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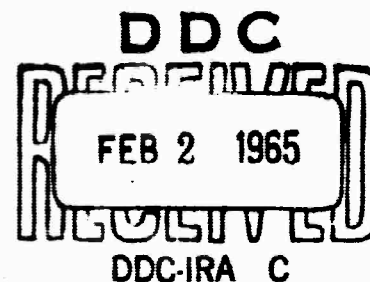
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CHEMILUMINESCENT MATERIALS

AMERICAN CYANAMID COMPANY
CENTRAL RESEARCH DIVISION
STAMFORD, CONNECTICUT



SEPTEMBER 1 - NOVEMBER 30, 1964

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SUMMARY

Progress in determining mechanisms of processes fundamental to chemiluminescence is reported with particular reference to:

(1) Studies of oxalyl chloride-hydrogen peroxide-9,10-diphenylanthracene chemiluminescence, (2) Exploratory studies of new potentially useful chemiluminescent reactions related to oxalyl peroxide decompositions, and (3) Synthesis and exploratory studies of new chemiluminescent systems based on the acridine and anthracene compound classes.

Quantitative luminosity and brightness data is summarized for representative β -nol and oxalyl chloride chemiluminescent systems. An initial brightness of 103 foot lamberts was obtained for a short-lived oxalyl chloride reaction.

An investigation of reactant concentration effects on quantum yields of light emission in the oxalyl chloride-hydrogen peroxide-9,10-diphenylanthracene system has confirmed conclusions previously drawn. Absolute values of the quantum yields, however, were significantly higher. Studies of fluorescer behavior in the system have shown that (1) at least three fluorescers remain predominantly unchanged following emission, (2) complex formation between oxalyl chloride or hydrogen peroxide and the fluorescer is essentially absent, and (3) oxalyl chloride is an important fluorescence quencher.

Continued investigations of oxalyl peroxide chemiluminescent systems have indicated that acyl-oxalyl peroxides are unstable. In related experiments the solid pyridine-oxalyl chloride complex was found

to provide chemiluminescence under conditions analogous to those used for oxalyl chloride itself. Moreover, thermal decomposition of the complex in the presence of a fluorescer was found to generate light without oxygen. It was also discovered that the complex promotes a moderately strong air-activated emission in certain solvents.

An exploratory synthesis effort designed to provide new chemiluminescent reactions from mechanistic hypotheses has produced four new chemiluminescent reactions based on acridine and dihydro-anthracene peroxides.

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.

To avoid excessive repetition, the objectives of a particular study are described in detail only in the report where the study is begun. The progress of a specific investigation can be followed conveniently over periods longer than a single quarter by referring to the Tables of Contents^{1,2,3,4,5}.

SECTION I

REACTION MECHANISMS IN CHEMILUMINESCENCE

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^{1,2,3,4,5,6}.



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.

1. Effect of Reactant Concentrations on Reaction Rates and Quantum Yields

In the previous report⁵ quantum yields and reaction rates were reported for a number of oxalyl chloride, hydrogen peroxide, 9,10-diphenylanthracene (DPA) experiments, where the concentrations of reactants were varied substantially. The results of that study are summarized below:

a) Reaction rates are linearly dependent on the oxalyl chloride concentration up to about 5×10^{-3} molar concentration.

b) Reaction rates very little with hydrogen peroxide concentration below about 10^{-2} molar concentration but increase substantially at higher concentrations.

c) Reaction rates are essentially independent of the fluorescer concentration.

d) Quantum yields are essentially independent of oxalyl chloride concentration below about 2×10^{-2} molar concentration.

e) Quantum yields increase with increasing hydrogen peroxide concentration according to the equation

$$\frac{1}{Q.Y.} = \frac{1}{K_a} + \frac{1}{K_b[H_2O_2]}$$

f) Quantum yields increase with increasing fluorescer concentration according to the equation

$$\frac{1}{Q.Y.} = \frac{1}{K_c} + \frac{1}{K_d[FL]}$$

Additional experiments with DPA have now been carried out to determine the reproducibility of the previous results. The new data is summarized in Table I. The previous conclusions were confirmed. Plots of $1/Q.Y.$ vs. $1/[H_2O_2]$ and $1/[FL]$ are shown in Figures I and II. Unexpectedly, however, the absolute magnitude of the reaction rate constants and quantum yield values obtained in the new experiments were appreciably and uniformly higher than those values determined earlier. The source of this disagreement is currently being sought.

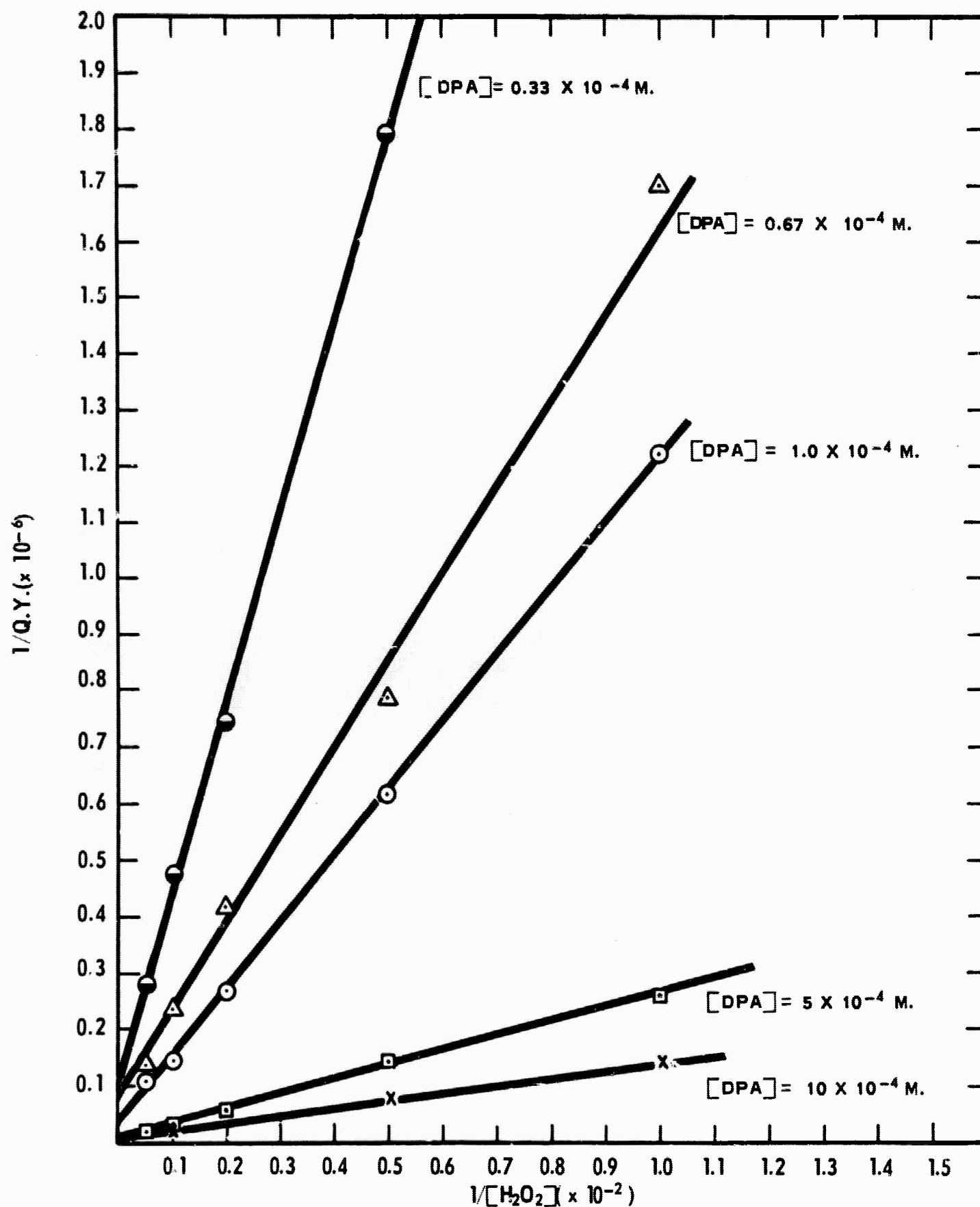
2. Stability of Fluorescers in the Oxalyl Chloride-Hydrogen Peroxide Reaction

A series of experiments were carried out where fluorescence spectra and intensities were determined for ethereal solutions of hydrogen peroxide containing the individual fluorescers 9,10-diphenylanthracene (DPA), 1,4-dimethoxy-9,10-diphenylanthracene (DMDPA), and rubrene both before and after reaction with oxalyl chloride. The fluorescence spectral distributions of the fluorescers were not changed following reaction with oxalyl chloride, and the intensities summarized in Table II show that these fluorescers are only about 10% consumed during the chemiluminescence process.

3. Examination of Possible Ground State Interaction between Fluorescent Hydrocarbons and Either Oxalyl Chloride or Hydrogen Peroxide

One of several possible mechanisms for the oxalyl chloride-hydrogen peroxide-fluorescent compound chemiluminescent reaction specifies the formation of an oxalyl chloride-fluorescer complex which provides chemiluminescence on reaction with hydrogen peroxide.

FIGURE 1
RELATIONSHIP BETWEEN QUANTUM YIELD AND 9,10-DIPHENYLANTHRACENE
(DPA) CONCENTRATIONS



$1/Q.Y. (x 10^{-2})$

FIGURE II
RELATIONSHIP BETWEEN QUANTUM YIELD AND H_2O_2 CONCENTRATION

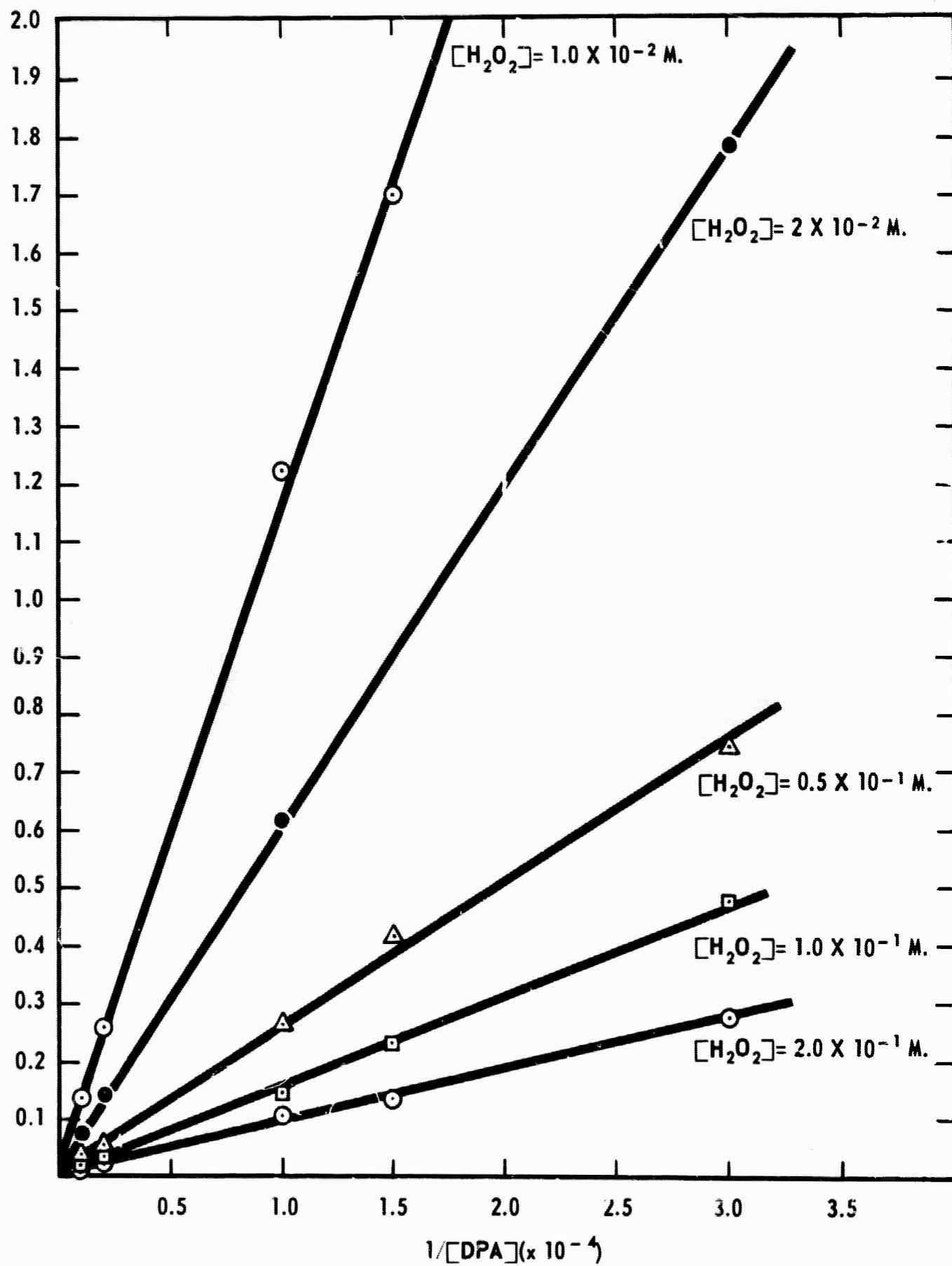


Table I

Variation of Reaction Rate and Chemiluminescence Quantum Yield
with Hydrogen Peroxide [H_2O_2] and 9,10-Diphenylanthracene [DPA]
Concentrations in Ether Solution^a

