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CHEMILUMINESCENT MATERIALS

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Progress in determining mechanisms of processes fundamental to chemiluminescence is reported with particular reference to the chemiluminescent systems (1) oxalyl chloride-hydrogen peroxide-fluorescer, (2) acyl-oxalic anhydride-hydrogen peroxide-fluorescer, (3) 9-chlorocarbonylacridinium salt-hydrogen peroxide, (4) tetracyanoethylene-hydrogen peroxide-fluorescer. Exploratory searches for new chemiluminescent materials are also reported.

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The following scientists made primary contributions to the technical effort:

M. M. Rauhut

L. J. Bollyky, R. A. Clarke, B. G. Roberts,
A. M. Semsel, R. H. Whitman.

Microanalyses were carried out under the direction of Dr. J. H. Deonarine; mass spectrometric analyses under the direction of Mr. T. E. Mead; computer analyses under the direction of Dr. D. W. Behnken; infrared analyses by Mr. N. B. Colthup; other spectroscopic work was supervised by Dr. R. C. Hirt.

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SUMMARY

Progress in determining mechanisms of processes fundamental to chemiluminescence is reported with particular reference to the chemiluminescent systems (1) oxalyl chloride-hydrogen peroxide-fluorescer, (2) acyl-oxalic anhydride-hydrogen peroxide-fluorescer, (3) 9-chlorocarbonylacridinium salt-hydrogen peroxide, (4) tetracyanoethylene-hydrogen peroxide-fluorescer. Exploratory searches for new chemiluminescent materials are also reported.

The effects of reactant concentrations on (1) have been determined quantitatively and unambiguously. Water in small concentrations was found to have a pronounced effect in increasing reaction rates and quantum yields. The quantum yield increases with increasing hydrogen peroxide and fluorescer, while the reaction rate is not appreciably altered. The quantum yield is seriously reduced by a phenolic free radical inhibitor.

Reaction (2) was found capable of generating quantum yields on the order of 10%, and is thus the most efficient non-biological chemiluminescence system now known. Effects of reactant concentrations on the quantum yields is discussed and stability data for several mixed oxalic anhydrides are provided. Reaction condition studies on reaction (3) have shown that quantum yields of 3.5% can be obtained in dilute solution, but that the efficiency decreases rapidly with increasing concentration. Investigations relating to the mechanism of (4) have resulted in the discovery of two new chemiluminescent reactions of moderate efficiency.

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 accomodate 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[1,2,3,4,5,6,7].

SECTION I

REACTION MECHANISMS IN CHEMILUMINESCENCE

PART 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[1,2,3,4,5,6,7,8].

$$Cl-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Cl + H_2O_2 \xrightarrow{\text{anthracene}} CO + CO_2 + HCl + Cl-\overset{O}{\overset{\|}{C}}-Cl$$

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 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 Water on Reaction Rates and Quantum Yields

Earlier work has indicated that water plays a major role in the oxalyl chloride-hydrogen peroxide-fluorescent compound chemiluminescent reaction[7]. Indeed, the influence of water is such that we have encountered considerable difficulty in reproducing reaction rate and quantum yield results in experiments carried out at low water concentrations. The magnitude of the water effect has now been demonstrated unambiguously. In Table I are summarized results obtained in experiments with constant oxalyl chloride, hydrogen peroxide, and 9,10-diphenylanthracene (DPA) concentrations where the solvent ether was dried in various ways. It is seen that reagent grade "anhydrous" ether is not nearly anhydrous enough to avoid influencing the results. Even ether "dried" by passage through an activated alumina column contains sufficient water to produce an easily observed change in reaction rate and quantum yield. The lowest rates and quantum yields were obtained using ether dried by distillation over lithium aluminum hydride under an argon atmosphere. The water concentration in ether prepared in this way was below the limit detectable by the usual Karl Fischer titration. Nevertheless, substantially different results were obtained from two separately prepared batches of hydride-dried ether. The difference between the two batches was shown to be the difference in water content by experiments (5) and (6) where water was deliberately added in concentrations large enough so that the residual water content of the ether could be neglected. As indicated in the Table, the rate and quantum yield results from the two batches of equally wet solvent agreed within experimental error.

TABLE I

The Effect of Ether from Various Sources on the Chemiluminescent Reaction of Oxalyl Chloride with H_2O_2 and DPA[a]

Source of Ether	H_2O conc ≃ (moles $l.^{-1}$)[b]	K^1 ($sec.^{-1}$)	Quantum Yield
1. Mallinckrodt reagent-grade anhydrous ether	2.76×10^{-2}	3.13×10^{-2}	1.78×10^{-4}
2. Mallinckrodt anhydrous ether passed through a 30 cm. Al_2O_3 (neutral) column.	0.79×10^{-2}	1.81×10^{-2}	0.61×10^{-4}
3. Mallinckrodt anhydrous ether distilled over $LiAlH_4$ under argon.	0.39×10^{-2}	1.93×10^{-2}[c]	0.41×10^{-4}
4. Mallinckrodt anhydrous ether distilled over $LiAlH_4$ under argon atmosphere.	$< 0.39 \times 10^{-2}$	1.13×10^{-2}[c]	0.14×10^{-4}
5. Standard concentration of aqueous ether added to #3.	4.96×10^{-2}	6.82×10^{-2}	2.85×10^{-4}
6. Standard concentration of aqueous ether added to #4.	4.96×10^{-2}	6.58×10^{-2}	2.65×10^{-4}

(a) Reactions carried out with 2.50×10^{-3} $\underline{M}$ oxalyl chloride, 2.2×10^{-2} $\underline{M}$ H_2O_2, and 2.3×10^{-4} $\underline{M}$ DPA.

(b) Analyzed by Karl Fischer technique.

(c) The first minute of the log I vs. time plot fell below the extrapolated linear portion of the decay line.

Other results showing the effect of added water on the reaction are summarized in Table II, and in Figures I and II. It is seen (Figure I) that the pseudo first order reaction rate constant increases approximately linearly with the square of the water concentration, and that (Figure II) the quantum yield increases linearly with water up to a concentration of about 3.7×10^{-2} molar and then levels off. The rate results might suggest a rate equation of the form

$$\frac{dX}{dT} = k[X] + k_2[X][H_2O]^2$$

where $k = 2.2 \times 10^{-2}$ sec.$^{-1}$ and $k_2 = 18.6$ l.^{2} mole^{-2} sec.$^{-1}$. More likely, however, the linear relationship in Figure I results from a coincidental combination of several factors derived from the complex reaction mechanism. The relationship between quantum yield and water concentration is of the type discussed previously[7].

