Reaction of 9,10-Diphenyl-9,10-dichloroanthracene with Lithium Dicyclohexyl Phosphide - Addition of 10 ml. (4.0 millimoles) of 0.4 M lithium dicyclohexyl phosphide³⁵ in ether to 0.40 g. (1.0 millimole) of 9,10-diphenyl-9,10-dichloroanthracene in 10 ml. of ether under nitrogen produced no light. Shaking the reaction mixture in the presence of oxygen was also non-luminescent. The reaction of lithium dicyclohexyl phosphide with oxygen is a known chemiluminescent reaction³⁵. Therefore, the result obtained indicates that a non-chemiluminescent reaction did occur between the phosphide and the chloroanthracene.

SECTION III

SPECTROSCOPY AND ENERGY TRANSFER

A. Recalibration of Spectroradiometer-Fluorimeter

Certain components of the radiometric equipment used for quantitative, absolute light measurements are subject to aging effects, and the instrument must be recalibrated periodically. The recalibration has been carried out as described in the Experimental Section. The new calibration factors agree to within 10% of the old, but the output intensity of the excitation source was found to have decreased about 15%. The new calibration curve is shown in Figure I.

As a test of the new calibration, the fluorescence quantum yield of quinine sulfate in 0.1 N sulfuric acid was measured and compared to an earlier measurement and a literature value. The data is summarized in Table I. The fluorescence yield as newly measured agrees well with our previous measurement and is 8% higher than the literature³⁶ value.

Table I

Fluorescence Yield of 10^{-3} Molar Quinine Sulphate in 0.1 N H_2SO_4

<u>Date of Experiment</u>	<u>Set of Factors Used</u>	<u>Quantum Yield</u>	<u>Literature Value³⁶ for Quantum Yield</u>
1-15-64	Old	0.60	0.55
5-14-64	New	0.60	

B. Oxalyl Chloride-Hydrogen Peroxide Chemiluminescence

Fluorescence Quenching Effects in the Oxalyl Chloride-Hydrogen Peroxide-9,10-Diphenylanthracene Reaction

In the previous report³ we showed that the excited state corresponding to the fluorescent additive in the above reaction was the emitting species. Since the over-all chemiluminescence yield is in part dependent on the fluorescence efficiency of the emitting species, it is important to know whether constituents of the reaction mixture are fluorescence quenchers. In the previous report we showed that the products from the reaction were not quenchers.

Experiments to determine the quenching effects of the starting materials, oxalyl chloride and hydrogen peroxide, are summarized in Table II. It is seen that oxalyl chloride is, in fact, a powerful quencher of 9,10-diphenylanthracene fluorescence. At an oxalyl chloride concentration of 6×10^{-3} molar the fluorescence efficiency drops to 24% of its unquenched value. It was also observed during the experiment that the exciting light used for the fluorescence measurements rapidly photolyzed oxalyl chloride. The photolysis products were not quenchers and after a brief excitation period the fluorescence efficiency returned to the unquenched value. Hydrogen peroxide had only a small fluorescence quenching effect.

Table II

The Quenching of the Fluorescence of
9,10-Diphenylanthracene in Ethereal Solutions^a

<u>Additive (Concentration)</u>	<u>Intensity of the 430 mμ</u> <u>Emission Band</u>		
	<u>Initial</u>	<u>At 5 Min.</u>	<u>At 10 Min.</u>
None	74.0	74.0	74.0
Oxalyl chloride (6.0×10^{-3} M) ^b	18.0	74.0	74.0
Oxalyl chloride (6.0×10^{-3} M) ^c	18.0	52.0	68.0
H ₂ O ₂ (0.1 M) ^b	70.0	70.0	70.0

a) 9,10-Diphenylanthracene concentration was 0.70×10^{-4} molar

b) Exposed continuously to exciting light¹

c) Masked from exciting light¹ between measurements

Quantum yield of the Oxalyl Chloride-Hydrogen Peroxide System
with Rubrene as the Acceptor

The quantum yield of a reaction of oxalyl chloride with hydrogen peroxide in ether containing rubrene and the quantum yield of the corresponding reaction with 9,10-diphenylanthracene are summarized in Table III. It is seen that rubrene is substantially more efficient than 9,10-diphenylanthracene in accepting excitation energy. Neither rubrene nor 9,10-diphenylanthracene were consumed under the conditions used. The over-all chemiluminescence reaction rate is not influenced by the acceptor as indicated in Table III and Figures II and III.

Table III

Quantum Yields of Oxalyl Chloride-Hydrogen Peroxide Reactions in Ether with Rubrene and with 9,10-Diphenylanthracene^a

<u>Acceptor</u>	<u>Fluorescence Quantum Yield</u>	<u>Chemiluminescence Quantum Yield</u>	<u>Pseudo First Order Rate Constant</u>
Rubrene	0.08	1.6×10^{-3}	$3.3 \times 10^{-2} \text{ sec}^{-1}$
9,10-Diphenyl-anthracene	0.75	0.22×10^{-3}	$3.2 \times 10^{-2} \text{ sec}^{-1}$

a) The concentrations were: oxalyl chloride = $4.12 \times 10^{-3} \text{ M}$; hydrogen peroxide = $1.10 \times 10^{-2} \text{ M}$; acceptor = $7.14 \times 10^{-4} \text{ M}$.

Distribution of Chemiluminescence between Two Acceptors

As discussed in the previous report³, criteria for efficient transfer to an acceptor in the oxalyl chloride-hydrogen peroxide system can be determined by experiments employing two acceptor species, where the ratio of transfer rate constants to the acceptors, k_a/k_p , can be obtained graphically from equation (1)³.

$$(1) \quad \frac{Q.Y.a}{Q.Y.b} = \frac{k_a[A]}{k_b[B]} \cdot \frac{F_a}{F_b}$$

To draw reliable conclusions regarding the chemical or physical characteristics of acceptors that determine transfer efficiencies, it is necessary to study a number of acceptor pairs. Chemiluminescence and fluorescence yield data for the pyrene-9,10-diphenylanthracene pair were reported in the previous report³. Corresponding results for a pyrene-anthracene system were determined during the current quarter.

Chemiluminescence quantum yields, (Q.Y.x), as functions of acceptor concentrations $[X]$, for acceptor pair experiments with pyrene and anthracene are summarized in Table IV. Fluorescence yield data (F_x in equation 1) for this system are summarized in Table V. Additional experiments are in progress and a detailed analysis will be presented in a forthcoming report.

Table IV

Chemiluminescence Quantum Yields for Oxalyl Chloride-Hydrogen Peroxide Reactions with Pyrene, Anthracene, and Pyrene-Anthracene Mixtures in Ether^a

Concentrations (Moles per Liter)		Chemiluminescence Yields ^b			
Pyrene	Anthracene	Pyrene Observed	Anthracene Observed	Corrected ^c	Total Corrected
2.32×10^{-2}	-	0.73×10^{-3}	-	-	0.73×10^{-3}
4.25×10^{-2}	-	0.87×10^{-3}	-	-	0.87×10^{-3}
-	0.93×10^{-4}	-	0.83×10^{-4}	0.87×10^{-4}	0.87×10^{-4}
-	2.34×10^{-3}	-	0.45×10^{-3}	0.55×10^{-3}	0.55×10^{-3}
-	1.57×10^{-2}	-	0.45×10^{-3}	0.55×10^{-3}	0.55×10^{-3}
4.25×10^{-2}	0.93×10^{-4}	$\sim 0.83 \times 10^{-3}$	$\sim 0.02 \times 10^{-3}$	$\sim 0.02 \times 10^{-3}$	0.85×10^{-3}
4.25×10^{-2}	2.34×10^{-3}	0.80×10^{-3}	0.10×10^{-3}	0.12×10^{-3}	0.92×10^{-3}
2.32×10^{-2}	1.57×10^{-2}	0.44×10^{-3}	0.31×10^{-3}	0.38×10^{-3}	0.82×10^{-3}

a) Ethereal oxalyl chloride was injected into ethereal hydrogen peroxide to obtain final concentrations of 0.93×10^{-2} molar and 1.70×10^{-1} molar, respectively.

b) Einsteins per mole of oxalyl chloride.

c) Corrected for absorption.