[DPA] Concentration $\times 10^4$ Molar	$H_2O_2 = 1 \times 10^{-2} M.$		$H_2O_2 = 2 \times 10^{-2} M.$		$H_2O_2 = 5 \times 10^{-2} M.$		$H_2O_2 = 10 \times 10^{-2} M.$		$H_2O_2 = 20 \times 10^{-2} M.$	
	$k',^b$ ($\times 10^2 \text{sec}^{-1}$)	Q.Y. ^c ($\times 10^3$)	$k',^b$ ($\times 10^2 \text{sec}^{-1}$)	Q.Y. ^c ($\times 10^3$)	$k',^b$ ($\times 10^2 \text{sec}^{-1}$)	Q.Y. ^c ($\times 10^3$)	$k',^b$ ($\times 10^2 \text{sec}^{-1}$)	Q.Y. ^c ($\times 10^3$)	$k',^b$ ($\times 10^2 \text{sec}^{-1}$)	Q.Y. ^c ($\times 10^3$)
0.33	7.3	0.026	8.0	0.056	9.5	0.13	13	0.21	20	0.36
0.67	7.7	0.059	8.4	0.13	9.5	0.24	12	0.43	21	0.74
1	7.6	0.082	8.2	0.16	9.5	0.38	12	0.68	21	0.92
5	7.6	0.39	8.2	0.71	9.3	1.7	12	3.2	22	6.2
10	7.2	0.73	8.2	1.4	9.3	3.0	13	5.4	20	8.6

^a Reactions were run with $2.33 \times 10^{-3} M$ oxalyl chloride in ether at $25^\circ C$.

^b k' = pseudo first order rate constant.

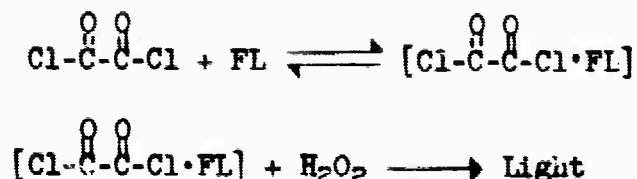
^c Q.Y. = quantum yield of chemiluminescence based on oxalyl chloride.

Table II		
Fluorescer	^a λ	Original Fluorescence Intensity ^c Fluorescence Intensity Following Chemiluminescent Reaction with Oxalyl Chloride ^b
Rubrene	550 m μ	60.0 55.0
1,4-Dimethoxy-9,10-diphenylanthracene	485 m μ	43.0 38.5

^a Wavelength for intensity measurement

^b Conditions: Fluorescer concentration = 1×10^{-4} M
 H_2O_2 concentration = 2.5×10^{-2} M
 OxCl₂ = 2.0×10^{-3} M

^c Arbitrary Units



Such a process would necessarily be characterized by alterations of the normal absorption spectrum of the fluorescent compound. Observation for spectral changes in this system is difficult, however, because ultra-violet light destroys oxalyl chloride by photolysis. An unchanged spectrum might thus lead to an erroneous conclusion. Spectral measurement is unambiguous, however, for the oxalyl chloride-rubrene system, since rubrene absorbs light in the visible portion of the spectrum at wavelengths where oxalyl chloride is unaffected. Measurements of the absorption spectrum of rubrene in pure ether solutions and in solutions containing a large excess of oxalyl chloride have given essentially identical spectral distributions and extinction coefficients. Thus there is evidently no complex formation in this system, and ground state complexes between oxalyl chloride and fluorescent hydrocarbons do not play a part in the chemiluminescent mechanism.

Absorption measurements of rubrene solutions in ether containing hydrogen peroxide similarly failed to show evidence of complex formation.

4. Fluorescence Quenching by Oxalyl Chloride

Evidence for fluorescence quenching by oxalyl chloride has been mentioned in previous reports.⁵ More definitive data has now been determined for quenching of rubrene in ether solution. The results show that substantial fluorescence quenching appears at oxalyl chloride

concentrations of 1×10^{-2} molar, but that only a 20% reduction of the unquenched intensity is seen at 10^{-3} molar oxalyl chloride. It should be noted that the quantum yield experiments in Part (A-1) were carried out at oxalyl chloride concentrations near 10^{-3} to minimize quenching effects.

SECTION I

EXPERIMENTAL

Quantum Yield and Rate Measurements

Appropriate stock solutions of the fluorescer, hydrogen peroxide and oxalyl chloride, were prepared in anhydrous ether which had been passed through an alumina column. Anhydrous hydrogen peroxide in ether was prepared by a method described by Greene and Kazan⁷ and analyzed iodometrically⁸. Ethereal solutions of distilled oxalyl chloride were analyzed gravimetrically by reaction with analine. The validity of the gravimetric method was determined as described in the following section.

Aliquots of fluorescer and hydrogen peroxide solutions were combined and mixed in a 3 ml. cylindrical cuvette, and 0.050 ml. of oxalyl chloride solution was injected. The timer was started and the solution was shaken and placed before the slit of the radiometer¹. This operation required about 8 seconds. The emission of a selected 5 mμ-wide spectral band bracketing wavelength λ' was recorded automatically as a function of time over several reaction halflives. Plots of log intensity vs. time were always linear. A typical plot has been illustrated previously³. The emission, $I_{\lambda'}^T$, in einsteins over the reaction lifetime for the 5 mμ-wide band was determined by the equation:

$$I_{\lambda'}^T = \frac{I_0}{k'} C q_{\lambda'}$$

where I_0 is the observed intensity extrapolated to zero time; k' is the pseudo first order rate constant; and C and $q_{\lambda'}$ are instrumental factors determined by the instrument calibration. I_0 and k' were calculated directly from the log intensity vs. time plots.

Total emission, E , in einsteins, over the entire spectral distribution and reaction lifetime is calculated from the formula:

$$E = I_{\lambda'}^T \left(\frac{\int_{\lambda_1}^{\lambda_2} I_{\lambda} W_{\lambda} q_{\lambda} d\lambda}{I_{\lambda'} W_{\lambda'} q_{\lambda'}} \right)$$

The integral is the area under the spectral distribution curve at an arbitrary time, T , calculated graphically or by computer. I_{λ} is the observed intensity at wavelength λ at time T ; W_{λ} is an instrumental factor determined by the instrument calibration, which converts I to watts at wavelength λ ; q_{λ} is the conversion factor to convert watts to quanta at wavelength λ ; $I_{\lambda'}$ is the observed intensity at time T and wavelength λ' , and $W_{\lambda'}$ and $q_{\lambda'}$ are the appropriate correction and conversion factors for λ' .

Some chemiluminescent reactions were too fast to measure the spectral distribution. It has been established previously² (for slower reactions) that the chemiluminescence spectrum is independent of time and identical to the fluorescence spectral distribution of the fluorescer. The spectral area per unit intensity at wavelength λ' was, therefore, determined from fluorescence measurements at each fluorescer concentration. Quantum yields were based on oxalyl chloride as the limiting reagent.

$$Q.Y. = \frac{E}{[\text{Oxalyl Chloride}]}$$

Determination of Oxalyl Chloride as Oxanilide

A solution of 14.1420 g. (11.147 millimoles) of freshly distilled oxalyl chloride in 100 ml. anhydrous benzene was prepared. A ten milliliter aliquot (1.1147 millimoles) of this solution was added to 25 ml. of anhydrous benzene containing 0.56 g. (6.0 millimoles) of aniline. After standing 30 minutes the white solid was collected on a tared sintered glass crucible, rinsed with ether, and stirred with 20 ml. of 5% NaHCO_3 solution for 10 min. in the crucible. The bicarbonate solution was removed by filtration and the white solid was washed well with water and dried in an oven at 110°C . for 1 hr. to obtain the oxanilide, m.p. $250-252^\circ$ (Lit⁹ m.p. $248-50^\circ$). Five separate determinations by this procedure gave $0.2639 \text{ g.} \pm 0.0004 \text{ g.}$ (98.5%). Theory: 0.2678 g.

Effect of Hydrogen Peroxide on the Absorption Spectrum of Rubrene in Ether

In an effort to detect complex formation between ground state rubrene and hydrogen peroxide, the absorption spectrum of 1.0×10^{-4} molar ethereal rubrene was measured in a 10 mm. cell on a Cary 14 spectrophotometer and compared to the absorption spectrum of 1.0×10^{-4} molar rubrene in ether containing 1.0 molar hydrogen peroxide. The absorption spectra and extinction coefficients for the two solutions were identical (within 2%) over the visible portion of the spectrum. Absorption by hydrogen peroxide occurred below 240 m μ .

The increase in fluorescence intensity with time after addition of oxalyl chloride results from photolysis of oxalyl chloride by the exciting ultraviolet light. No change is observed during periods when the light is off. Similar results were obtained for oxalyl chloride quenching of 1,4-dimethoxy-9,10-diphenylanthracene.

Fluorescence Quenching of Rubrene by Oxalyl Chloride

The fluorescence of approximately 9×10^{-4} molar solutions of rubrene in ether was excited by ultraviolet light in the standard radiometer. The intensity of emission at 550 mμ was recorded. Oxalyl chloride was added, and the fluorescence intensity was immediately remeasured. Fluorescence intensities were then continuously measured as a function of time until a constant value was obtained. The results are summarized below.

Fluorescence Intensity Before Addition of OxCl ₂ (550mμ)	OxCl ₂ Conc. (moles/liter) after Addition	Fluorescence Intensity after Addition of OxCl ₂ (550 mμ)	Time Lapse Before Fluorescence Intensity Became Constant	Final Fluorescence Intensity (550 mμ)
47.0	2×10^{-3}	37.6	2 seconds	46.5
40.0	1×10^{-2}	19.2	1 hour	36

Effect of Oxalyl Chloride on the Absorption Spectrum of Rubrene in Ether

In an effort to detect complex formation between ground state rubrene and oxalyl chloride, the absorption spectrum of 1.0×10^{-4} molar ethereal rubrene was measured in a 10 mm. cell on a Cary 14 spectrophotometer and compared to the absorption spectrum of 1.0×10^{-4} molar rubrene in ether containing 1.0 molar oxalyl chloride. The absorption spectra and extinction coefficients for the two solutions were identical (within 2%) over the visible portion of the spectrum. Additional absorption by oxalyl chloride was observed below 375 mμ.