2. Effect of Hydrogen Peroxide on the Reaction Rate and Quantum Yield

Reaction rate and quantum yield results from experiments where the hydrogen peroxide concentration was varied independently of oxalyl chloride, DPA, and water are summarized in Table III. It is evident from the results that the reaction rate is independent of hydrogen peroxide concentration. (The small upward trend in the pseudo first order rate constant is almost certainly a consequence of residual water in the hydrogen peroxide stock solution.) The quantum yield, however, increases approximately linearly with increasing hydrogen peroxide concentration in the range studied.

Results from a related series of experiments are summarized in Table IV.

Figure 1

EFFECT OF WATER ON THE PSEUDO FIRST ORDER INTENSITY DECAY CONSTANT
(DATA FROM TABLE II)

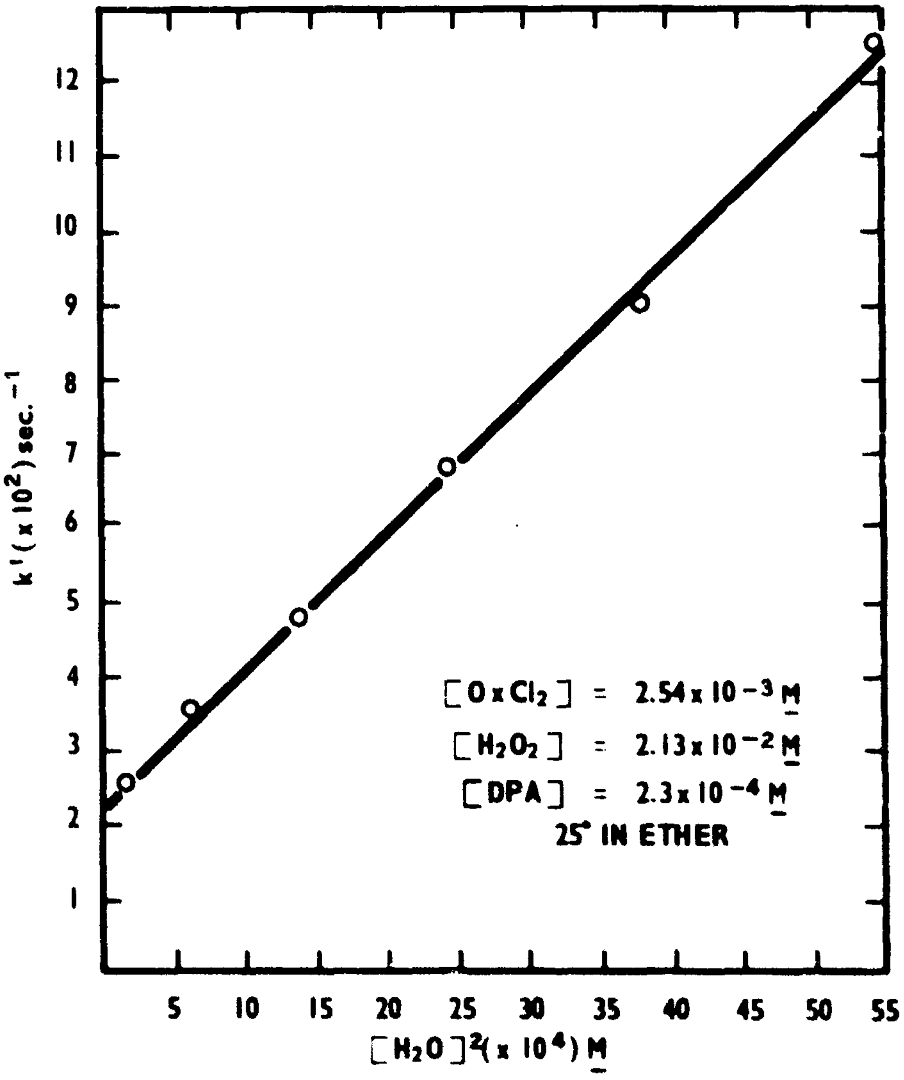


Figure II

EFFECT OF WATER ON QUANTUM YIELD
(DATA FROM TABLE II)