Table VFluorescence Quantum Yields for
Anthracene and Pyrene in Ether^a

<u>Compound</u>	<u>Concentration (Moles/Liter)</u>	<u>Fluorescence Quantum Yield</u>	
		<u>Observed</u>	<u>Corrected^b</u>
Pyrene	2.32×10^{-2}	0.16	0.16
Pyrene	4.25×10^{-2}	0.14	0.14
Anthracene	0.93×10^{-4}	0.26	0.26
Anthracene	2.34×10^{-3}	0.22	0.25
Anthracene	1.57×10^{-2}	0.13	0.14

a) The solutions contained 1.70×10^{-1} molar hydrogen peroxide.

b) Fluorescence yields corrected for self-absorption. See Experimental.

C. Energy Transfer in 3-Aminophthalhydrazide Chemiluminescence

In the previous report³ we described chemiluminescence quantum gain produced by the addition of disodium fluorescein to the aqueous 3-aminophthalhydrazide-potassium persulfate-hydrogen peroxide-sodium carbonate chemiluminescent reaction. It was also pointed out, however, that self-absorption and self-quenching of fluorescein at the high concentrations required, seriously complicated interpretation of the results. In a search for a more suitable system for analysis of non-radiative energy transfer, we have carried out a 3-aminophthalhydrazide-hydrogen peroxide reaction in a dimethylsulfoxide-benzene mixture containing rubrene. The results are summarized in Table VI.

Table VI

Effect of Rubrene on 3-Aminophthalhydrazide Chemiluminescence

<u>3-Aminophthalhydrazide (moles per liter)</u>	<u>Rubrene (moles per liter)</u>	<u>Chemiluminescence Yield</u>
1×10^{-2}	None	2.8×10^{-3}
1×10^{-2}	2×10^{-2}	4.4×10^{-3} ^a

a) Total emission derived from rubrene. Not corrected for self-absorption.

As indicated in the table, the chemiluminescence yield is substantially increased by the presence of rubrene. Unfortunately, a portion of the rubrene was observed to precipitate during the course of the reaction, thus obscuring the quantitative aspect of the experiment. The result, however, clearly indicates the occurrence of

non-radiative energy transfer. Efforts are continuing to find a system suitable for quantitative study.

SECTION III

EXPERIMENTAL

Recalibration of the Spectroradiometer-Fluorimeter - The calibration of the photomultiplier tube was carried out as described previously^{1,2} using a 500 watt N.B.S. standard lamp and a ferrioxalate actinometer solution³⁷. The factor to convert the energy entering the monochromator to total energy emitted by the sample was obtained using a translucent 12 volt spherical light bulb closely approximating the dimensions of the radiometric cuvette. The bulb was first immersed in a ferrioxalate actinometer solution (10 mm. depth all around it) and the ferrous ions per minute produced by the totally absorbed light were determined. The bulb was then placed in the position of the sample [see Figure 1, p. 34, Technical Report No. 1¹] and a 10 mm. deep actinometer solution placed behind the entrance slit to the monochromator. The ferrous ions produced per minute were determined. These two figures gave the required "spherical" factor. The loss in the instrument monochromator was determined using external monochromatic light from a "Farrand" monochromator and measuring the light behind the entrance and exit slits of the spectrofluorimeter. A barrier layer cell and a micro-voltmeter were used for this measurement.

The new calibration factors for conversion of observed intensities to absolute microwatts and quanta/sec agree to within 10% of the previously determined factors.

The B.L.B. U.V. lamps used as "exciting lights" during fluorescence measurements were found to have aged and their total output had dropped by approximately 15-20%.

The new calibration factors (Figure 1) have been introduced into the computer programs and will be used for all quantum yield determinations until further recalibration is required.

Fluorescence Quantum Yield Measurements - The experimental procedures and calculations were those previously described². In some cases it was desirable to correct quantum yields for self-absorption. This correction was made using the following formula:

$$\text{Q.Y. corrected} = (\text{Q.Y. observed}) \left(\frac{I_{\lambda}^{\text{ob}}}{\int_{\lambda_1}^{\lambda_2} I^{\text{ob}} d\lambda} \right) \left(\frac{\int_{\lambda_1}^{\lambda_2} I^{\circ} d\lambda}{I^{\circ} \lambda} \right)$$

I_{λ}^{ob} is the observed intensity from the sample to be corrected at a wavelength, λ , chosen well above the absorption band so that it is not appreciably reabsorbed, and $\int_{\lambda_1}^{\lambda_2} I_{\lambda}^{ob} d\lambda$

is the corresponding integrated spectral area. I°_{λ} and

$\int_{\lambda_1}^{\lambda_2} I^{\circ}_{\lambda} d\lambda$ are the corresponding values for a dilute solution of the

sample where self-absorption at short wavelengths is not appreciable. These corrections are small (see Table V) for front-surface fluorimetry. Such corrections are valid only when the fluorescence yield of the sample is relatively low. In other cases an additional correction must be made to take into account the emission produced by reabsorption. This secondary correction was not needed for the results reported in this report.

Chemiluminescence Quantum Yields for Reactions of Oxalyl Chloride with Hydrogen Peroxide in the Presence of Rubrene and 9,10-Diphenylanthracene - The experiments summarized in Table III were carried out essentially as described previously³. Kinetic plots of log intensity (observed) vs. time are shown in Figures II and III. The emission of the 430 mμ band was used to follow the decay rate in the 9,10-diphenylanthracene experiment; the 550 mμ band was used for rubrene.

Chemiluminescence Yields of the Oxalyl Chloride-Hydrogen Peroxide Reaction in Ethereal Solution with Pyrene and Anthracene as Mixed Acceptors - The experimental procedure and method for calculation of results for the experiments summarized in Table III were those described in the previous report. The emission intensities at 400 mμ and 500 mμ, respectively, were used to calculate separate anthracene and pyrene yields. Yields, corrected for self-absorption, were obtained from the following equation:

$$Q.Y. \text{ corrected} = Q.Y. \text{ observed} \left(\frac{I_{\lambda}}{\int_{\lambda_1}^{\lambda_2} I d\lambda} \right) \left(\frac{\int_{\lambda_1}^{\lambda_2} I^{\circ} d\lambda}{I^{\circ}_{\lambda}} \right)$$

I_{λ} is the observed time-integrated intensity at 400 mμ and $\int_{\lambda_1}^{\lambda_2} I d\lambda$

is the integrated spectral area. I°_{λ} and $\int_{\lambda_1}^{\lambda_2} I^{\circ} d\lambda$ are the

corresponding values obtained in fluorescence experiments in dilute solution. This equation has the effect of replacing a spectral area which is erroneously small because of reabsorption at short wavelength,

with a theoretically valid and constant spectral area. This correction can be substantial in chemiluminescence experiments (see Table III) because emission from a significant depth of solution occurs and short wave length emission is subject to serious reabsorption. Pyrene dimer emission is not reabsorbed and no correction is needed in this case.

Spectral distributions for the experiments in Table III are shown in Figures IV, V, and VI. A typical rate curve is shown in Figure VII.