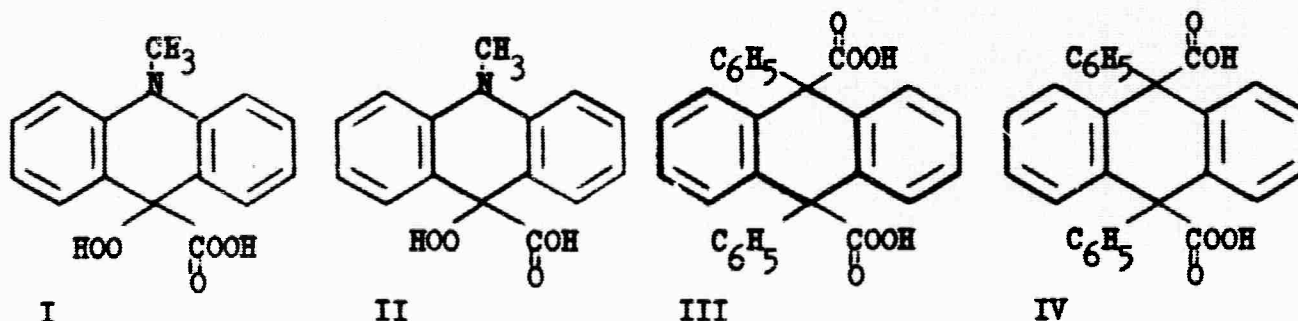
SECTION II

STRUCTURAL CRITERIA FOR CHEMILUMINESCENT COMPOUNDS

PART A

Relationship of Peroxides to Chemiluminescence

While chemiluminescence is observed during oxidations of a variety of apparently unrelated organic compounds, with the exception of electron transfer luminescence (see Section I), appreciable emission is observed only from oxidations involving oxygen or hydrogen peroxide. The action of oxygen or hydrogen peroxide in chemiluminescence seems best explained in terms of the formation of essential peroxidic intermediates¹. Preceding reports⁵ described in detail the evidence leading to this conclusion. In an effort to establish detailed criteria bearing on the relationship of peroxide structure to chemiluminescence efficiency, attempts have been made to synthesize several types of peroxides predicted on the basis of supplementary hypotheses to exhibit chemiluminescent decomposition. Recent effort has been concentrated on the preparation of precursors to the four peroxides shown below. While the peroxide literature suggests that

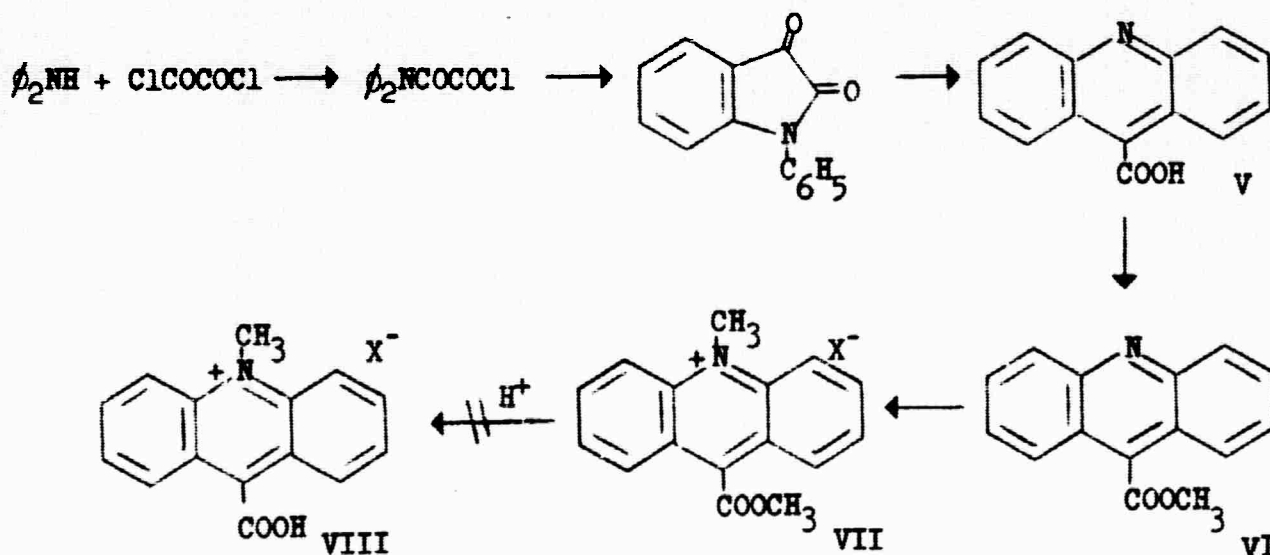


peroxides I through IV would have little stability, it appeared feasible to prepare stable precursors which would permit their unambiguous preparations in situ, and permit examination of their decompositions for chemiluminescence. These compounds would be expected to decompose to the known fluorescent products, N-methylacridone (from I and II) and 9,10-diphenylanthracene (from III and IV).

Though our work remains incomplete, precursors to III and IV have been isolated and shown to undergo chemiluminescent reactions with hydrogen peroxide; the synthesis of precursors to I and II is considered imminent. Moreover, during investigations of routes to I and II, two new chemiluminescent reactions have been uncovered.

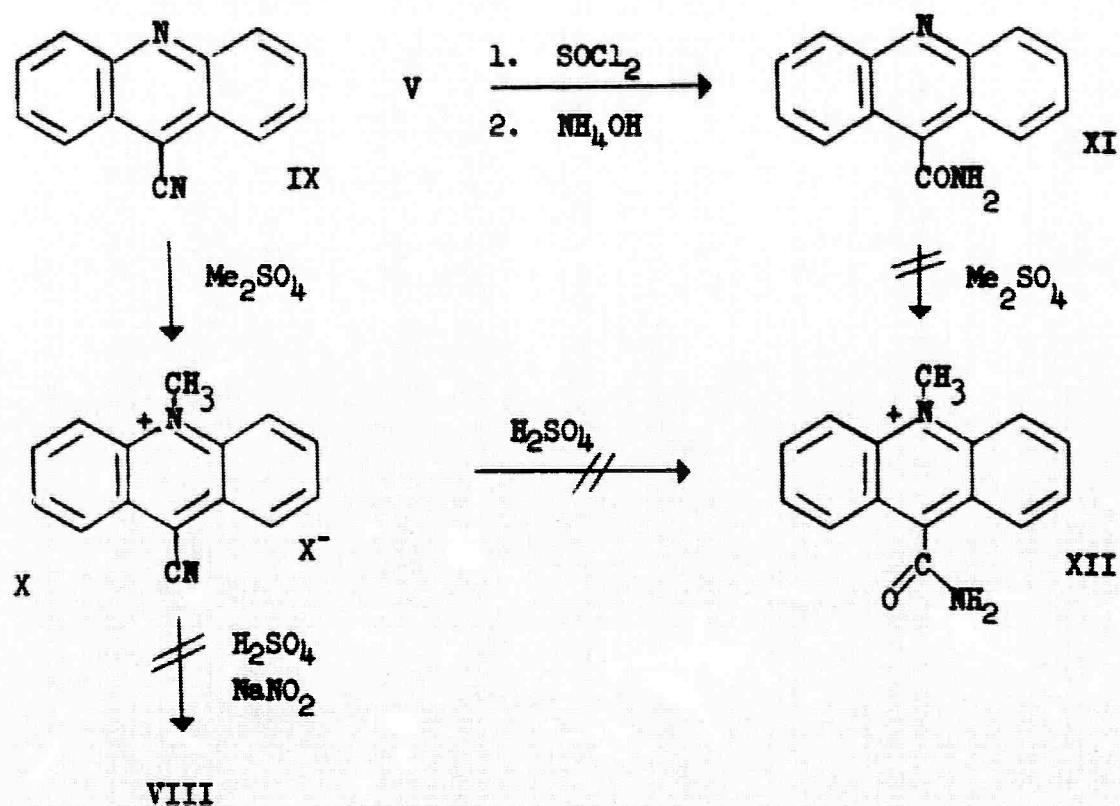
1. Peroxides Based on the Acridine System

In Technical Report No. 5⁵ we described early attempts to synthesize precursors to I and II by the route outlined below.

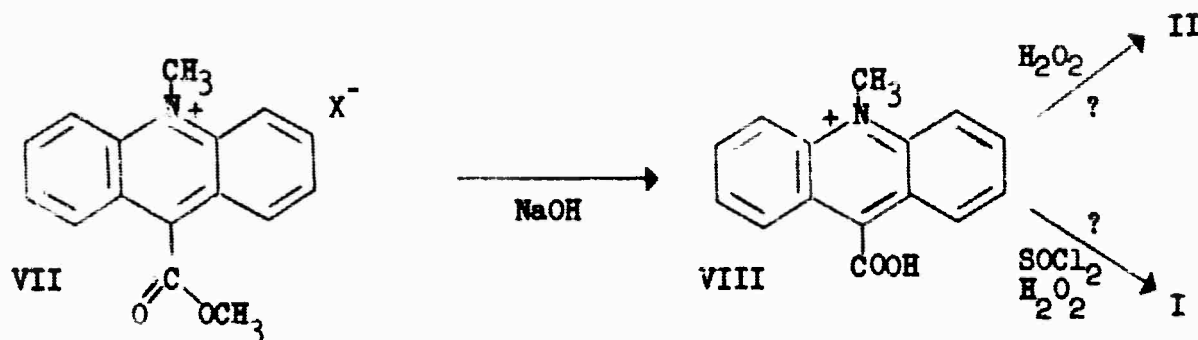


This route was temporarily blocked when VII proved to be completely resistant to the acid hydrolysis conditions normally applicable to

hindered esters. Alternative methods of protecting the acid function were investigated, as shown below, but without success. Thus, whereas the cyanoacridine IX could be readily methylated to X, subsequent acid



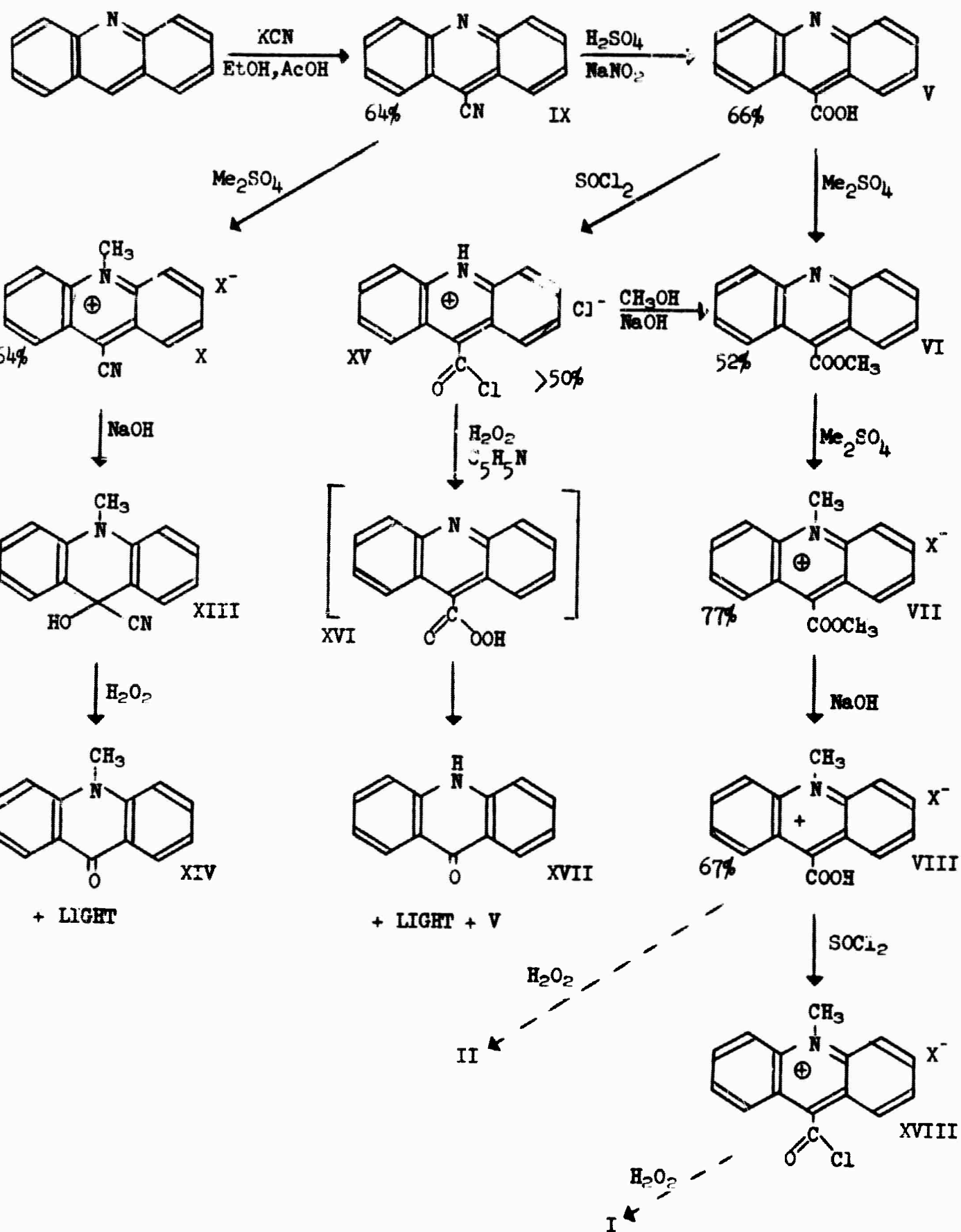
hydrolysis of the cyano group failed; the only isolable product was N-methylacridone. The alternative approach, conversion of the acid V to amide XI, followed by methylation and deamination to VIII, failed at the methylation step. We have recently reexamined the route via the ester VII and have found that hydrolysis can be achieved with surprising ease under alkaline conditions. Attempts to convert VIII to I and



II are currently in progress. During these synthetic investigations other possible pathways to chemiluminescent intermediates were examined. Chart I gives a summary of the successful synthetic procedures established, together with two new chemiluminescent reactions which have been discovered. It should be noted that a much more convenient method of preparation of the acridine acid V via cyanoacridine IX is currently being employed.