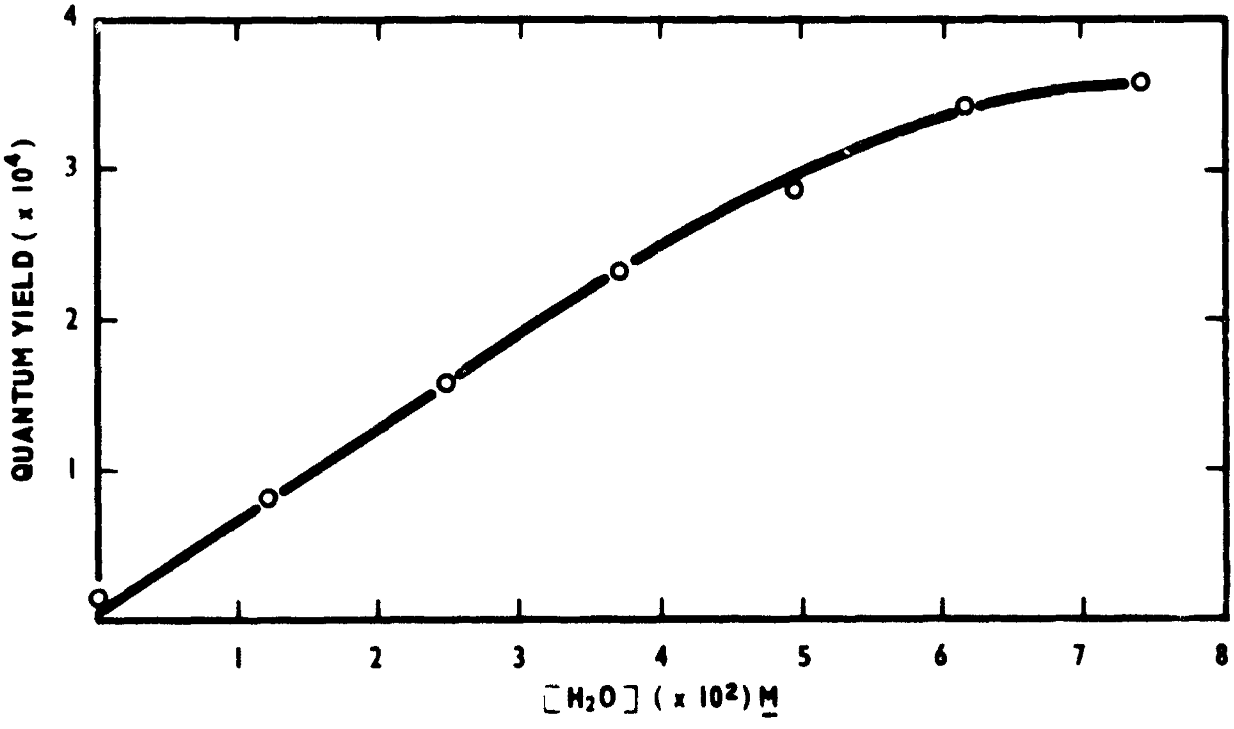


TABLE II

Effect of Water on Oxalyl Chloride-Hydrogen Peroxide Chemiluminescence[a]

$[H_2O]$ ($\times 10^2$ Molar)	K^1 ($sec.^{-1} \times 10^2$)	Quantum Yield ($\times 10^4$)
< 0.4[b]	1.93[c] (1.13[d])	0.41 (0.14[d])
1.23	2.60[e]	0.80
2.46	3.53	1.59
3.69	4.75	2.33
4.96	6.82 (6.58[d])	2.85 (2.65[d])
6.15	9.04	3.43
7.38	12.50	3.57

(a) The reactions were carried out with 2.54×10^{-3} M oxalyl chloride, 2.13×10^{-2} M H_2O_2, and 2.3×10^{-4} M DPA, at 25° where the amount of water specified was added prior to injection of oxalyl chloride.

(b) Lower limit of analysis by Karl Fischer method.

(c) Log I vs. T plot was linear only after 30 sec. of reaction. Earlier intensities were below the extrapolated linear plots.

(d) Result from separately prepared "anhydrous ether".

(e) Log I vs. T plot was linear after 15 sec. of reaction.

TABLE III

Effect of Hydrogen Peroxide Concentration on Oxalyl Chloride-Hydrogen Peroxide Chemiluminescence[a]

$[H_2O_2]$ (x 10^2 Molar)	k^1 (sec.$^{-1}$ x 10^2)	Quantum Yield (x 10^4)
1.0	1.8	0.85
2.0	1.8	1.5
5.0	1.9	4.3
10.0	2.1	8.6

(a) Reactions were carried out with 2.42 x 10^{-3} M oxalyl chloride, and 2.0 x 10^{-4} M DPA in alumina-dried ether at 25°.

TABLE IV

Effect of Hydrogen Peroxide on Reaction Rate and Quantum Yield in Systems Containing Water[a]

$[H_2O_2]$ (x 10^2 molar)	k^1 (sec.$^{-1}$ x 10^2)	Q^F (x 10^4)	Q_W^F (x 10^4)	F_W	Q_W^T (x 10^4)	Q_W^T/Q^T
1.0	6.4	0.35	2.6	.59	4.4	5.1
2.0	6.5	0.66	4.6	.59	7.8	5.2
5.0	6.7	1.8	10.0	.55	18	4.2
5.0[b]	7.5	-	-		6.6	1.5
10.0	7.6	4.0	13.2	.55	24	2.8

(a) Reactions were carried out with 2.42 x 10^{-3} M oxalyl chloride and 2.0 x 10^{-4} M DPA in ether at 25°. After 30 sec. of reaction water was injected to provide a water concentration of 3.44 x 10^{-2} M. Q^F = The fractional quantum yield observed before water injection; Q_W^F = The fractional quantum yield observed after water injection; F_W = The fraction of total reaction measured after water injection; Q_W^T = The calculated total quantum yield for the reaction in the presence of water; Q^T = The total quantum yield in the absence of added water.

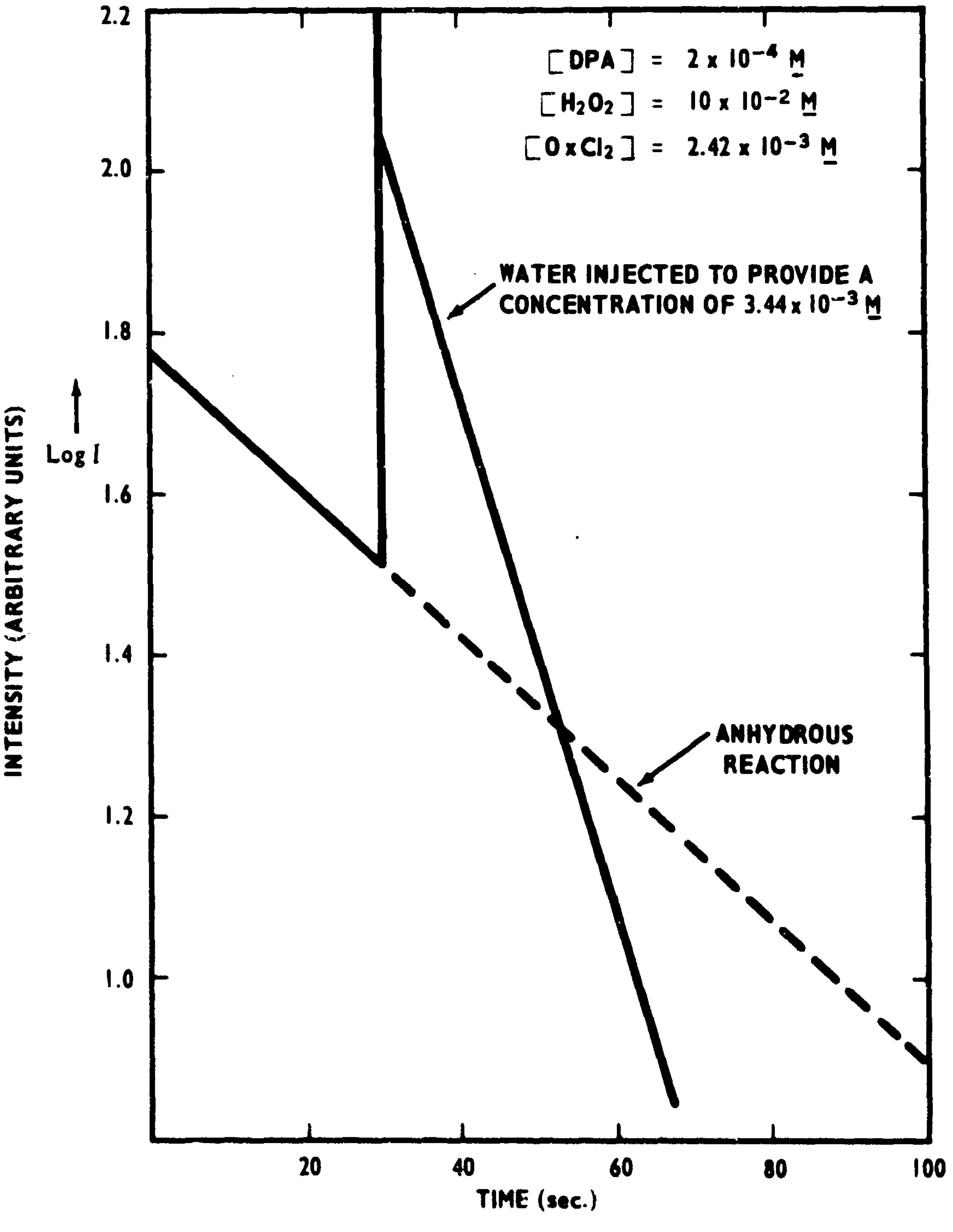
(b) Water was added before oxalyl chloride injection to provide 3.44 x 10^2 M water.