Energy Transfer in 3-Aminophthalhydrazide Chemiluminescence -

Stock Solutions

- | | |
|---|--------------------------|
| A. 3-Aminophthalhydrazide in dimethyl sulfoxide | - 2.5×10^{-2} M |
| B. Rubrene in benzene | - 2.0×10^{-2} M |
| C. Triton B in methanol | - 40% |
| D. Hydrogen Peroxide in tertiary butanol | - 2 M |

Solution D (0.50 ml.) was added to a 25-ml. flask containing 4.0 ml. of solution A, 5.0 ml. of solution B and 0.50 ml. of solution C. The timer was started with the last addition. After mixing, 3 ml. of this solution was transferred to the cuvette cell¹ and the decay rate of the 585 mμ band followed (Figure VIII). A wavelength distribution was also taken (Figure IX). The decay curve became first order after 6 minutes and the emission for this period was calculated using Simpson's rule of integration.

The calculation of quantum yield of chemiluminescence has been described previously³.

The experiment was repeated with pure benzene replacing solution B. The results are summarized in Table III

FIGURE 1

CALIBRATION CURVE SHOWING FACTORS USED TO CONVERT OBSERVED EMISSION INTENSITIES AT INDIVIDUAL WAVELENGTHS TO ABSOLUTE QUANTA/SEC. EMITTED

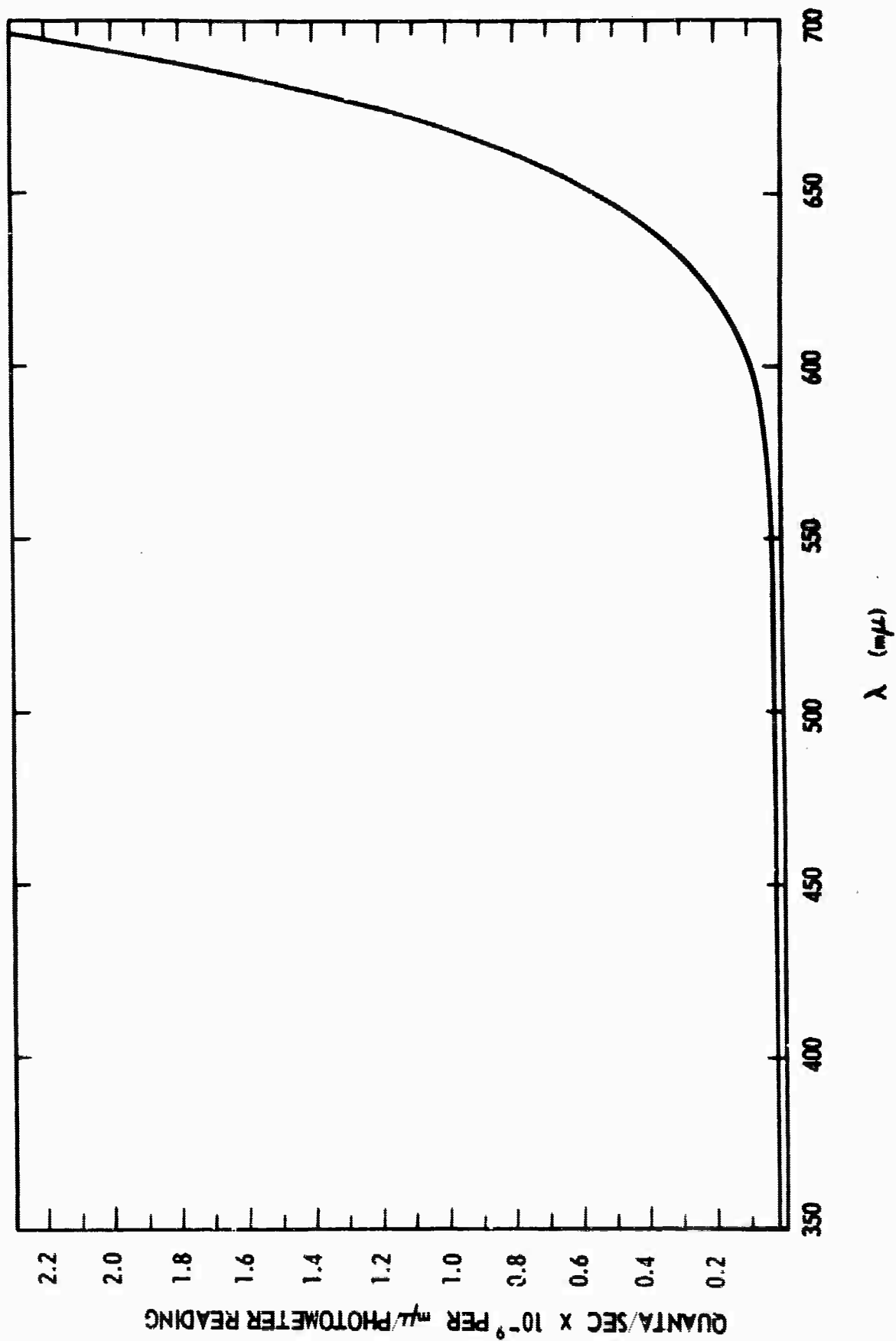


FIGURE II

RATE OF OXALYL CHLORIDE ($4.12 \times 10^{-3} \text{ M}$) HYDROGEN PEROXIDE ($1.10 \times 10^{-2} \text{ M}$)
9,10-DIPHENYLANTHRACENE ($7.14 \times 10^{-4} \text{ M}$) REACTION IN ETHER