As indicated above, the cyanoacridine IX is readily methylated to the salt X. On treatment with aqueous base it affords a white solid, believed to be the pseudobase, XIII (structure proof in progress). This pseudobase dissolved in ethanol reacts with aqueous hydrogen peroxide to give a moderately strong blue emission with a lifetime in the range of twenty to thirty minutes. Recently McCapra and Richardson¹⁰ reported a somewhat similar chemiluminescent reaction between 9-cyano-N-methylacridinium nitrate and hydrogen peroxide. However, these authors failed to isolate the pseudobase XIII and suggested that it is not a precursor to chemiluminescence. We plan to investigate the mechanistic aspects of this reaction in detail. The

Chart I

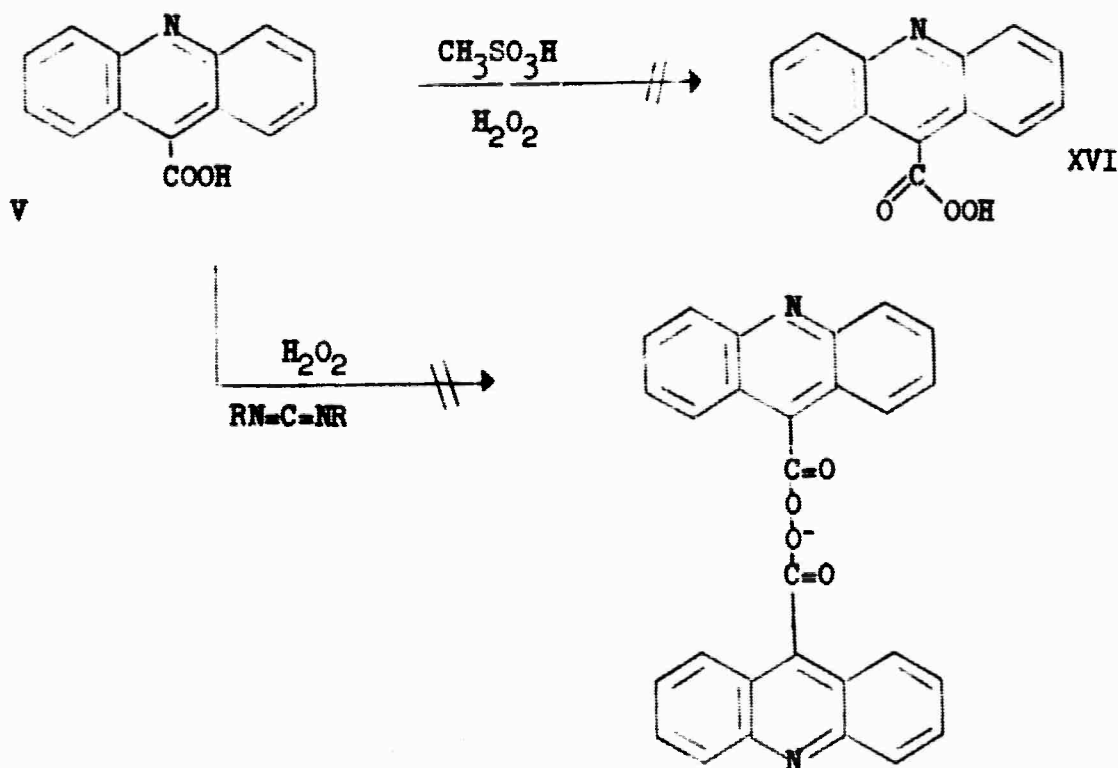


product thus far isolated is the expected emitting species--N-methylacridone, XIV.

The second new chemiluminescent reaction involves conversion of the acid V to the acid chloride-hydrochloride salt, XV, which, when dissolved in pyridine and treated with aqueous hydrogen peroxide, generates a moderately strong, long-lived blue light emission. Products isolated thus far are the acid, V, and the likely emitter, acridone, XVII.

Peracid derivatives such as XVI have not been isolated.

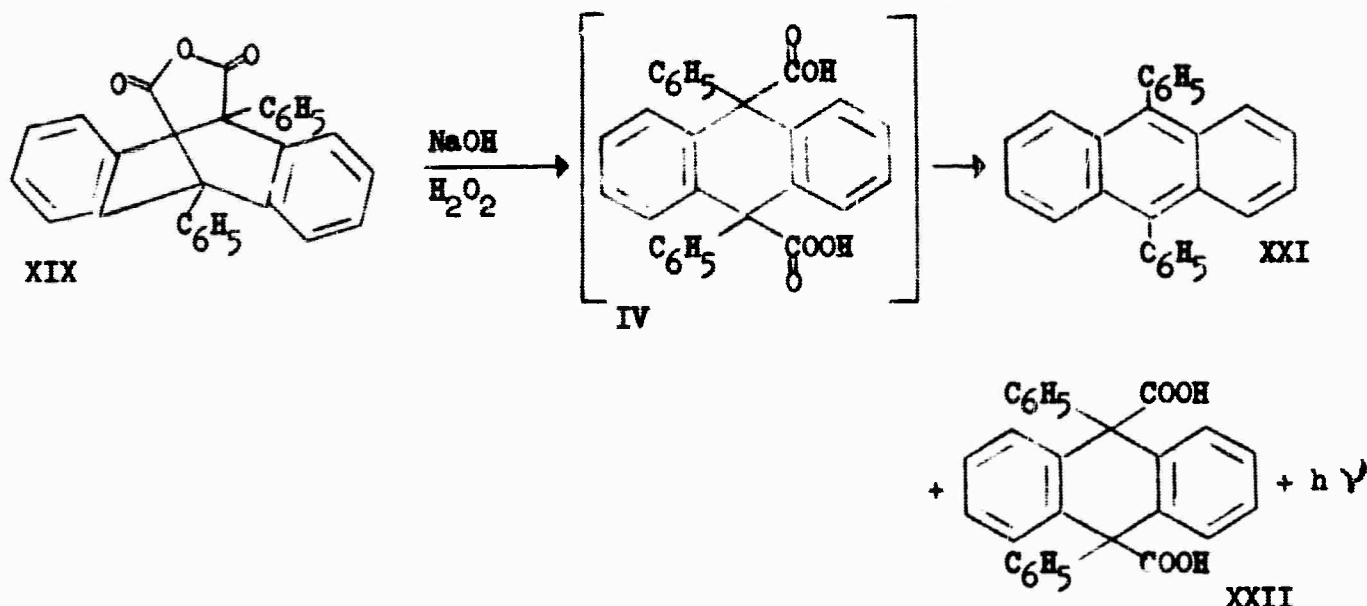
Alternative methods of in situ synthesis are also being investigated. Conventional methods of preparing peracids and peroxides have thus far failed, however, indicating that such peroxides are indeed unstable. Thus unreacted acid, V, was recovered from the reaction of

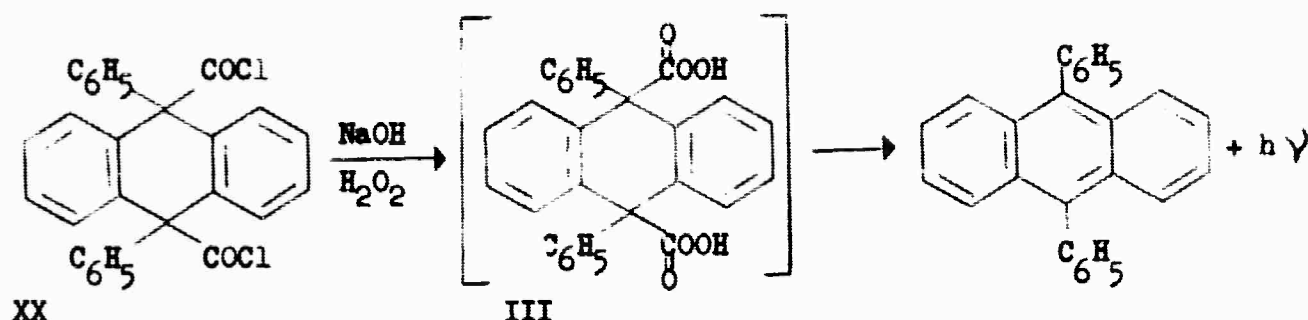


V with hydrogen peroxide in methane sulfonic acid. Reaction of V with anhydrous hydrogen peroxide and dicyclohexylcarbodiimide gave a product having peroxide activity (liberation of iodine from sodium iodide in acetic anhydride). However, infrared evidence indicated the material to be predominantly unchanged V. Light emission was not observed when the product was treated with hydrogen peroxide and base. Further investigation of peroxy derivatives of the acridine acid V are planned.

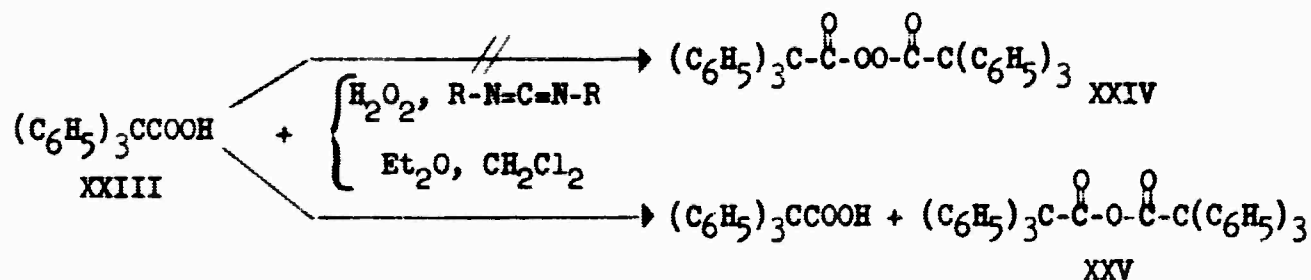
2. Peracids Based on the Anthracene System

We previously reported⁵ the isolation of the bridged anhydride, XIX (precursor of IV), and the bis (acid chloride) XX (precursor of III). Both compounds have now been shown to undergo chemiluminescent reactions under certain conditions. Reaction of XIX or XX with aqueous alkaline hydrogen peroxide generates a medium intensity, brier chemiluminescent emission, evidently derived from decomposition of peroxide IV. Alternatively when ethanol solutions of





XIX or XX were treated with hydrogen peroxide and pyridine, chemiluminescence was not observed. Both reactions afforded mixtures of the anthracene, XXI, and diacid, XXII. This apparent contradiction will be given further attention. Peracid derivatives have not been isolated. In a related experiment an attempt was made to convert triphenylacetic acid XXIII to the peroxide XXIV; peroxidic products were not isolated, and only triphenylacetic acid and a compound believed to be the anhydride XXV were obtained. However, when the



reaction was carried out in the presence of 9,10-diphenylanthracene, a weak emission of light was observed.