In this series hydrogen peroxide was varied in experiments where a constant water concentration was introduced 30 seconds following the onset of reaction. This procedure was adopted to minimize direct reaction of water with oxalyl chloride. The observed effect of water injection is shown in Figure III. As indicated in Table IV, the fraction of total reaction measured in the presence of water (F_W) varied from 55% to 59% and this fraction was used to estimate the complete quantum yield of the aqueous system (Q_W^T). In agreement with the previous series, it is seen that the hydrogen peroxide concentration has at most a minor effect on the reaction rate, and in further agreement, the quantum yield increases substantially as the hydrogen peroxide concentration increases. A comparison of the k^1 and Q_W^T values with the quantum yield and rate values in Table III, reemphasizes the effect of water on the reaction rate and quantum yield. However, it is clear from the ratios of $Q^T{}_W/Q^T$ that the influence of water on the quantum yield decreases at higher hydrogen peroxide concentrations.

Also indicated in Table IV is the result from an otherwise identical experiment where the water was added prior to injection of oxalyl chloride. The observed quantum yield is not only smaller than the calculated quantum yield for the experiment with delayed water addition, it is even smaller than the observed quantum yield (Q_W^F) corresponding to only 55% of the total reaction. The result clearly shows that at the water and hydrogen peroxide concentrations investigated, water competes seriously with hydrogen peroxide at an early reaction stage to divert a key reactant into a non-chemiluminescent pathway. This "key reactant" is probably oxalyl chloride itself.

Figure III

TYPICAL DECAY PLOT SHOWING THE EFFECT OF WATER INJECTION



3. The Effect of Hydrogen Peroxide and DPA Concentrations on the Reaction Rate and Quantum Yield

The results of a series of experiments where the hydrogen peroxide and DPA concentrations were independently varied over substantial ranges at approximately constant water concentration, are summarized in Table V. It is seen that the reaction rate is essentially unaffected by the hydrogen peroxide or DPA concentrations. The quantum yield, however, increases with increasing DPA concentration throughout the range studied and increases with increasing hydrogen peroxide concentration up to a concentration of about 2.3 x 10^{-1} molar. These results are in essential agreement with results of previously reported experiments[6,7], where the water concentration was not carefully controlled.

The Effect of 2,6-Di-t-butyl-4-methylphenol (DBMP) on the Reaction Rate and Quantum Yield

The effect of the free radical inhibitor DBMP on the reaction is indicated in Table VI. These reactions in dimethylphthalate solution did not provide simple Log intensity vs. time plots, and lifetimes are indicated with reference to the time required for the intensity to decrease by 1/2 its maximum value. It is clear from the approximate constancy of this half intensity period (as well as from the intensity vs. time plots) that DBMP does not affect the reaction rate. The quantum yield, however, is drastically reduced with increasing DBMP. As indicated in the previous report[7] this result is not a consequence of fluorescence quenching of the fluorescer by DBMP, and therefore suggests a non-rate determining free radical chain process. The possibility of interference by an ionic route is unlikely, but has not been eliminated. We will investigate this point.

TABLE V

Effect of Hydrogen Peroxide and 9,10-Diphenylanthracene (DPA) n Reaction Rate and Quantum Yield[a]

$[H_2O_2]$ (M/L x 10^2)	[DPA] (M/L)							
	5.0×10^{-5}		7.5×10^{-5}		16.7×10^{-5}		50.00×10^{-5}	
	k^1 (sec.$^{-1}$ x 10^2)	Q.Y. (x 10^4)	k^1 (sec.$^{-1}$ x 10^2)	Q.Y. (x 10^4)	k^1 (sec.$^{-1}$ x 10^2)	Q.Y. (x 10^4)	k^1 (sec.$^{-1}$ x 10^2)	Q.Y. (x 1[illegible])
5.21	9.2	2.1	8.9	3.2	9.7	7.3	7.0	17
10.42	7.6	3.3	8.3	4.6	8.7	11	6.7	27
15.63	---	---	---	---	7.8	14	6.4	34
23.41	7.4	3.8	7.3	5.4	7.0	15	6.1	38
36.63	6.6	3.8	7.5	6.5	6.8	15	7.1	45
57.6^b	7.2	4.4	7.9	6.5	7.7	15	7.1	39
78.5^c	8.1	4.0	8.9	6.3	8.4	15	8.0	40

(a) Oxalyl chloride concentration = 1.92×10^{-3} M; water concentration = 1.2×10^{-2} M except where noted.