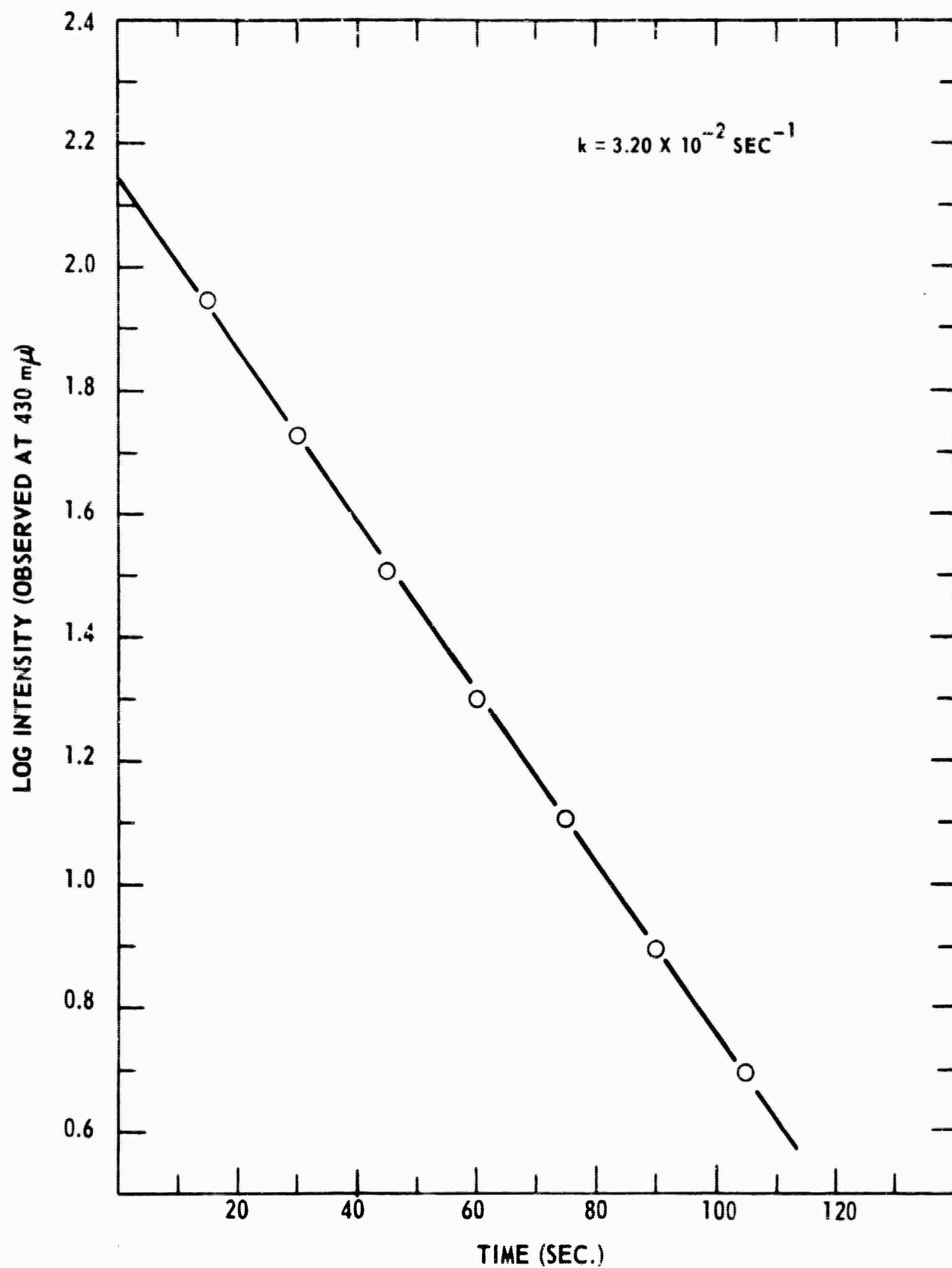


FIGURE III

RATE OF OXALYL CHLORIDE ($4.12 \times 10^{-3} \text{ M}$)—HYDROGEN PEROXIDE ($1.10 \times 10^{-2} \text{ M}$)—RUBRENE ($7.14 \times 10^{-4} \text{ M}$)—9,10-DIPHENYLANTHRACENE ($7.14 \times 10^{-4} \text{ M}$) REACTION IN ETHER

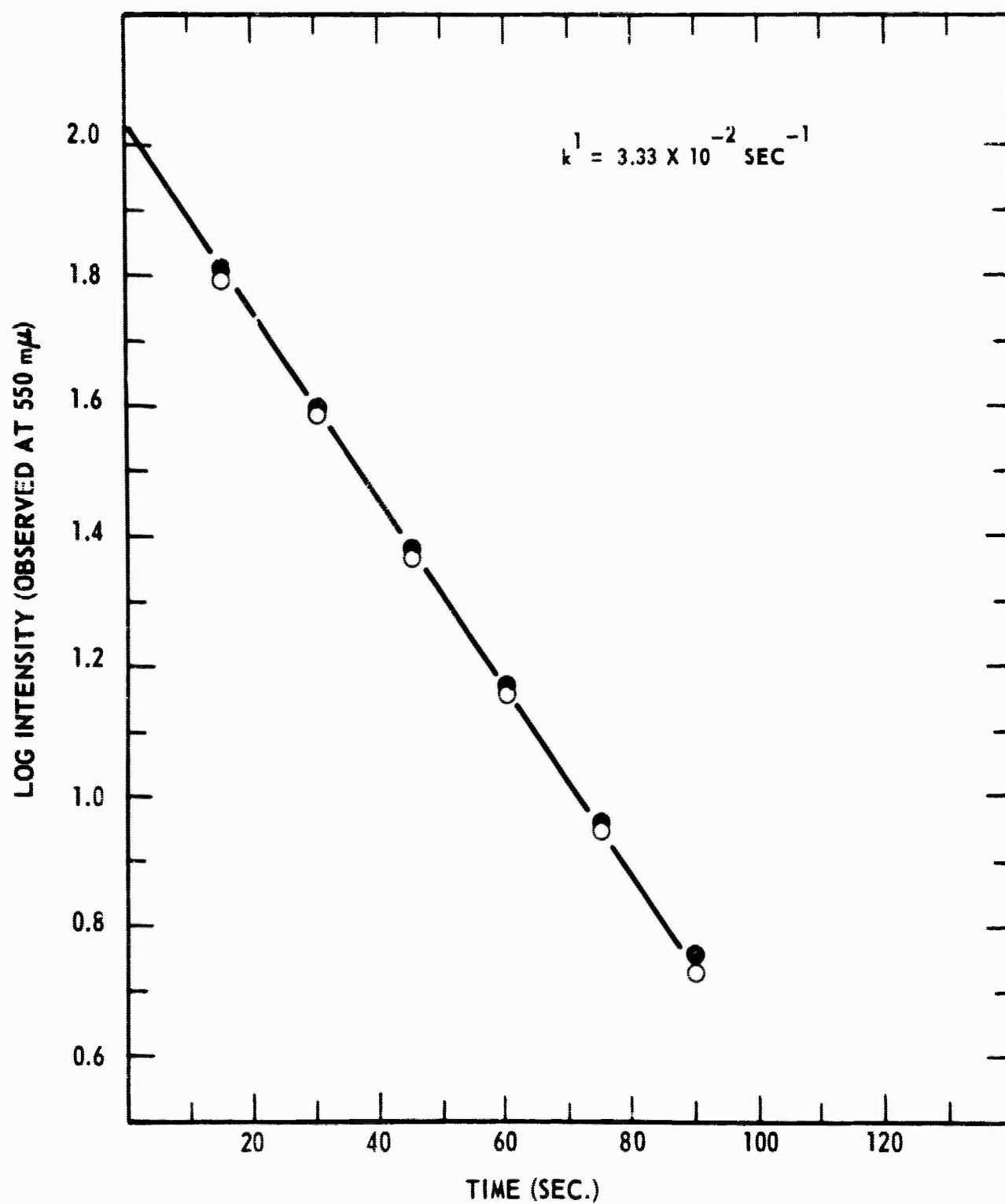


FIGURE IV

SPECTRAL DISTRIBUTION AT ONE MINUTE FROM START OF OXALYL CHLORIDE ($0.93 \times 10^{-2} \text{ M}$)
HYDROGEN PEROXIDE ($1.70 \times 10^{-1} \text{ M}$) ACCEPTOR EXPERIMENTS IN ETHER