SECTION IIA

EXPERIMENTAL

9-Cyanoacridine¹¹ - In a 3-l. round-bottom flask equipped with a condenser, 178.2 g. of acridine (1 mole), 100 g. of potassium cyanide (1.5 mole) and 100 g. of acetic acid (1.6 mole) were mixed in 1 liter of 95% ethanol. The mixture was heated under reflux for two hours. After filtering the brown slurry, the collected solid was allowed to stand in air overnight. Recrystallization from ethanol yielded 130 g. (64%) of yellow needles, m.p. 181-183°, (Lit.¹¹, m.p. 181°).

Acridine-9-carboxamide

1. From 9-Cyanoacridine¹² - A solution of 5 g. (0.024 mole) of 9-cyanoacridine in 10 ml. of conc. sulfuric acid was heated on a steam bath for two hours. The dark orange solution was poured over ca 50 g. of ice. The yellow solid which formed was collected by filtration. The filtrate was neutralized with 3 N aqueous ammonium hydroxide, effecting the precipitation of a second crop of yellow solid. Infrared spectra indicated the first solid (0.97 g.) was the bisulfate salt of the desired amide; the second solid (3.23 g.) was the free base, m.p. 262-264° (Lit.¹² m.p. 263-4°). The total yield was 4.2 g. (78%).

2. From 9-Chlorocarbonylacridine Hydrochloride - A mixture of 7.45 g. (0.027 mole) of 9-chlorocarbonylacridine hydrochloride and 50 ml. of conc. ammonium hydroxide in a 100-ml. Erlenmeyer flask was heated on a steam bath for two hours. The solid was collected and recrystallized from ethanol to obtain 3.81 g. (64%) of yellow crystals, m.p. 262-264°.

Acridine-9-carboxylic Acid - To a solution of 4.2 g. of acridine-9-carboxamide (0.019 mole) in 20 ml. of conc. sulfuric acid was added at 0°, 5 g. (0.053 mole) of sodium nitrite in small portions. The solution was heated on a steam bath for two hours, then poured over ca 50 g. of ice. The yellow solid which formed was collected and dried in vacuo. The infrared spectrum of the product [3.6 g., 65%, m.p. 281° dec. (Literature reports on m.p. vary from 279°-300°)] agreed with previous spectra of the known product.

Attempted Methylation of Acridine-9-carboxamide - Dimethyl sulfate, ca 30 ml., was distilled directly into a 100-ml. round-bottom flask. A condenser, drying tube and nitrogen inlet were fitted into the flask and 3.8 g. of acridine-9-carboxamide was added. After heating the resultant slurry on a steam bath for three hours, the solid was collected on a Buchner funnel. The infrared spectrum of the product indicated that it was acridinium-9-carboxamide methosulfate. Hydrolysis of this amide gave only acridine-9-carboxylic acid.

9-Cyano-N-methylacridinium Bisulfate - In a 50-ml. round-bottom flask 5.9 g. of 9-cyanoacridine (0.035 mole) was combined with 20 ml. of dimethyl sulfate and the mixture was heated on a steam bath for two hours. A dark orange solution formed, and a red solid crystallized after cooling. The infrared spectrum of the solid (7.42 g., 64%) indicated the desired product had been obtained as the methosulfate salt. On recrystallization from acetonitrile (50% recovery) the infrared spectra indicated the product was present as the bisulfate salt, m.p. dec. above 150°, the anion apparently having hydrolyzed during the extended boiling prior to recrystallization.

Anal. Calcd. for $C_{15}H_{12}N_2SO_4$: C, 56.95; H, 3.82; N, 8.85;

S, 10.13.

Found: C, 57.03; H, 3.76; N, 8.92;

S, 10.29.

Hydrolysis of 9-Cyano-N-methylacridinium Methosulfate - A solution of 3.1 g. (0.01 mole) of 9-cyano-N-methylacridinium methosulfate in 20 ml. of fuming sulfuric acid was heated on a steam bath for two hours. The solution was then treated with 5 g. of sodium nitrite, and heating was continued for two additional hours. The solution was poured over 100 g. of ice to obtain a brown gummy solid. The solid was filtered and excess 95% ethanol was added to the filtrate. Yellow needles of N-methylacridone, m.p. 202-4° (Lit.¹⁴, m.p. 201-3°), crystallized and were collected. Identification was confirmed by infrared spectroscopy. The spectrum of the gummy solid indicated it too was crude N-methylacridone.

Solution of a 1-g. sample of 9-cyano-N-methylacridinium methosulfate in cold sulfuric acid, followed by pouring over ice and precipitation by ethanol, also led to N-methylacridone as the sole isolable product.

9-Carboxy-N-methylacridinium Chloride - A solution of 21 g. (0.058 mole) of 9-carbomethoxy-N-methylacridinium methosulfate⁵ in 200 ml. water was added to 200 ml. of 10% sodium hydroxide. The deep purple solution was heated for two hours on a steam bath, and the hot mixture was filtered. The dark amber filtrate was acidified with conc. hydrochloric acid, yielding a dark green solution from which yellow needles precipitated. The solid was collected on a Buchner, washed with isopropanol and dried in vacuo to yield 13.3 g. (84%) of product, m.p. dec. slowly above 205°. The infrared spectrum is in agreement with that expected for the product. Analysis pending.

9-Chlorocarbonylacridine Hydrochloride (XV) - In a 100-ml. flask, 8 g. of the partially hydrated sodium salt of acridine-9-carboxylic acid (30-33 mmole) was added to 50 ml. of thionyl chloride and the mixture heated on a steam bath for four hours. A clear brown

solution was obtained. The mixture was added to excess hot methylene chloride and the precipitated sodium chloride was filtered off. The filtrate was concentrated on a steam bath and heptane was added to precipitate the product. Filtration and drying afforded 7.45 g. of the yellow product, m.p. 218-218.5°. The yield based on anhydrous starting material was 82%.

Anal. Calcd. for $C_{14}H_9NOCl_2$: C, 60.5; H, 3.24; N, 5.03;

Cl, 25.5.

Found: C, 59.45; H, 3.42; N, 5.24;

Cl, 25.4.

Action of Aqueous Hydrogen Peroxide on 9-Chlorocarbonyl Acridine Hydrochloride (XV) In Pyridine - One gram of XV was dissolved in 20 ml. of pyridine in a test tube. One half of this solution was added to 10 ml. of a cold solution of 30% aqueous hydrogen peroxide. A steady light emission was observed changing from bright blue to blue-green with a lifetime of the order of 10 min., no solids separated and a mild gas evolution was observed. A similar result but more intense light emission was obtained using the remainder of the pyridine solution and reversing the order of addition. The two reaction mixtures were combined, 100 ml. of water was added and the solution was extracted twice with 100 ml. of ether. During the second extraction an orange-yellow solid precipitated from the aqueous phase which was separated and filtered. The solid was extracted with hot ethanol to leave a tan powder (ca. 300 mg.) which exhibited an infrared spectrum superimposable with that of acridine-9-carboxylic acid. The ether extracts were dried over magnesium sulfate, filtered and evaporated to afford a pale brown oil. Trituration of the oil with water gave a pale yellow solid. Filtration and recrystallization of the solid from aqueous ethanol yielded 150 mg. of acridanone, identified by its characteristic infrared spectrum.

Action of Sodium Peroxide and Hydrogen Peroxide on 9,10-Diphenyl-9,10-dihydroanthracene-9,10-dicarboxylic Anhydride⁷ - A solution of 200 mg. of the anhydride⁷ (XIX, 0.5 mmole) in 10 ml. of tetrahydrofuran was added in three portions at 1-min. intervals to a test tube containing a cold solution of 800 mg. of sodium peroxide (10 mmoles) in 10 ml. of water. No light emission was detected in the first few seconds, but rapid development of a blue-violet fluorescence was observed. After ca. 30 secs. a blue emission was observed from the upper liquid phase. On shaking the emission occurred throughout the mixture and a white gelatinous solid separated. Filtration afforded a white solid which had an infrared spectrum identical with that of the hydrated disodium salt of 9,10-diphenyl-9,10-dihydroanthracene-9,10-dicarboxylic acid. The filtrate on standing afforded pale yellow crystals of 9,10-diphenylanthracene, identified by its infrared spectrum.

When a few mg. of the anhydride (XIX) were dissolved in 5 ml. of tetrahydrofuran and added to 10 ml. of a 1 M solution of hydrogen

peroxide in ether, no light emission or fluorescence was observed. The addition of 1 ml. of pyridine caused immediate fluorescence to develop, but no light emission, and the mixture became turbid. After standing for 24 hours, the mixture had evaporated to 3-4 ml. and a white crystalline solid had separated. The latter was filtered and dried and shown to be 9,10-diphenyl-9,10-dihydroanthracene-9,10-dicarboxylic acid by its infrared spectrum. A further crop of crystals was obtained from the filtrate on standing, and infrared evidence indicated that this product was again mainly the diacid, but contaminated with a small amount of 9,10-diphenylanthracene.

Action of Dicyclohexylcarbodiimide and Hydrogen Peroxide on Triphenylacetic Acid - In an ice-bath-cooled 100-ml. flask fitted with a condenser and drying tube, 2.26 g. of dicyclohexylcarbodiimide (11 mmole) was suspended in 15 ml. of ether. A solution of 1.7 g. of 90% hydrogen peroxide (approx. 50 mmole) was added together with a few small crystals of 9,10-diphenylanthracene. At an internal temperature of 4° 25 ml. of methylene chloride and 2.9 g. of triphenylacetic acid (10 mmole) were added, the latter appeared to be insoluble. After 20 min. the temperature had reached 10° and a weak, diffuse light emission was observed. After a further 30 min. at 5-10°, no light emission could be detected. The mixture was stirred for a total period of two hours when the acid still appeared insoluble and the mixture was stored in a icebox overnight. Filtration of the white insoluble solid and copious washing with methylene chloride and ether afforded 2.2 g. of dicyclohexylurea, m.p. 230-231°, infrared spectrum identical to that of authentic material. The filtrate and washings were extracted successively with saturated aqueous solutions of ammonium chloride, sodium carbonate and sodium chloride, the organic layer separated, dried over magnesium sulfate and filtered. The filtrate was evaporated to yield a white powder, the infrared spectrum of which exhibited absorption bands typical of a carboxylic acid (1700 cm^{-1}) and an acid anhydride ($1815, 1740\text{ cm}^{-1}$). A test for peroxides (sodium iodide and acetic anhydride) proved negative. Fractional crystallization from ether/heptane afforded a first crop of pure triphenylacetic acid, m.p. 263-265°; and a second crop of material believed to be triphenylacetic anhydride, m.p. 174.5-176.5°. This latter identification is to be confirmed.

Chemiluminescent Reaction of "Pseudobase" (XIII) with Hydrogen Peroxide - A mixture of 0.1 g. of 9-cyano-N-methylacridinium bisulfate, 3 ml. of 20% sodium hydroxide and 20 ml. of 95% ethanol was heated in a 50 ml. flask until solution was complete. The yellow needles which crystallized after cooling were collected. The infrared spectrum conforms to that expected for the "pseudobase" structure (XIII). Analysis pending.

An ethanolic solution of this product was treated with 30% hydrogen peroxide and provided a medium, blue, long-lived light emission.

SECTION II

PART B

New Chemiluminescent Compounds Based on the Oxalic Acid System

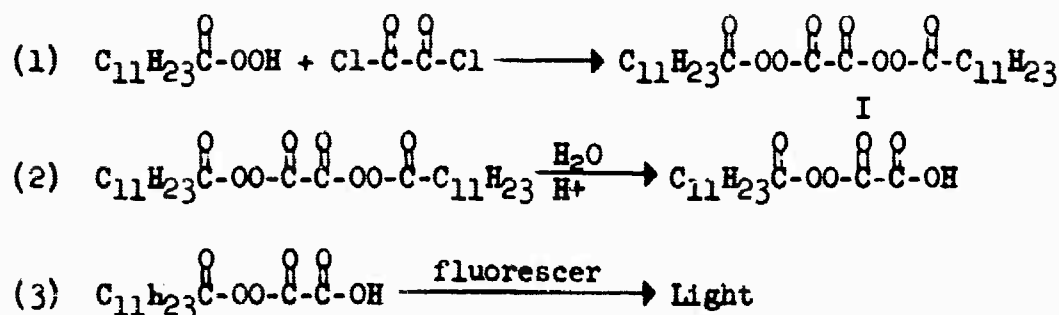
An investigation of the mechanism by which chemiluminescence is produced in the reaction oxalyl chloride with hydrogen peroxide (see Section I) has clearly implicated a peroxyoxalic acid as a key intermediate. Indeed a number of peroxyoxalate derivatives have been found to provide chemiluminescence on decomposition^{2,3,4,5}. To further expand our understanding of this general chemiluminescent process, we are continuing to study the structural requirements bearing on chemiluminescent efficiency.