(b) Water concentration = 2.1×10^{-2} M.

(c) Water concentration = 2.5×10^{-2} M.

TABLE VI

The Effect of a Free Radical Inhibitor* on the Oxalyl Chloride + H_2O_2 + Fluorescer Chemiluminescence Reaction in Dimethylphthalate Solution

Molar Concentration of Inhibitor	First half-life in sec.	Ft. Lamberts at maximum intensity	Quantum Yield
0	87	0.64	4.13×10^{-2}
0.67×10^{-3}	95	0.48	3.80×10^{-2}
2.0×10^{-3}	84	0.33	2.34×10^{-2}
1×10^{-2}	65	0.09	0.65×10^{-2}
1.5×10^{-2}	73	0.08	0.48×10^{-2}
ca. 2.0×10^{-2}	68	0.05	0.29×10^{-2}

---

* 2,6-di-_t_-butyl-4-methylphenol

DPA = 5×10^{-4} _M_; H_2O_2 = 0.2 _M_; Oxalyl chloride = 2.42×10^{-3} _M_.

The intensity during the first 2 mins. for all the above reactions fell below the linear extrapolated log I vs. time plot.

SECTION I - PART A

EXPERIMENTAL

Materials

Anhydrous Ether. - (Mallinckrodt Reagent Grade, Anhydrous) was further dried by passage through a 30 cm. neutral alumina column[9], or by distillation over lithium aluminum hydride under argon. Residual water was estimated by the Karl Fischer method[10].

Oxalyl Chloride. - (Aldrich) was distilled through a 10 x 1 cm. Vigreaux column under argon to obtain a fraction, b.p. 64° (1 atm.) (Lit.[11], b.p., 63.5-64° (763 mm.). Standard solutions of oxalyl chloride in ether or dimethylphthalate (1.11×10^{-1} M to 1.50×10^{-1} M) were analyzed gravimetrically by conversion to oxanilide with excess aniline. This reaction was shown to be quantitative in preliminary large scale experiments.

Anhydrous Hydrogen Peroxide in ether was prepared from 98% hydrogen peroxide (Becco Chemical Division, FMC Corp.) dissolved in ether to a concentration of 25%, and dried by shaking 16 hours with excess anhydrous magnesium sulfate[12]. Water estimation of the dried solution by infrared analysis at 1640 cm.$^{-1}$ indicated that residual water was below 2.9×10^{-2} M. Standard solutions of hydrogen peroxide (0.758 M to 1.65 M) were prepared from this solution and anhydrous ether and were analyzed iodometrically[13].

9,10-Diphenylanthracene (DPA) (Aldrich) was recrystallized from abs. ethanol-chloroform to obtain material, m.p. 250-251° (Lit.[14], m.p. 250-251°).

2,6-Di-t-butyl-4-methylphenol (Koppers Co., Inc.) was sublimed in vacuo to obtain material melting at 69-70° (lit.[15], m.p. 69-70°).

Chemiluminescence Experiments

In general, the experiments were carried out by combining appropriate aliquots of standard etheral solutions of hydrogen peroxide, DPA and water with an appropriate volume of ether in a 3 ml. stirred cylindrical cuvette. The volume of ether used was chosen to make the final volume 3.00 ml. which exactly filled the cuvette. The cuvette was placed in the spectroradiometer and an appropriate aliquot of standard ethereal oxalyl chloride was injected from an all-glass syringe. The intensity of emission of a selected 5 mμ-wide wavelength span was measured as a function of time from the point of oxalyl chloride injection. The reaction temperature was 25° to within one degree. The radiometer, its calibration, and the calculation of rates and quantum yields have been previously described[1,2,4].

The experiments in Table I were all carried out with the same standard solutions. The ether added to obtain the desired concentrations was treated as described in the table and amounted to 83% of the final volume.

The experiments in Table IV were carried out by injecting a constant 0.20 ml. of 5.16 x 10^{-1} M water in ether after 30 sec. of reaction. "Fractional quantum yields" from the anhydrous (Q^F) and wet (Q_W^F) parts of the experiments were calculated separately in the usual way[7]. The fraction of total reactions measured in the presence of water (F_W) was estimated from the formula

$$F_W = 1 - \frac{Q^F}{Q}$$

where Q is the quantum yield for the anhydrous reaction (Table III).

The total quantum yield for the aqueous part of the reaction was estimated from the formula

$$Q_W^T = \frac{Q_W^F}{F_W}$$

SECTION I

PART B

Chemiluminescence from Mixed Oxalic Anhydrides

In previous reports we have described a series of efficient new chemiluminescent reactions based on the decomposition of monoperoxyoxalic acid and certain of its derivatives in the presence of a fluorescer, such as 9,10-diphenylanthracene (DPA). While efficient, these reactions are in general unsuitable for practical use because of their short emission lifetimes. It is clear, however, that a reaction producing a monoperoxyoxalic acid derivative by a slow process, would accomodate the goal of long-lived emission.

In the previous report[7] we described a series of exploratory experiments, which examined the possibility of producing monoperoxyoxalic acid derivatives by reaction of hydrogen peroxide with certain oxalic acid derivatives including esters, anhydrides, and Lewis-base oxalyl chloride complexes. Results with triphenylacetic-oxalic anhydride were particularly encouraging, providing strong intensities over extended periods. A more detailed study of oxalic anhydride chemiluminescence is thus being carried out to determine the effects of electronic and steric structural factors on anhydride stability, rate of reaction with hydrogen peroxide, ease of hydrolysis, and chemiluminescence efficiency.