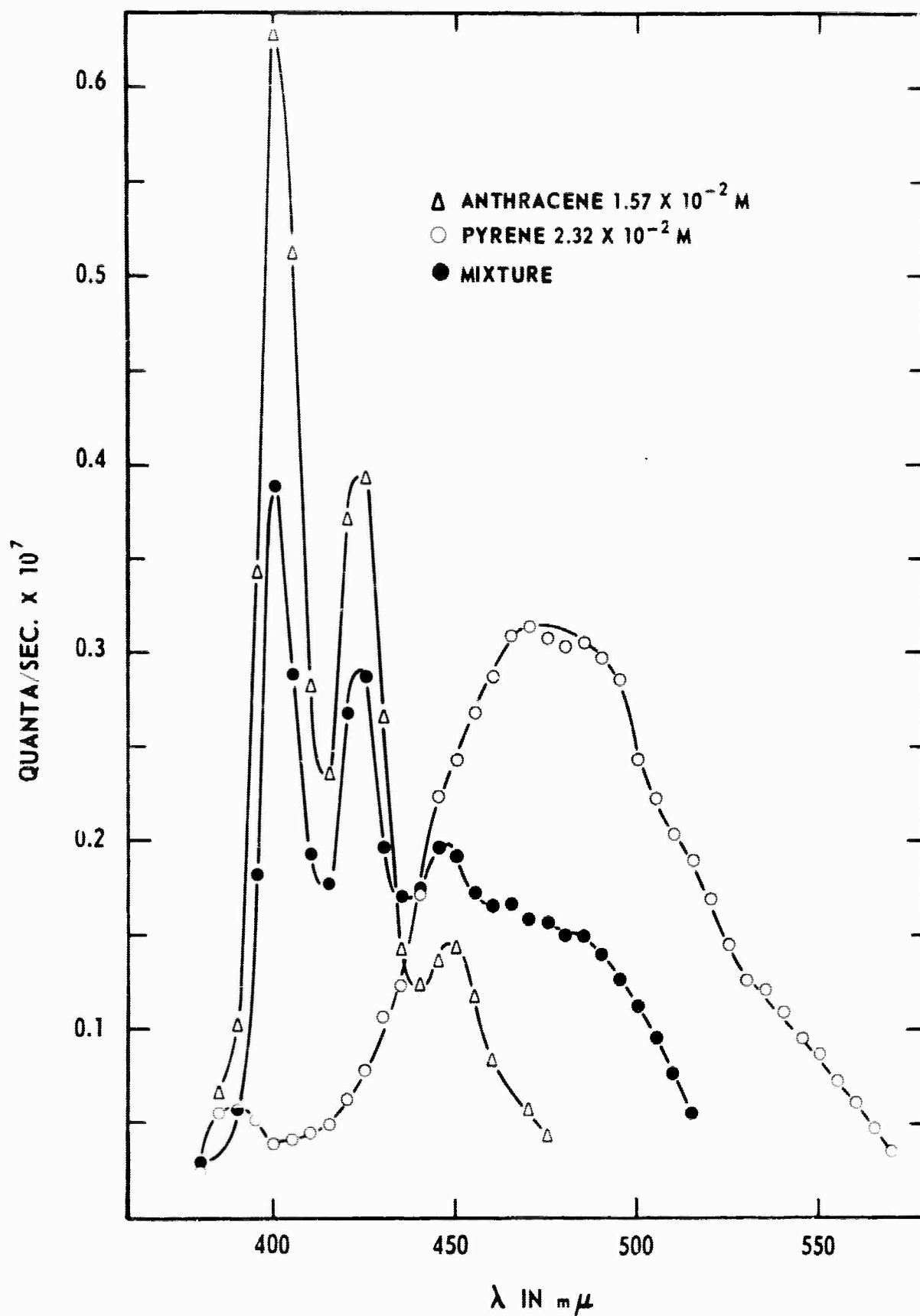


FIGURE V

SPECTRAL DISTRIBUTION AT ONE MINUTE FROM START OF OXALYL CHLORIDE ($0.93 \times 10^{-2} \text{ M}$)

HYDROGEN PEROXIDE ($1.70 \times 10^{-2} \text{ M}$) ACCEPTOR EXPERIMENTS IN ETHER

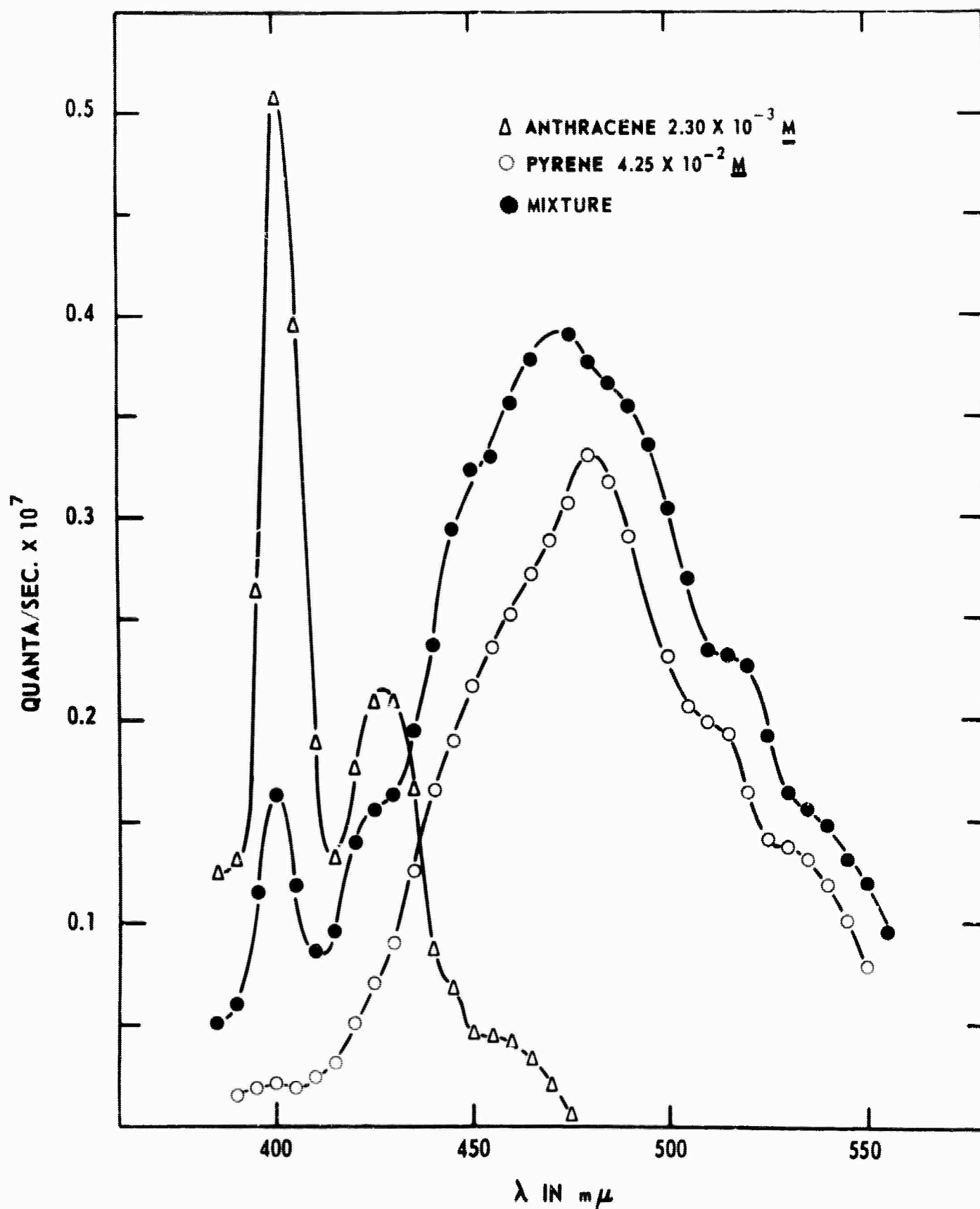


FIGURE VI

SPECTRAL DISTRIBUTION AT ONE MINUTE FROM START OF OXALYL CHLORIDE ($0.93 \times 10^{-2} \text{ M}$)
HYDROGEN PEROXIDE ($1.70 \times 10^{-1} \text{ M}$) ACCEPTOR EXPERIMENTS IN ETHER