Moreover, chemiluminescent systems now available have serious defects, barring many uses for practical lighting. These defects include short lifetimes, difficult operating procedures, and efficiencies that approach but fall short of the efficiency required for a broadly practical system. The present study therefore includes an initial effort to provide new chemiluminescent systems which will provide long-lasting light on contact with air or water.

1. Attempts to Isolate Acylperoxides of Oxalic Acid

Mechanism studies on the oxalyl chloride-hydrogen peroxide-fluorescent compound chemiluminescent system³ have indicated that peroxides of the structure $R-\overset{\overset{O}{\parallel}}{C}-OO-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-OH$ decompose spontaneously to provide light in the presence of a fluorescent compound. Thus a reaction which provides such a peroxide by a relatively slow process

should also provide a long-lived chemiluminescent system. Step (2) in the following sequence is one of a large number of possibilities that are being investigated to this end.



Peroxyauric acid does not generate chemiluminescence when combined with oxalyl chloride in ether solution containing a fluorescer at room temperature regardless of the reactant ratio. When such mixtures are subsequently treated with water, however, bright emission is obtained. This observation suggested that the peroxide I might be sufficiently stable to isolate. Moreover, ditertiarybutyldiperoxyoxalate, a peroxide of related structure, has been isolated by a similar procedure¹⁹. Our attempts to prepare peroxide I in the experiments described below have given discouraging results, however, indicating that such peroxides are insufficiently stable for isolation and storage.

(a) Reactions of Peroxyauric Acid with Oxalyl Chloride

Oxalyl chloride was treated with peroxyauric acid in ether, petroleum ether or in the absence of solvent⁵ and in the presence or absence of pyridine. As indicated in Table I peroxyoxalates were not isolated in any of the experiments; only lauric acid and dilauryl peroxide were obtained after evaporation of the solvent under reduced pressure.

Table I

Attempted Preparation of Lauryl Oxalyl Peroxides

<u>Mode of Addition of Reactants</u>	<u>Solvent</u>	<u>Temp.</u>	<u>Base</u>	<u>Reaction Time</u>	<u>Products</u>
Cl-CO-CO-Cl added to 2 PLA	Ether	0° - 25°	None	1/2 hr.	LA + LP
Cl-CO-CO-Cl added to 2 PLA	Pet. ether	0°	None	1/2 hr.	LA + LP
3Cl-CO-CO-Cl added to PLA	Pet. ether	0°	Pyridine	1 hr.	LA + LP
Cl-CO-CO-Cl added to 2 PLA	Pet. ether	0°	Pyridine	1 hr.	LP
Cl-CO-CO-Cl added to 2 PLA	Pet. ether	0°	None	1 hr.	PLA
2PLA added to Cl-CO-CO-Cl	Pet. ether	0°	None	1 1/2 hr.	PLA
PLA added to Cl-CO-CO-Cl	None	0°	None	18 hrs.	LA

PLA = peroxyauric acid
LA = lauric acid
LP = lauryl peroxide

In addition, only lauric acid was obtained from the reaction of a pyridine-oxalyl chloride complex with peroxyauric acid. (See later discussion of the preparation and properties of this complex.)

(b) Reaction of Potassium Peroxylaurate with Oxalyl Chloride

The potassium salt of peroxyauric acid was prepared under anhydrous conditions by the titration of potassium triphenylmethide with peroxyauric acid in 1,2-dimethoxyethane. The freshly prepared solution of the potassium salt was treated with oxalyl chloride and the solution

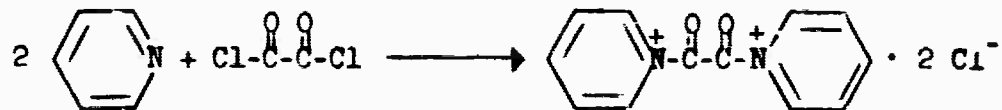
evaporated to dryness under reduced pressure. The solid product obtained was a complex mixture but non-peroxidic. This experiment will be repeated under other conditions.

(c) Reaction of Oxalic Acid with Dicyclohexylcarbodiimide and Peroxylauric Acid

Application of the powerful carbodiimide method of peroxide synthesis⁷ to the preparation of dilauroyldiperoxyoxalate from oxalic acid and peroxyauric acid gave only dilaurylperoxide and dicyclohexylurea. Neither oxalyl peroxides nor oxalic acid were obtained.

2. Chemiluminescence from the Pyridine Complex of Oxalyl Chloride

Pyridine has long been known to form a 2:1 "complex" with oxalyl chloride. The complex is a yellow hygroscopic solid decomposing at 118-120°.¹⁶



This complex was examined for chemiluminescence under a variety of conditions as described below.

(a) Reactions with Peroxides

Reaction of the pyridine-oxalyl chloride complex with several peroxides in the presence of a fluorescer was found to generate chemiluminescence as indicated in Table II.

Table II

Oxalyl Chloride-Pyridine Complex Peroxide System

<u>Solvent</u>	<u>Co-reactant</u>	<u>Temp.</u>	<u>Atmosphere</u>	<u>Chemiluminescence Intensity</u>
Tetrahydrofuran	H ₂ O	25°	Air	None
Tetrahydrofuran	H ₂ O ₂ (30%)	25°	Air	M
Ether	Peroxy-lauric acid	25°	Argon	MW
Pet. ether	Peroxybenzoic acid	-70°	Argon	None
Pet. ether	Peroxybenzoic acid	0°	Argon	None
Pet. ether	Peroxybenzoic acid	25°	Argon	VW
Ether	Peroxybenzoic acid	25°	Argon	W
Ether	Peroxybenzoic acid	-70°	Argon	VW
Ether	9,10-Diphenylanthracene Photooxide	25°	Argon	None
Ether (no fluorescer)	9,10-Diphenylanthracene Photooxide	25°	Argon	None

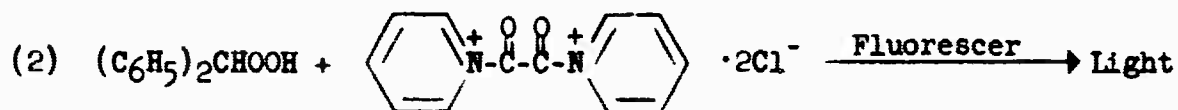
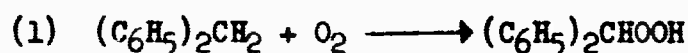
Test: Approximately 2 - 3 mg. of the complex was added to a solution of 1 mg. 9,10-diphenylanthracene and about 5 mg. of co-reactant in 5 ml. solvent maintained at the desired temperature. Chemiluminescence was observed visually. Classification is based on oxalyl chloride-hydrogen peroxide taken as strong (S). Other designations are M = medium, W = weak, VW = very weak, barely visible

Reaction of the complex with water is vigorous but non-chemiluminescent. Reaction with hydrogen peroxide, however, provides a medium intensity emission. Reactions with peroxy-lauric and peroxybenzoic acids produced evident but less intense emissions, which are temperature dependent. The failure of 9,10-diphenylanthracene photooxide to provide chemiluminescence eliminates it as an essential

intermediate derived from the fluorescer.

(b) Oxygen Promoted Chemiluminescence from Pyridine-Oxalyl Chloride Complexes

The observation in the preceding section that organic peroxides react with the pyridine oxalyl chloride complex to produce light indicates that a reaction which can provide such a peroxide in a system containing the complex would also be chemiluminescent. One of a large number of possibilities for achieving such a process is illustrated in the following equations:



An initial investigation of the above process has demonstrated that the reaction of oxygen with the pyridine-oxalyl chloride complex and diphenylmethane in the presence of the free radical initiator α, α' -azobisisobutyronitrile (AIBN) and a fluorescer such as 9,10-diphenylanthracene (DPA) at 80° generates a medium intensity, long-lived emission. The intensity of the emission can be controlled by the concentration of initiator, the oxygen pressure, and by the reaction temperature. A large number of free radical initiators, fluorescers, and hydroperoxide precursors are expected to be active in this process and are being studied. The practical advantages of a bright, long-lived, oxygen activated chemiluminescent system are evident.

(c) Chemiluminescence Thermal Decompositions of the Oxalyl Chloride

Pyridine Complex

Chemiluminescent emission was observed from the thermal decomposition of the pyridine-oxalyl chloride complex under certain conditions even when oxygen was excluded. The results of a number of experiments are summarized in Table III. As noted in the table, the temperature required for decomposition varies markedly with the solvent. Best chemiluminescent intensities were obtained in diphenyl or triphenylmethane, suggesting the involvement of a free radical reaction with solvent. This conclusion is reinforced by observations that chemiluminescent intensity is substantially increased in the presence of a free radical initiator α, α' -azobisisobutyronitrile and decreased by the presence of the free radical inhibitors, 2,6-t-butyl-4-methylphenol and hydroquinone.

Chemiluminescence was not observed from decompositions of solid mixtures of the complex with fluorescers or in glycerine or benzene solutions. A protic solvent would be expected to react with the complex similarly to water in a dark reaction. The relatively low boiling point of benzene may explain the lack of chemiluminescent reaction in that solvent.

The two main products of the decomposition are pyridine hydrochloride and carbonmonoxide.

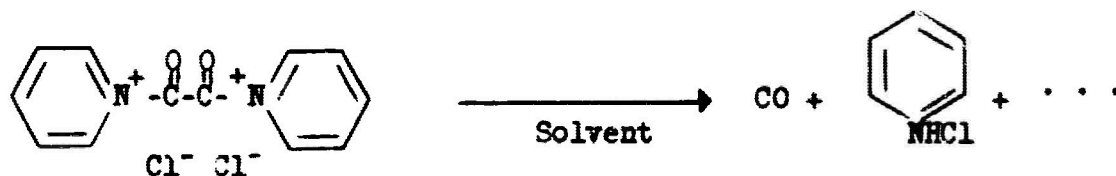


Table III

Thermal Decomposition of Oxalyl Chloride Pyridine Complex (1:2)

<u>Solvent</u>	<u>Temp.</u>	<u>Atmosphere</u>	<u>Chemiluminescence Intensity</u>	<u>Remarks</u>
(C ₆ H ₅) ₂ CH ₂	25°	N ₂	MS	
(C ₆ H ₅) ₂ CH ₂	25°	Ar	MS	
(C ₆ H ₅) ₂ CH ₂	25°	Ar	M	Hydroquinone inhibitor added
(C ₆ H ₅) ₂ CH ₂	25°	Ar	VW	t-Bu cresol inhibitor added
(C ₆ H ₅) ₂ CH ₂	85°	Ar	MS	
(C ₆ H ₅) ₂ CH ₂	85°	Ar	S	Azobisisobutyronitrile initiator added
(C ₆ H ₅) ₂ CH ₂	85°	Ar	MW	Hydroquinone inhibitor added
(C ₆ H ₅) ₂ CH ₂	85°	O ₂	S	Azobisisobutyronitrile initiator added
(C ₆ H ₅) ₂ CH ₂	140°	Ar	S	
(C ₆ H ₅) ₃ CH	140°	Ar	MW	
Paraffin	140°	Ar	W	
p-Cl ₂ C ₆ H ₄	53°	Ar	VW	
p-Cl ₂ C ₆ H ₄	140°	Ar	VW	
Cl-C ₆ H ₅	25°	Ar	VW	
Cl-C ₆ H ₅	130°	Ar	W	
Benzene	80°	Ar	None	
Glycerine	140°	Ar	None	
No solvent	120°	Ar	None	

Test: Approximately 3 mg. of the complex was added to the solution of 1 mg. 9,10-diphenylanthracene fluorescer in 5 ml. solvent maintained under the desired atmosphere. Chemiluminescence was observed visually. Classification is based on oxalyl chloride-hydrogen peroxide taken as strong (S). Other designations are M = medium, W = weak, VW = very weak, barely visible

Most of the experiments were carried out in an argon atmosphere and all solvents used were carefully purified and distilled as well as tested for the absence of peroxide. The standard potassium iodide method (2),¹⁷ as well as the more sensitive chemiluminescence reaction of oxalyl chloride with peroxides, was used to establish that peroxides were not present. The appearance of chemiluminescence under these conditions indicates that oxygen or peroxides are not essential to the chemiluminescence process. This conclusion, however, requires additional verification.