Three oxalic anhydrides (Structure I) have been prepared and examined in preliminary fashion.

$$\mathrm{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R}$$

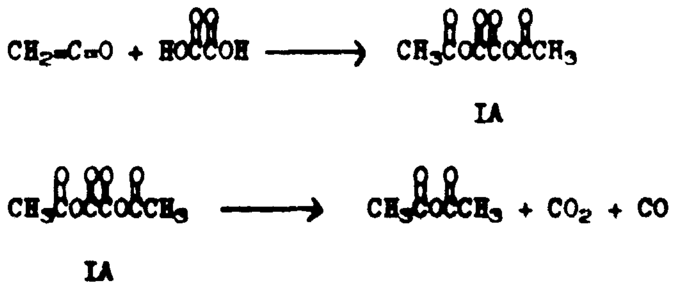
Ia: $R=CH_3$

Ib: $R=(C_6H_5)_3C$

Ic: $R=C_6H_5$

The three anhydrides were found to vary markedly in thermal stability. hydrolytic reactivity, and chemiluminescence efficiency. The poor chemiluminescence results obtained from Ic were discussed in the previous report[7]. Current results are summarized below.

1. Acetic-oxalic anhydride (IA) was readily prepared from oxalic acid and ketene at -50°C. The product appeared to be essentially pure and was stable over an extended period when stored as a solid below its melting point of about -5°. At higher temperatures, however, the liquid anhydride decomposed slowly to acetic anhydride in agreement with earlier work by Edwards and Henly[16].



$$\mathrm{CH_2{=}C{=}O + HO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3}$$

IA

$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 + CO_2 + CO}$$

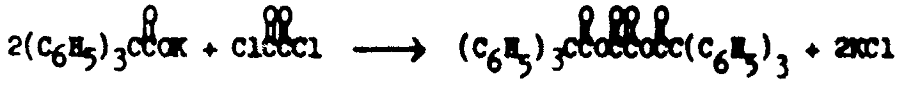
IA

Thermal decomposition of the pure liquid anhydride is appreciable even at 0° and is complete after a few hours at 25°C. However, the decomposition is significantly slower in dilute solution. A study of the decomposition in 1,2-dimethoxyethane solution was carried out where the concentrations of IA, acetic anhydride and acetic acid were determined as a function of time by infrared analysis. The results are summarized in Tables I. As indicated in the Table, decomposition was found to be catalyzed by base (pyridine or potassium acetate) but was not affected by free radical inhibitors.

Potential acid catalysis of decomposition is particularly disadvantageous to the stability of IA since small amounts of acetic acid will generally be present in IA solutions as a consequence of hydrolysis. An effort was thus made to stabilize IA in ether by the use of excess ketene which would tie up acetic acid as acetic anhydride. Substantial decomposition of IA occurred, however, even under these conditions, suggesting that IA is inherently unstable above its melting point.

The instability of IA in solution has prevented quantitative measurement of its chemiluminescence efficiency in reactions with hydrogen peroxide. Qualitative observations, however, indicate that its chemiluminescence efficiency is close to the 10% efficiency obtained with IB (see below).

2. Bistriphenylacetic-oxalic Anhydride (IB) was prepared from potassium triphenylacetate and oxalyl chloride in benzene solution.



$$2(C_6H_5)_3C\overset{O}{\overset{\|}{C}}OK + Cl\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Cl \longrightarrow (C_6H_5)_3C\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}C(C_6H_5)_3 + 2KCl$$

IB

TABLE Ia

Decomposition of Diacetic Oxalic Anhydride in 1,2-Dimethoxyethane

Initial IA* Concentration (moles l.$^{-1}$)	1.15 Molar			0.575 Molar			0.115 Molar		
Time (hours)	[IA] (%)	Acetic Anhydride (%)	Acetic Acid (%)	[IA] (%)	Acetic Anhydride (%)	Acetic Acid (%)	[IA] (%)	Acetic Anhydride (%)	Acetic Acid (%)
0.05	96**	0	4	93	0	7	92	0	8
0.4	94**	0	6	90	2	8	90	0	10
1.8	80**	13	7	87	3	10	87	0	13
2.25	90**	2	8	85	5	10	81	3	16
22	31 ***	11	58	58	27	15	65	15	20
67	7 ***	13	80	15	65	20	35	40	25

---

* IA - Diacetic oxalic anhydride.
** Reaction temperature: 26°
*** Reaction temperature: 17-23°

TABLE Ib

Decomposition of Diacetic Oxalic Anhydride in the Presence of Acid, Base, or Free Radical Inhibitor in 1,2-Dimethoxyethane**

[IA]* (Moles $1.^{-1}$)	Additive	Additive Conc. (Moles $1.^{-1}$)	% [IA]* Remaining			
			0.25 hrs.	0.50 hrs.	2.25 hrs.	6.0 hrs.
5.6×10^{-3}	acetic acid	3.5×10^{-3}	100		75	
5.3×10^{-3}	acetic acid	1.2×10^{-2}	100		74	
4.6×10^{-3}	acetic acid	3.5×10^{-2}			0	
1.15×10^{-1}	none	---	94		90	
1.36×10^{-1}	pyridine	2.5×10^{-1}	0			
1.36×10^{-1}	potassium acetate	5×10^{-1}	0			
1.36×10^{-1}	2,6-di-t-butyl-4-methylphenol	4×10^{-2}	100	94	84	69

---

* Diacetic Oxalic Anhydride

** Temperature range: 26.0° - 26.3°C.

As indicated in Figure I, a prominent feature of the reactions was the appearance of a variable but discrete induction period lasting up to 19 minutes following admixture of reactants. The possibility that the observed induction period was a consequence of a free radical inhibitor present as a trace impurity was investigated with an experiment where the inhibitor 2,6-di-t-butyl-4-methylphenol (DTBMP) was deliberately added. As indicated in Table III, however, the inhibitor appeared to reduce, rather than lengthen the induction period, although the quantum yield was substantially reduced. Since DTBMP does not quench DPA emission[7], the result indicates tentatively that a key fast step may, indeed, be of free radical chain character, but that the rate determining step responsible for the induction period is an ionic process. Additional studies will be carried out to bear on this point and to determine the cause of the induction period.

The results of a series of rate and quantum yield measurements, carried out in dimethylphthalate (DMP) are summarized in Tables IV, V, and VI. The reproducibility of these results is significantly better than those reported above for reactions in 1,2-dimethoxyethane. Moreover, in contrast to the experiments in 1,2-dimethoxyethane, induction periods were usually absent in DMP except for several experiments in Table VI. A typical light intensity vs. time curve is given in Figure III.

An independent infrared assay of the anhydride solution was prevented by the strong absorption of the solvent DMP in the carbonyl region. To minimize random variations resulting from varying IB concentrations, each experimental set was carried out from a single IB stock solution. Comparison of results from different experimental sets is of doubtful value.