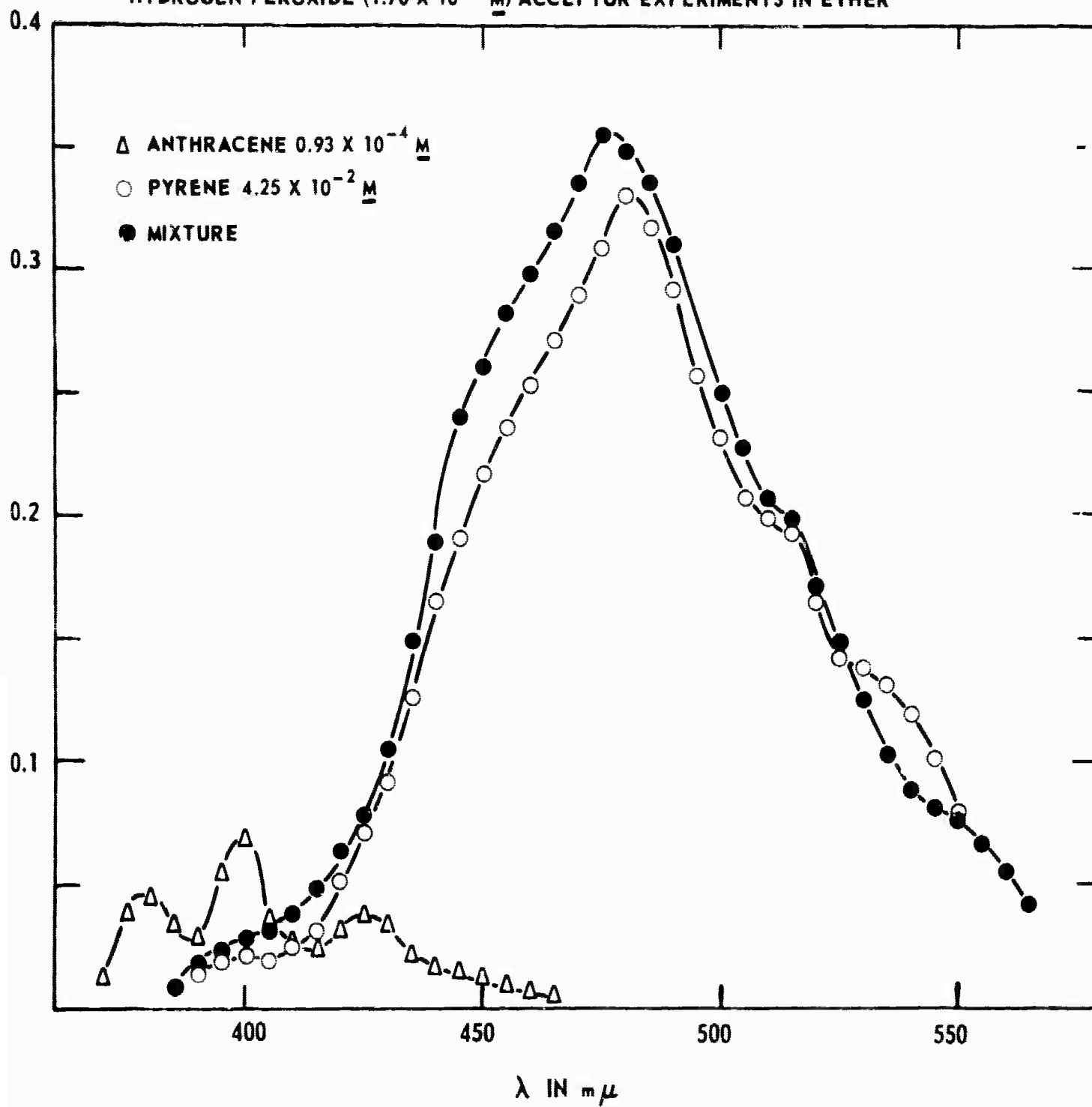


FIGURE VII

RATE OF OXALYL CHLORIDE (0.93×10^{-2} M)—HYDROGEN PEROXIDE
(1.70×10^{-1} M) REACTION IN ETHER CONTAINING 4.25×10^{-2} M PYRENE