Chemiluminescence from thermal decomposition of pyridine complexes of acid chlorides is not confined to the oxalyl chloride complex. The acetyl chloride pyridine complex also enters a free radical chemiluminescence thermal decomposition, even though it fails to produce light on reaction with peroxides. These results are summarized in Table IV.

Table IV
Acetylchloride-Pyridine Complex

<u>Solvent</u>	<u>Co-reactant</u>	<u>Temp.</u>	<u>Atmosphere</u>	<u>Chemiluminescence Intensity</u>	<u>Remarks</u>
$(C_6H_5)_2CH_2$	None	90°	Ar	VW	
$(C_6H_5)_2CH_2$	None	90°	Ar	VW	Azobisisobutyronitrile added
$(C_6H_5)_2CH_2$	None	90°	Ar	None	Hydroquinone added
Ether	Perlauric acid	25°	Ar	None	
Ether	H ₂ O ₂ (90%)	25°	Ar	None	

Tests were carried out as in Tables II and III.

SECTION IIB

EXPERIMENTAL

Pyridine-Oxalyl Chloride Complex (2:1) - A solution of 0.6 g. (0.005 mole) of oxalyl chloride in 25 ml. dry petroleum ether was added dropwise with stirring to 0.8 g. (0.01 mole) pyridine in 25 ml. dry petroleum ether at 25°. The reaction was protected from moisture with a "Drierite" drying tube.

The yellow precipitate, which formed immediately during addition, was filtered under nitrogen, washed with petroleum ether, and dried under vacuum to obtain 1.0 g. (71.4%) of product, m.p. 118.5-120.0°; resolidification, then partial melting 140-42° (Lit.¹⁶ m.p. 118-20°; solidification, melting 137-40°).

Elementary Anal Calculated: C, 50.54; H, 4.35; N, 9.83; Cl, 24.87.

Obtained: C, 50.91; H, 3.53; N, 9.72; Cl, 24.66.

Pyridine-Acetylchloride Complex (1:1) - A solution of 0.8 g. (0.01 mole) of acetylchloride in 10 ml. of dry petroleum ether was added dropwise to a stirred solution of 0.8 g. (0.01 mole) of pyridine in 10 ml. dry petroleum ether precooled to 0° under argon. The reaction mixture was stirred 1/2 hr. at 0°. The precipitate, which began to form almost immediately, was collected on a filter under argon, washed with petroleum ether, and dried to obtain 0.6 g. (38.7%) of product whose infrared spectrum is in agreement with that expected for the desired product as compared to the spectrum of the oxalyl chloride complex.

Peroxy¹⁸lauric Acid - To a slurry of 30 g. (0.15 mole) of lauric acid in 72 g. (0.75 mole) of methanesulfonic acid at 40°, was added 16.6 g. (0.45 mole) of 90% hydrogen peroxide during 20 minutes. The temperature was maintained at 40° with stirring for 40 minutes. Then crushed ice was added slowly to the reaction mixture maintaining the temperature 25°. The mixture was filtered, and the collected material washed well with cold water and dried under vacuum to obtain 34.8 g. (100%) of peroxyacid, m.p. 50-51° (Lit.¹⁸ m.p. 50-50.5°). The product was crystallized from petroleum ether.

A solution of 0.3 g. (0.0025 mole) of oxalyl chloride in 10 ml. anhyd. ether was added slowly to a stirred solution of 1.05 g. (0.005 mole) of peroxy¹⁸lauric acid precooled to 0° under argon. Gas evolution was noted. The reaction temperature was allowed to rise to 25° over 1/2 hr., then the reaction was stirred an additional 1/2 hr. The solution was evaporated to dryness under reduced pressure. Products obtained from the reaction were analyzed by infrared analysis and were found to be lauric acid and lauroyl peroxide, together with small amounts of peroxy¹⁸lauric acid; oxalic acid derivatives were not detected.

A solution of 0.3 g. (0.0025 mole) of oxalyl chloride in 10 ml. anhyd. petroleum ether was added slowly under argon to a stirred solution of 1.05 g. (0.005 mole) peroxyauric acid in 10 ml. anhyd. petroleum ether precooled to 0°. Gas evolution was noted. The reaction was stirred 1/2 hr. at 0°, then evaporated to dryness under reduced pressure. The products obtained from the reaction were analyzed by infrared spectroscopy and found to be approximately 70% lauric acid and 30% lauroyl peroxide; no desired product obtained was detected.

To a stirred solution of 0.53 g. (0.0025 mole) of peroxyauric acid and 0.2 g. (0.0025 mole) of pyridine in 25 ml. anhydrous petroleum ether cooled to 0° under argon, was slowly added a solution of 0.15 g. (0.00125 mole) of oxalyl chloride in 25 ml. petroleum ether. The reaction mixture was stirred 1 hr. at 0°, then the precipitated pyridine hydrochloride was filtered off, and the filtrate evaporated to dryness. The solid residue was analyzed by infrared spectroscopy and found to be lauric acid (approximately 50%) and lauroyl peroxide (approximately 40%); no desired product was detected.

A solution of 0.53 g. (0.0025 mole) of peroxyauric acid and 0.2 g. (0.0025 mole) of pyridine in 25 ml. anhydrous petroleum ether was added slowly to a stirred solution of 0.9 g. (0.0075 mole) of oxalyl chloride in 25 ml. petroleum ether precooled to 0° under argon. The reaction mixture was stirred 1 hr. at 0°. The pyridine hydrochloride precipitate was filtered off, and the filtrate evaporated to dryness under reduced pressure at room temperature. The product was analyzed by I.R. spectroscopy and found to be mainly lauroyl peroxide, with some lauric acid present; no desired product obtained.

To a stirred solution of 0.53 g. (0.0025 mole) of peroxyauric acid in 25 ml. dry petroleum ether precooled to 0°, a solution of 0.15 g. (0.00125 mole) of oxalyl chloride in 25 ml. dry petroleum ether was added slowly under argon. The reaction mixture was stirred 1 hr. at 0°, then evaporated to dryness under reduced pressure without external heat. The residue was found by infrared spectroscopy to be pure unchanged peroxyauric acid; apparently no reaction had taken place.

A solution of 0.53 g. (0.0025 mole) of peroxyauric acid in 25 ml. dry petroleum ether was added slowly to a stirred solution of 0.90 g. (0.0075 mole) of oxalyl chloride in 25 ml. dry petroleum ether under argon precooled to 0°. The reaction was stirred 1.5 hrs. at 0°, then evaporated to dryness under reduced pressure using no external heat. The residue was found by infrared spectroscopy to be pure unchanged peroxyauric acid; no reaction had taken place.

Peroxyauric acid (0.53 g., 0.0025 mole) and oxalyl chloride (0.15 g., 0.00125 mole) were mixed at 0° in a dry atmosphere. The reaction mixture was stirred 1.5 hrs. at 0° under reduced pressure, then allowed to stand 18 hrs. at 0°. The residue was analyzed by I.R. spectroscopy to be a mixture of lauric acid and lauroyl peroxide, with a small amount of peroxyauric acid; no desired product was obtained.

The oxalyl chloride-pyridine complex (1:2) (0.0025 mole) was freshly prepared in 60 ml. dry tetrahydrofuran to the stirred slurry of the complex, a solution of 1.05 g. (0.005 mole) peroxylic acid in 40 ml. dry tetrahydrofuran was added under argon. The reaction mixture was stirred for 1 hr. at 25° C. then filtered to recover a white solid whose infrared spectrum agreed with that of pyridine hydrochloride. The filtrate was evaporated to dryness under reduced pressure at room temperature. The solid residue was analyzed by I.R. spectroscopy and found not to contain any of the desired dilauryl oxalyl chloride.

Potassium triphenylmethide (approximately 0.0025 mole) was prepared by the reaction of elemental potassium with triphenylmethane in dry glyme in a dry atmosphere. The potassium triphenylmethide solution was titrated with 0.1 M peroxylic acid in dry glyme to form the salt of the peroxy acid. The amount of peroxylic acid required was 0.001 mole. The glyme solution of the peroxylic acid salt was cooled to 0° under argon, then a solution of 0.15 g. (0.00125 mole) of oxalyl chloride in 25 ml. dry glyme was added dropwise with stirring. The reaction was stirred 1 hr. at 0°, then the solvent was evaporated under reduced pressure. The residue was analyzed by I.R. spectroscopy and was found to be a mixture containing, in addition to triphenylmethane, a compound with an ionized carboxyl and a non-peroxidic unknown; apparently no desired compound was obtained.

A solution of 0.45 g. (0.005 mole) of oxalic acid and 2.16 g. (0.01 mole) of peroxylic acid in 90 ml. anhydrous ether and 90 ml. dichloromethane was added in one portion to a stirred solution of 2.06 g. (0.01 mole) of dicyclohexylcarbodiimide in 20 ml. anhydrous ether precooled to 0°. The reaction mixture was stirred 22 hrs. at 0° in a dry atmosphere. The precipitated dicyclohexylurea was collected on a filter and washed three times with 20 ml. portions of dichloromethane. Dicyclohexylurea (1.15 g., 50%) m.p. 233-4° (Lit.⁷ m.p. 233-4°) was obtained. The I.R. spectrum agreed with that of an authentic sample. The combined organic solutions were evaporated to dryness under vacuum. The residue from the reaction was mainly lauroyl peroxide with smaller amounts of dicyclohexylcarbodiimide dicyclohexylurea; no oxalic acid was recovered nor desired peroxidic product detected.

SECTION III

BRIGHTNESS AND LIFETIMES OF CHEMILUMINESCENT SYSTEMS

Chemiluminescence quantum yield data is of major importance in determining chemiluminescence mechanisms and in assessing the potential practical value of a chemiluminescent system. However, such data does not directly provide a measure of visual brightness, since chemiluminescence brightness is a function of reaction rate sample thickness and spectral distribution as well as quantum yield.

To assist other laboratories in interpreting the quantum output and the brightness of the systems under investigation, these reports will contain, in addition to quantum yield data, light output in the following units:

1. Brightness - Initial brightness is reported in foot lamberts using the photopic scale for eye sensitivity. In order that the significance of any given brightness measurement be properly evaluated, it is accompanied by data on (a) lifetime (expressed at the time to half brightness or by giving a plot of brightness vs. time), (b) the concentration of reagents used (in weight per cent or moles per liter), and (c) the thickness of the sample.

2. Quantum Output - Initial chemiluminescent output in terms of total quanta (in einsteins) emitted per cc. per second with a frequency response curve, and, as before, lifetime and concentration information.

Conversion of Quantum Units to Photometric Units - In our laboratory it is convenient to first calculate the over-all time-integrated luminosity of a chemiluminescent system in units of

lumen-seconds per ml. (L^T) from the formula:

$$L^T = \phi C \times 10^{-3} \frac{A_L}{A_q}$$

In this formula ϕ is the quantum yield in einsteins per mole, C is the concentration of limiting reactant in moles per liter, A_L is the area of the spectral distribution curve at an arbitrary time T (providing that the spectral distribution is not a function of time) in units of lumens, and A_q is area under the spectral distribution curve at time T in units of quanta per second.

A_L and A_q can be calculated graphically or by computer from the integrals:

$$A_L = \int_{\lambda_1}^{\lambda_2} I_{\lambda} W_{\lambda} Y_{\lambda} d\lambda$$

$$A_q = \int_{\lambda_1}^{\lambda_2} I_{\lambda} W_{\lambda} q_{\lambda} d\lambda$$

where I_{λ} is the observed intensity at time T and wavelength λ , W_{λ} is an instrumental factor, determined by the calibration, which converts I_{λ} to energy units in watts, and Y_{λ} and q_{λ} are the appropriate conversion factors for converting watts to lumens and to einsteins per second. λ_1 and λ_2 are, of course, the wavelength limits of the spectral distribution curve.