Yields of crude product were good, but considerable losses were encountered during purification steps leading to analytical grade material. The solid product appears to be stable on storage for extended periods at room temperature provided anhydrous conditions are maintained. In dilute solution in 1,2-dimethoxyethane, however, infrared analysis indicates that IB is slowly lost by conversion to triphenylacetic acid as indicated in Figure 1.

Results of other experiments bearing on the stability of IB in 1,2-dimethoxyethane solution are summarized in Table II. Triphenylacetic acid (TPA acid) apparently has little effect on the conversion of IB to TPA acid, but pyridine initiates a rapid decomposition to triphenylacetic anhydride (TPA anhydride).

A preliminary set of quantum yield measurements has been completed on the triphenylacetic oxalic anhydride-hydrogen peroxide-9,10-diphenylanthracene (DPA) system in 1,2-dimethoxyethane and in dimethylphthalate solutions. The results of experiments in 1,2-dimethoxyethane are summarized in Table III and a typical intensity decay plot is shown in Figure II. Since the anhydride was hydrolyzed readily by the traces of moisture present even in freshly distilled 1,2-dimethoxyethane infrared assay of the anhydride was carried out on the stock solutions used in the experiments to monitor the actual starting concentrations of the anhydride and its hydrolysis product, triphenylacetic acid.

In spite of this independent concentration analysis, the quantum yield and rate results show moderate scatter. Quantum yields on the order of 5 to 9 per cent were obtained, however, substantiating the high efficiency of the system.

TABLE II

Stability of Bistriphenylacetic Oxalic Anhydride in 1,2-Dimethoxyethane, and in the Presence of Acid or Base[a]

Initial IB Concentration (moles $l.^{-1}$)	2×10^{-2} M			2×10^{-2} M			2×10^{-2} M		
Additive + Concentration (moles $l.^{-1}$)	NONE			1×10^{-2} M TPA* acid			1×10^{-2} M pyridine		
Time (hours)	[IB][b] (%)	TPA Acid[c] (%)	TPA[c] Anhydride (%)	[IB][b] (%)	TPA Acid[c] (%)	TPA[c] Anhydride (%)	[IB][b] (%)	TPA Acid[c] (%)	TPA[c] Anhydride (%)
0.05	83	19	0	54	46	0	9	34	57
0.38	79	21	0	52	47	0	6	33	57
1.83	62	36	0	42	56	0	4	36	60
2.95	52	43	0	39	62	0	2	38	60
20.0	0	100	0	0	100	0	0	41	70

---

a) IB: Bistriphenylacetic oxalic anhydride, reaction temperature: 26.2°.
*TPA: triphenylacetic