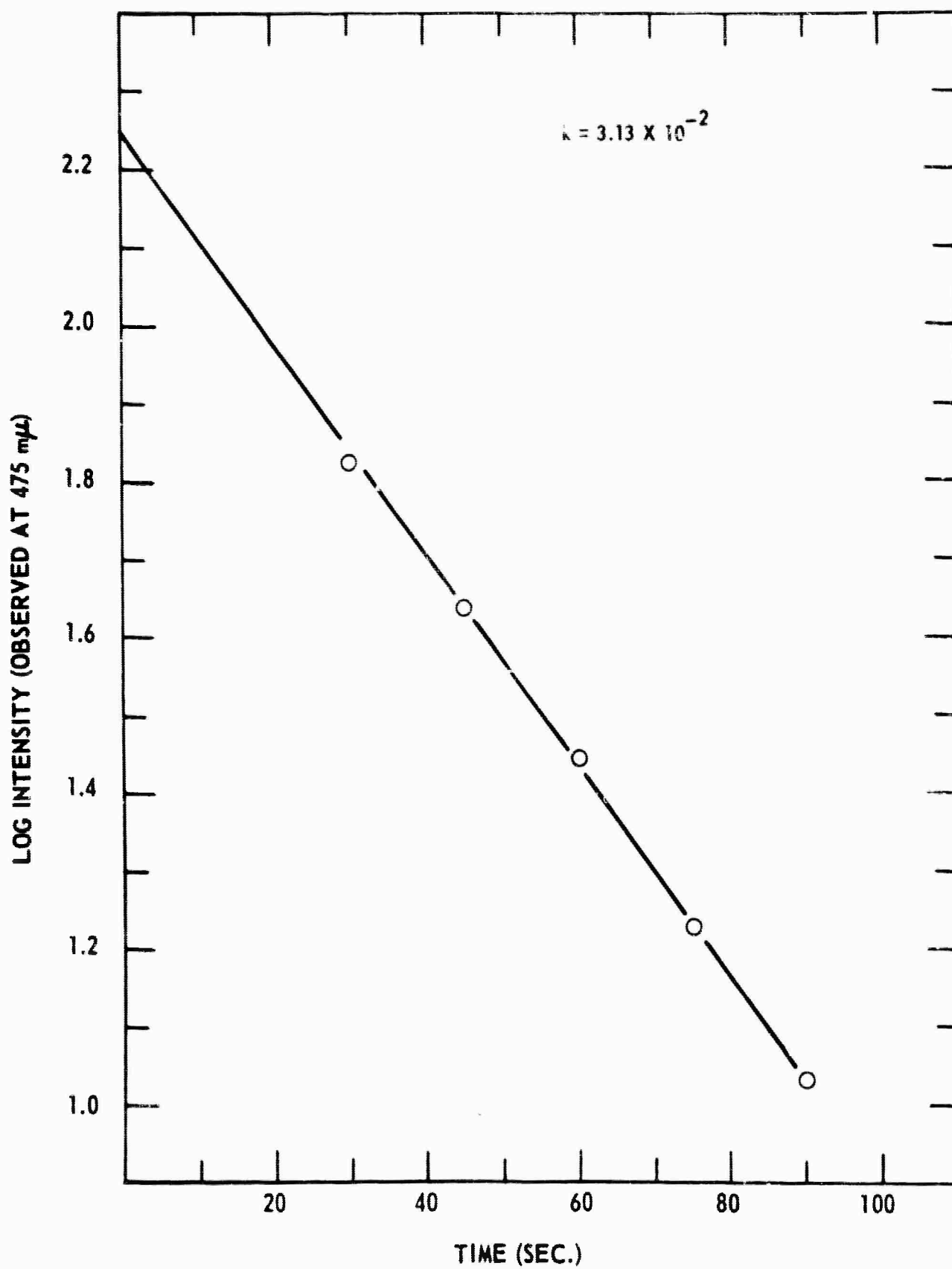
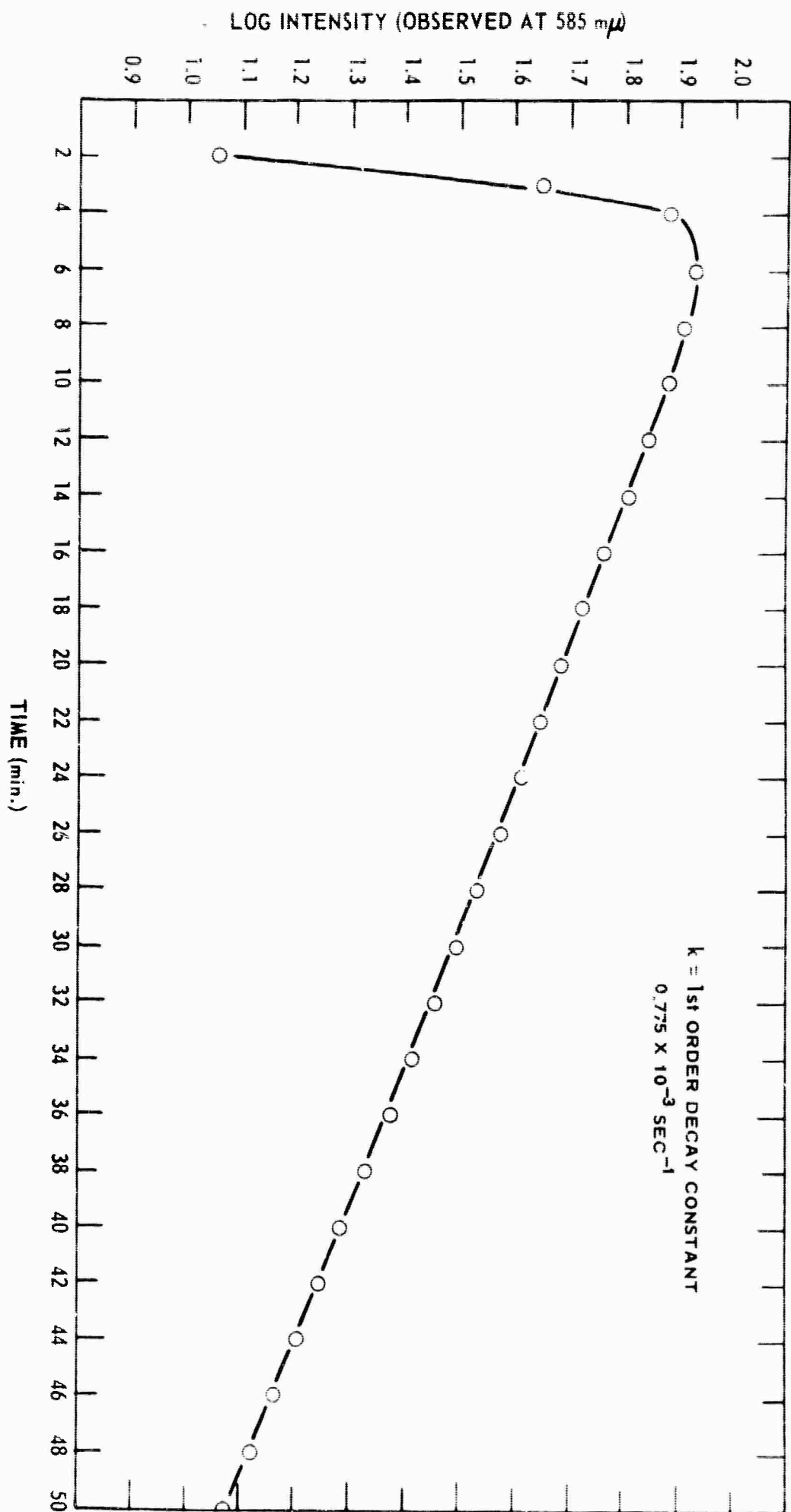
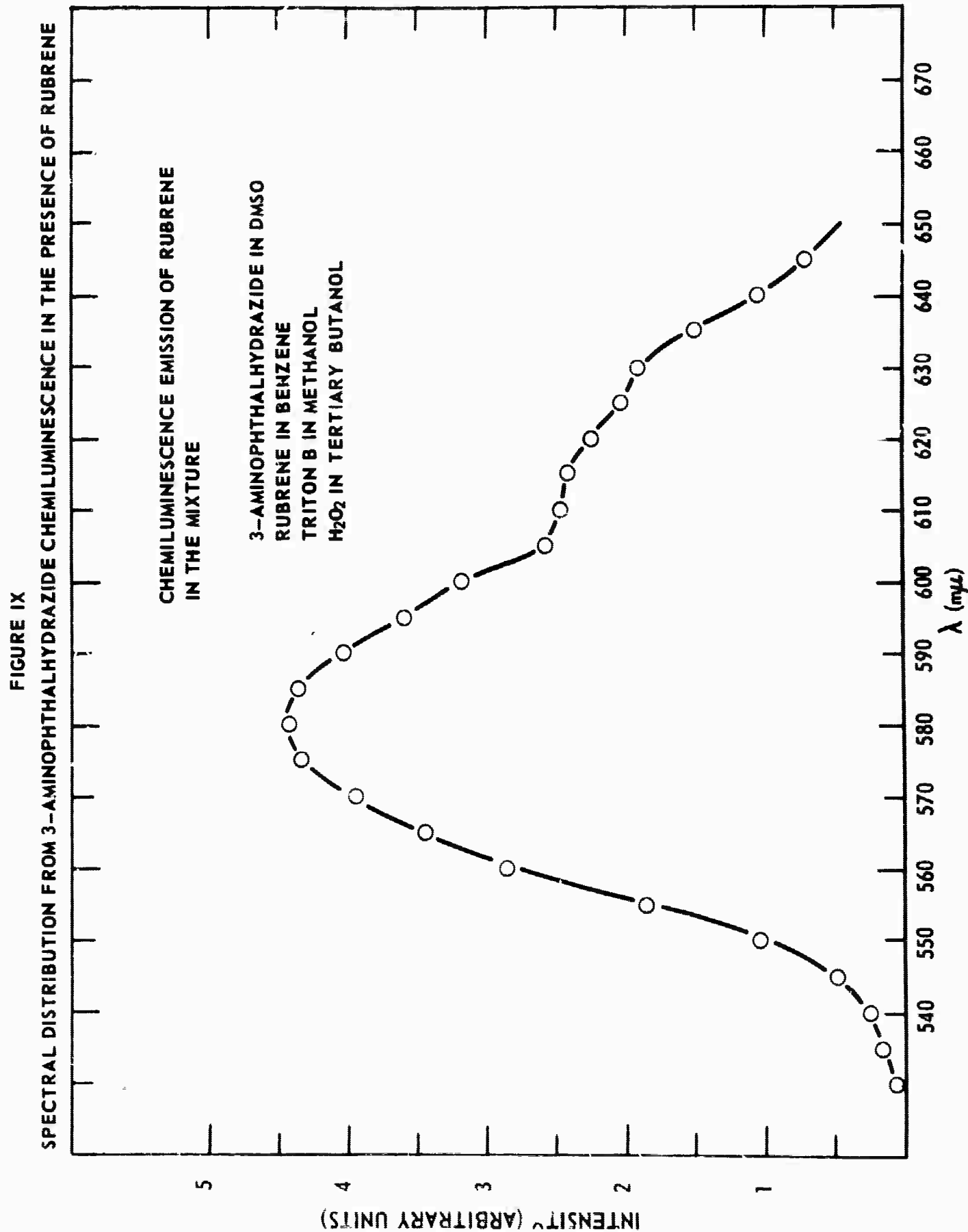


FIGURE VIII
REACTION OF 3-AMINOPHTHALHYDRAZIDE IN DMSO + RUBRENE IN BENZENE + H₂O₂
IN TERTIARY BUTANOL + TRITON B IN METHANOL





REFERENCES

1. American Cyanamid Company, "Chemiluminescent Materials," Technical Report No. 1, Contract Nonr 4200(00).
2. American Cyanamid Company, "Chemiluminescent Materials," Technical Report No. 2, Contract Nonr 4200(00).
3. American Cyanamid Company, "Chemiluminescent Materials," Technical Report No. 3, Contract Nonr 4200(00).
4. E. A. Chandross, Tetrahedron Letters, No. 12, 761 (1963).
5. E. N. Harvey, J. Phys. Chem., 33, 1456 (1929); V. Vojil, Chem. Listy, 48, 520 (1954); Chem. Abs., 48, 8674 (1954).
6. J. Kroh, B. C. Green, J. W. T. Spivlas, J. Am. Chem. Soc., 83, 2201 (1961).
7. E. H. White, J. Chem. Ed., 34, 275 (1957).
8. E. H. White, "Light and Life," W. D. McElroy and B. Glass, Ed., The Johns Hopkins Press, Baltimore, 1961, p. 185.
9. E. H. White, D. Iafirion, H. H. Kagi, J. H. M. Hall, J. Am. Chem. Soc., 86, 940 (1964).
10. E. H. White and M. M. Bursey, J. Am. Chem. Soc., 86, 941 (1964).
11. Dufraisse, L. Velluz, Compt. Rend., 209, 516 (1939).
12. A. Etienne, G. Bichet, Compt. Rend., 228, 1134 (1949).
13. Y. Lepage, Ann. Chim. (Paris) 13, 1137 (1959).
14. H. D. Zook, T. J. Russo, J. Am. Chem. Soc., 82, 1258 (1960).
15. Siegfried Hunig, Max Kiessel, Ber., 91, 380 (1958).
16. F. G. Germuth, J. Am. Chem. Soc., 51, 1555 (1929).
17. A. Robertson, W. A. Waters, J. Chem. Soc., 1578 (1948).
18. Pittsburg Plate Glass Company
19. P. D. Bartlett, R. E. Pincock, J. Am. Chem. Soc., 82, 1769 (1960).
20. G. Wittig, R. W. Hoffmann, Ber., 95, 2718 (1962).
21. Y. Lepage, Ann. Chim. (Paris) 13, 1137 (1959).
22. C. Dufraisse, L. Velluz, R. Demuyzck, Compt. Rend., 215, 111 (1942).