Initial (Zero-time) Luminosity - For first or pseudo first order reactions the initial (zero-time) luminosity, L , in lumens per ml. is calculated from

$$L = k' L^T$$

where k' is the first order rate constant.

Brightness - In principle it can be misleading to report chemiluminescent output using a standard photometric unit for brightness. Brightness is usually applied to surfaces which obey Lambert's law, that is, that the emission per unit solid angle is proportional to the cosine of the angle between the direction of observation and the surface normal. This cosine law is not obeyed by a chemiluminescent system, since chemiluminescence is emitted not from a surface but from various points in a bulk liquid and also because the light emitted is refracted on passing through a liquid-air or liquid-glass interface. The practical effect of this difference is that the brightness of a chemiluminescent sample of uniform thickness varies with the angle of observation, becoming brighter as the observer moves away from the surface normal. By contrast, the brightness of a uniformly diffusing surface is the same at all angles.

The brightness measurements reported here refer only to that light which leaves a flat transparent surface at an angle sufficiently close to the surface normal so that the lack of a cosine dependence is not experimentally significant. Also the light measured includes no light reflected from rear or side surfaces. This is accomplished by using a sample cell with flat parallel transparent faces and measuring light output only for portions of the surface sufficiently far from the edges to eliminate the possibility of including light reflected from the side walls.

Photometric luminance (or brightness) is defined as a measure of the luminous flux per unit solid angle leaving a surface at a given point in a given direction per unit of projected area. The foot

lambert is then defined as a unit of photometric luminance equal to $1/\pi$ candella per square foot of emitting surface. When the surface obeys Lambert's law, the total emission or flux from one side of a planar surface of one foot lambert brightness and 1 square foot area is then equal to 1 lumen. This light is obviously emitted into a hemisphere with maximum flux perpendicular to the surface (at the pole of the hemisphere) and zero flux at the rim or equator of the hemisphere. It can be shown, however, that a chemiluminescent sample with a 1 square foot area and a brightness of 1 foot lambert measured normal to the surface will have a total emission of $2n^2$ lumens over the same hemisphere or $4n^2$ lumens over a total sphere where n is the index of refraction of the solvent. Because of this relationship, it is possible to calculate the brightness normal to a chemiluminescent surface when total emission in lumens per cc. is known by using the following formula:

$$B = \frac{929 Ld}{4n^2}$$

In this equation, B is given in foot lamberts, L in lumens per cc., d is sample thickness in centimeters and n is the refractive index of the sample.

In principle, then, it is possible to calculate brightness for chemiluminescent solutions of any thickness, knowing the quantum yield, rate constant, concentration and spectral distribution or the total lumens per cc. measured in a cell of any geometry and to convert brightness at one thickness to brightness at another thickness. This assumes, however, that brightness will be strictly proportional to sample thickness. In practice this is not always the case, particularly if fluorescent additives are used to shift the wavelength distribution of

emitted light. In this case, as sample thickness is decreased, the fraction of the original light absorbed by the fluorescer may fall off, resulting in a color shift and a departure from linearity in brightness response. Similarly, if solutions are colored, increased thickness will give less than calculated brightness.

We prefer to make our measurements in cells of 1 cm. thickness and report data at that thickness. For most systems 10 per cent of that brightness could be achieved in a 1 mm. thickness, although an increase in fluorescer concentration might be required.

Initial luminosity and brightness data and reaction half-lives for two "luminol" chemiluminescent systems are summarized in Table I. The first experiment in the table gives a typical brightness for the normal deep blue emission. In the second experiment the blue emission is converted to yellow by emission-reabsorption transfer to fluorescein; the result emphasizes the importance of spectral distribution to brightness. Brightness data for these reactions as determined directly by a commercial brightness meter is also provided in the table. Reasonable but not excellent agreement was obtained. Spectral distributions for luminol and luminol-fluorescein are shown in Figure 1.

Representative luminosity and brightness data for oxalyl chloride-hydrogen peroxide-fluorescer chemiluminescent reactions is summarized in Table II. The substantial brightness available from rubrene systems should be evaluated with reference to the very short reaction lifetime. On the other hand, the concentrations of reagents used are very low, and substantially higher light levels can be obtained

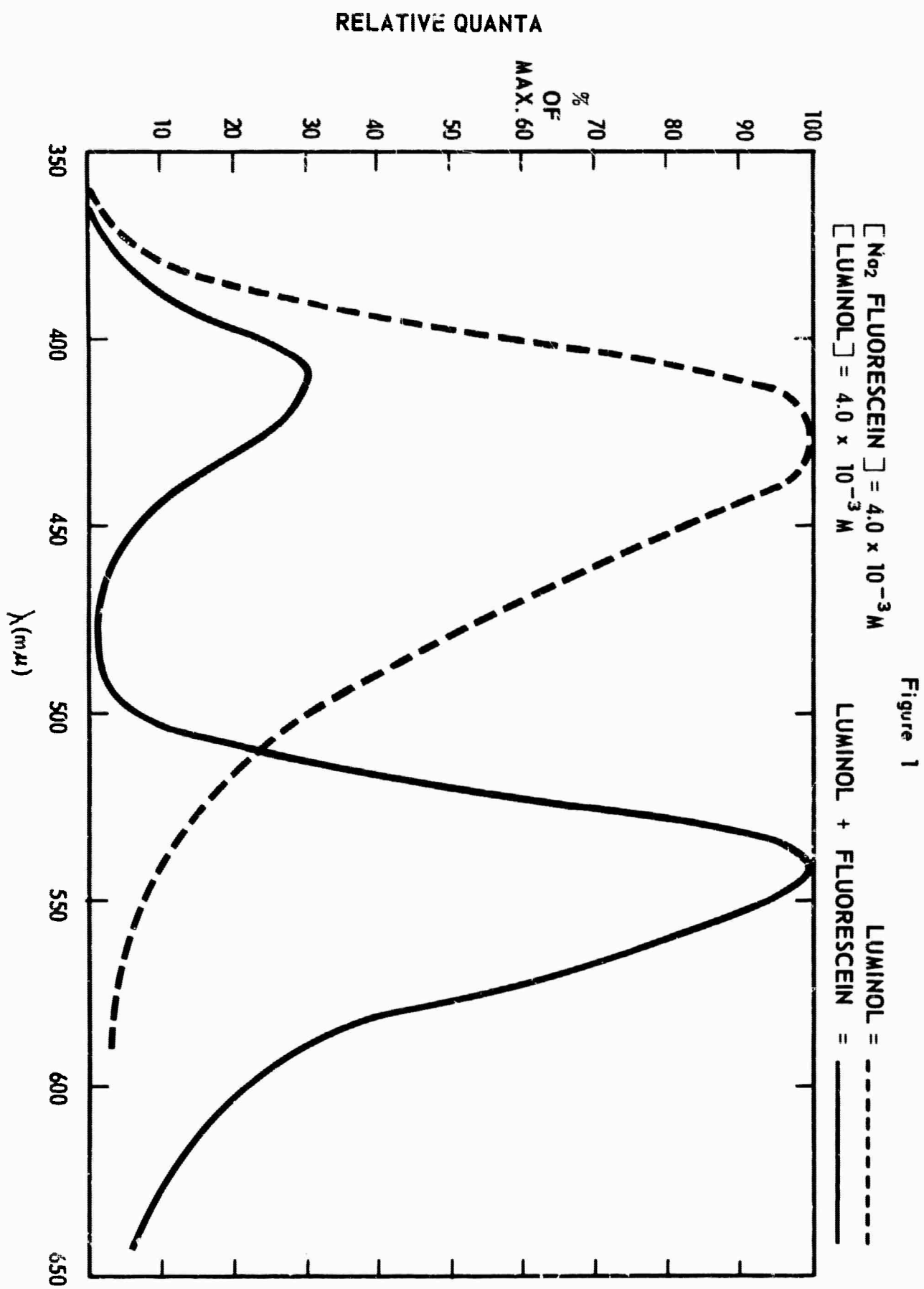


Table I

Luminol Luminosity Data^a

Luminol Conc.	Fluorescein Conc.	First Order Half-life (min.)	Chemiluminescence Quantum Yield	Initial Emission Rate (einsteins sec ⁻¹ ml ⁻¹)	Initial Luminosity (lumens per cc.)	Initial Brightness for 1 cm. Thickness (foot lamberts)	
						From Q.Y. Data ^b	Direct Measurement ^c
$4 \times 10^{-3} M$	Zero	18	0.78×10^{-2}	2.0×10^{-11}	0.38×10^{-3}	0.050	0.036
$4 \times 10^{-3} M$	$6 \times 10^{-4} M$	15	0.72×10^{-2}	2.2×10^{-11}	2.62×10^{-3}	0.34	0.241

^a Reactions were carried out with 6×10^{-2} molar $K_2S_2O_8$ and 3×10^{-2} molar H_2O_2 in 0.1 M aqueous potassium carbonate solution.

^b Einsteins can be converted to quanta by multiplying by 6.02×10^{23} .

^c Determined directly by a commercial brightness meter (Photoresearch Corp., Hollywood, California) Model UB 1/2.

Table II

Luminosity and Brightness Data for Representative Oxalyl Chloride-Hydrogen Peroxide-Fluorescer Reactions in Ether at 25°

Fluorescer Conc. moles/liter	H ₂ O ₂ Conc. moles/liter	Oxalyl Chloride Conc. moles/liter	Half-life in Secs.	Chemiluminescence Quantum Yield	Initial Luminosity (lumens per cc.)	Brightness (Foot Lamberts for 1 cm. Thickness)	Initial Quantum Emission Rate Einsteins sec ⁻¹ ml ⁻¹)*
Rubrene							
0.11×10^{-4}	1.00×10^{-2}	2.20×10^{-3}	13.8	0.41×10^{-3}	0.38×10^{-2}	0.5	$.453 \times 10^{-10}$
0.49×10^{-4}	2.00×10^{-2}	2.20×10^{-3}	12.0	2.00×10^{-3}	2.53×10^{-2}	3.3	2.55×10^{-10}
1.00×10^{-4}	5.00×10^{-2}	2.20×10^{-3}	10.9	7.85×10^{-3}	1.08×10^{-1}	14.1	1.10×10^{-9}
6.00×10^{-4}	2.00×10^{-1}	2.20×10^{-3}	7.5	3.21×10^{-2}	7.91×10^{-1}	103.0	6.58×10^{-9}
9,10-Diphenylanthracene							
0.33×10^{-4}	1×10^{-2}	2.33×10^{-3}	9.6	0.26×10^{-4}	0.23×10^{-3}	0.03	$.439 \times 10^{-11}$
1×10^{-4}	5×10^{-2}	2.33×10^{-3}	7.3	0.38×10^{-3}	0.46×10^{-3}	0.06	$.840 \times 10^{-10}$
5×10^{-4}	1×10^{-1}	2.33×10^{-3}	5.6	3.24×10^{-3}	0.53×10^{-2}	0.69	$.934 \times 10^{-9}$
10×10^{-4}	2×10^{-1}	2.33×10^{-3}	3.5	0.86×10^{-2}	2.36×10^{-2}	3.08	4.05×10^{-9}
1,4-Dimethoxy-9,10-diphenylanthracene							
0.14×10^{-4}	1×10^{-2}	2.01×10^{-3}	10.5	0.19×10^{-3}	1.31×10^{-3}	0.17	$.252 \times 10^{-10}$
0.28×10^{-4}	2×10^{-2}	2.01×10^{-3}	10.6	0.63×10^{-3}	4.46×10^{-3}	0.58	$.828 \times 10^{-10}$
1.00×10^{-4}	5×10^{-2}	2.01×10^{-3}	9.2	2.86×10^{-3}	2.32×10^{-2}	3.03	$.435 \times 10^{-9}$
2.80×10^{-4}	1×10^{-1}	2.01×10^{-3}	7.8	5.96×10^{-3}	5.70×10^{-2}	7.42	1.066×10^{-9}

* To convert to Quanta sec⁻¹ml⁻¹ multiply by 6.02×10^{23} .

at higher concentrations of the limiting reagent, oxalyl chloride.

Spectral distributions for 9,10-diphenylanthracene³ and for 1,4-dimethoxy-9,10-diphenylanthracene⁵, have been pictured previously. An emission distribution for rubrene will be provided in the next report.

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