23. C. Dufraisse, L. Velluz, Bull. Soc. Chim., 171 (1942).
24. A. Wilson, L. Bini, R. Hofstadter, Anal. Chem., 33, 1135 (1961).
25. I. M. Kolthoff and J. J. Lingane, "Polarography", Vol. 1, Interscience Publishers, N. Y., 1952.
26. See C. A. Parker and C. G. Hatchard, J. Phys. Chem., 66, 2506 (1962).
27. See H. Linschitz and E. W. Abrahamson, Nature, 172, 909 (1957).
28. N. D. Scott, J. F. Walker and V. L. Hansley, J. Am. Chem. Soc., 58, 2442 (1936).
29. See D. E. Paul, D. Lippin and S. I. Weissman, J. Am. Chem. Soc., 78, 116 (1956); G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, Rec. trav. chim., 75, 487 (1956).
30. V. L. Hansley, Ind. Eng. Chem., 43, 1759 (1951); A. Carrington, and F. Dravnick, and M. C. R. Symons, J. Chem. Soc., 947 (1959).
31. M. Polanyi and G. Shay, Z. Phys. Chem., B1, 30 (1928).
32. M. Balkanski and F. Gaus, "Luminescence of Organic and Inorganic Materials," H. P. Kallmann and G. M. Spruch, Eds., John Wiley & Sons, New York, 1962, p. 318; B. Brocklehurst, G. Porter, J. M. Yates, J. Phys. Chem., 68, 203 (1964).
33. E. Bergmann, O. Blum-Bergmann and A. F. Christiani, Ann., 483, 80 (1930).
34. W. L. Semon and D. Craig, J. Am. Chem. Soc., 58, 1278 (1936).
35. K. Issleib and A. Tzschuch, Chem. Ber., 92, 1118 (1959).
36. W. J. Melhuish, New Zealand J. Sci. Tech. Bull., 37, 142 (1955).
37. C. A. Parker, Proc. Roy. Soc., A220, 104 (1953); C. G. Hatchard, C. A. Parker, ibid, A235, 518 (1956).

DISTRIBUTION LIST

<u>NO. COPIES</u>	<u>NO. COPIES</u>
Commanding Officer Office of Naval Research Branch Office The John Crerar Library Building 86 East Randolph Street Chicago 1, Illinois (1)	Air Force Office of Scientific Research (SRC-E) Washington 25, D.C. (1)
Commanding Officer Office of Naval Research Branch Office 346 Broadway New York 13, New York (1)	Commanding Officer Harry Diamond Laboratories Washington 25, D. C. Attn: Technical Information Office Branch 012 (1)
Commanding Officer Office of Naval Research Branch Office 1030 East Green Street Pasadena 1, California (1)	Office, Chief of Research & Development Department of the Army Washington 25, D. C. Attn: Physical Sciences Division (1)
Commanding Officer Office of Naval Research Branch Office Box 39 Navy #100 Fleet Post Office New York, New York (7)	Chief, Bureau of Ships Department of the Navy Washington 25, D. C. Attn: Code 342C (2)
Director, Naval Research Laboratory Washington 25, D. C. Attn: Technical Information Officer (6) Chemistry Division (1) Mr. R. Kirk (Code 6440) (1)	Chief, Bureau of Naval Weapons Department of the Navy Washington 25, D. C. Attn: Technical Library (4) Mr. R. Diggins (RMMO-3) (1)
Chief of Naval Research Department of the Navy Washington 25, D. C. Attn: Code 425 (2)	Defense Documentation Center Headquarters Cameron Station Alexandria, Virginia (20)
DDR&E Technical Library Room 3C-128, The Pentagon Washington 25, D. C. (1)	Director of Research U.S. Army Signal Research & Development Laboratory Fort Monmouth, New Jersey (1)
Technical Director Research & Engineering Division Office of the Quartermaster General Department of the Army Washington 25, D. C. (1)	Naval Radiological Defense Laboratory San Francisco 24, California Attn: Technical Library (1)
Research Director Clothing & Organic Materials Division Quartermaster Research & Engineering Command U. S. Army Natick, Massachusetts (1)	Naval Ordnance Test Station China Lake, California Attn: Head, Chemistry Division (1) Dr. G. W. Leonard (Code 4501) (1) Mr. S. D. Little (Code 3534) (1)

<u>NO. COPIES</u>	<u>NO. COPIES</u>
Commanding Officer Army Research Office Box CM, Duke Station Durham, North Carolina Attn: Scientific Synthesis Office (1)	Chief of Naval Research Department of the Navy Washington 25, D. C. (1) Attn: Code 421 (1) Code 440 (1) Code 450 (1) Code 461 (1)
Brookhaven National Laboratory Chemistry Department Upton, New York (1)	Dr. Charles E. Waring University of Connecticut Department of Chemistry Storrs, Connecticut (1)
Atomic Energy Commission Division of Research Chemistry Programs Washington 25, D. C. (1)	Dr. Emil H. White Department of Chemistry Johns Hopkins University Baltimore, Maryland (1)
Atomic Energy Commission Division of Technical Information Extension Post Office Box 62 Oak Ridge, Tennessee (1)	Dr. Ferd E. Williams Department of Physics University of Delaware Newark, Delaware (1)
U.S. Army Chemical Research and Development Laboratories Technical Library Army Chemical Center, Maryland (1)	Dr. J. E. Castle E. I. duPont de Nemours & Co. Central Research Department Wilmington, Delaware (1)
Director, ARPA The Pentagon Washington 25, D. C. Attn: Dr. Gene V. Mock (4) COL. Harry E. Tabor (2)	Mr. R. T. Reilly Limited War Laboratory Aberdeen Proving Grounds, Maryland (1)
Inspector of Naval Material 181 Middle Street Bridgeport 3, Connecticut (1)	Dr. Daniel Grafstein 1150 McBride Avenue General Precision, Inc. Little Falls, New Jersey (1)
Naval Ammunition Depot Crane, Indiana Attn: Code 34 (1)	Remote Area Conflict Information Center Battelle Memorial Institute 505 King Avenue Columbus, Ohio 43201 (1)
Naval Ordnance Laboratory White Oak Silver Spring, Maryland Attn: Mr. B. E. White (Code WE) (1)	Remote Area Conflict Information Center Battelle Memorial Institute 1755 Massachusetts Avenue, N.W. Washington, D. C. 20036 (1)

NO. COPIES

Dr. A. W. Berger
Monsanto Research Corporation
Boston Laboratories
Everett, Massachusetts 02149 (1)

Dr. Henry Linschitz
Department of Chemistry
Brandeis University
Waltham, Massachusetts (1)

United States Air Force
Research and Technology Division
Eglin Air Force Base, Florida 32542
Attn: Code ATCC (1)

Dr. F. H. Johnson
Department of Biology
Princeton University
Princeton, New Jersey (1)

Dr. W. H. Urry
Department of Chemistry
University of Chicago
Chicago, Illinois (1)