b) Per cent of added IB remaining

c) Per cent of theoretical yield based on IB

Figure 1

DECOMPOSITION OF TRIPHENYLACETIC OXALIC ANHYDRIDE IN 1,2-DIMETHOXYETHANE SOLUTION AS A FUNCTION OF TIME

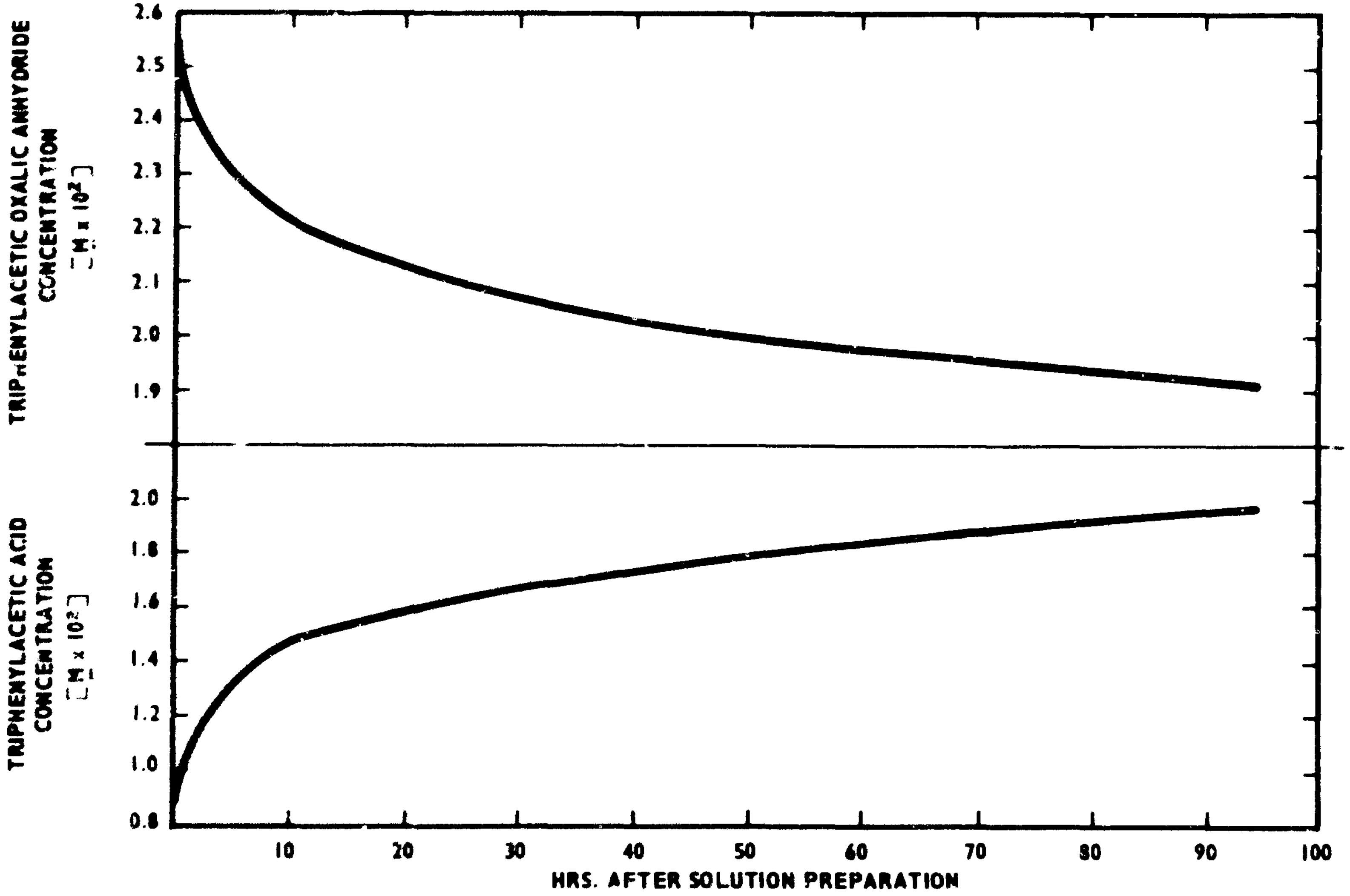


Figure 11

CHEMILUMINESCENCE FROM TRIPHENYLACETIC ANHYDRIDE IN 1,2-DIMETHOXYETHANE

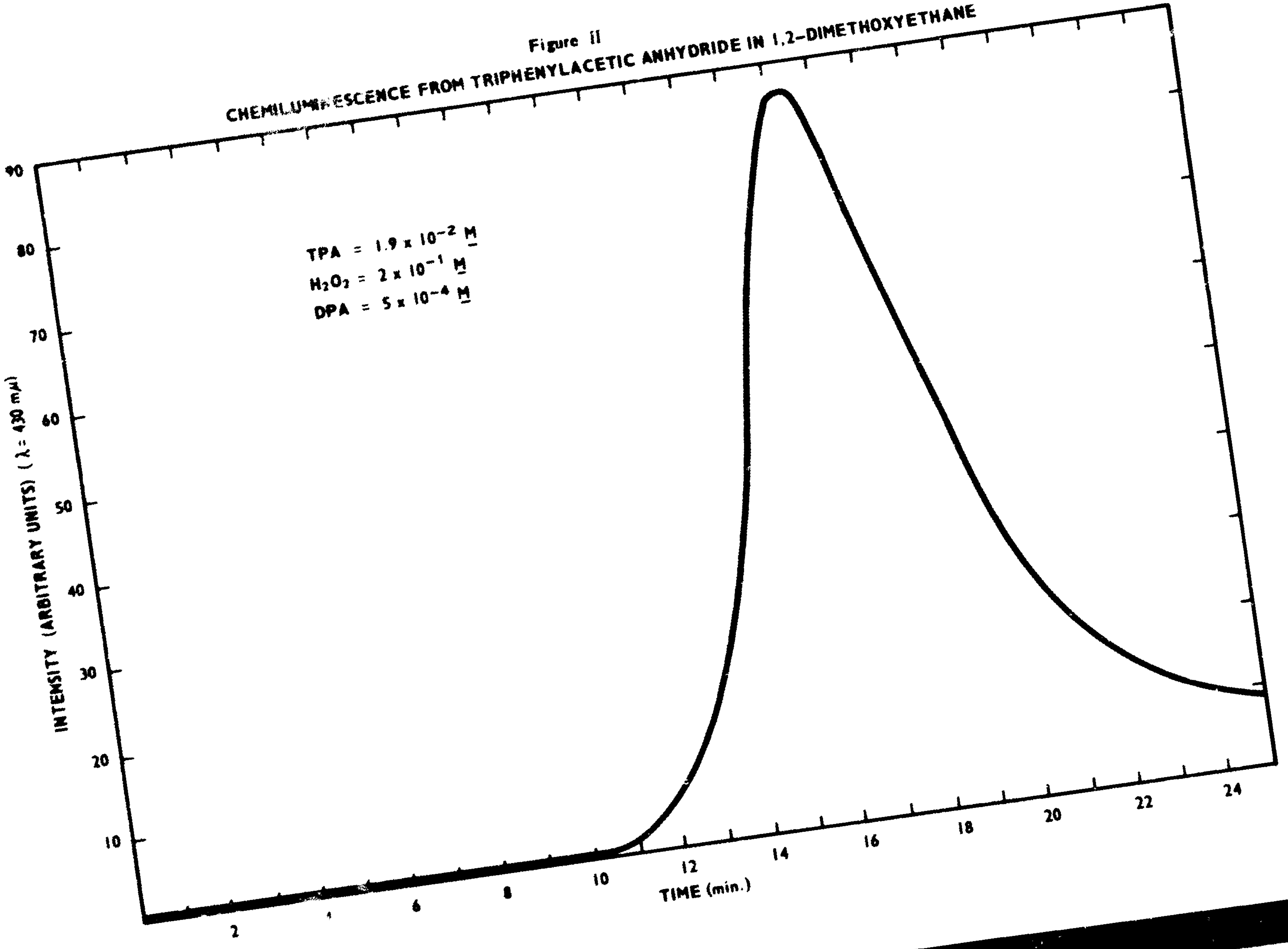


TABLE III

Quantum Yield of Chemiluminescence from Bistriphenylacetic Oxalic Anhydride-Hydrogen Peroxide Reaction in 1,2-Dimethoxyethane Containing 9,10-Diphenylanthracene[a]

$[(C_6H_5)_3C\overset{O}{\overset{\|}{C}}\text{-}O\overset{O}{\overset{\|}{C}}]_2$[b] (mole l.$^{-1}$)		$[(C_6H_5)_3C\overset{O}{\overset{\|}{C}}OH]$[c] (mole l.$^{-1}$)	$[H_2O_2]$ (mole l.$^{-1}$)	t_1[d] (min.)	$t_{1/2}I$[e] (min.)	Quantum Yield (Einstein/mole anhydride)	
A	B					A	B
1.7×10^{-2}	1.18×10^{-2}	0.92×10^{-2}	0.5	19	0.5	6.1×10^{-2}	8.8×10^{-2}
"	1.17×10^{-2}	0.99×10^{-2}	0.5	16	0.5	4.3×10^{-2}	6.2×10^{-2}
"	1.17×10^{-2}	0.99×10^{-2}	0.5	16	0.5	4.6×10^{-2}	6.6×10^{-2}
"	1.16×10^{-2}	0.99×10^{-2}	0.5	14	3.5	5.1×10^{-2}	7.5×10^{-2}
" [f]	1.16×10^{-2}	0.99×10^{-2}	0.5	8	0.7	0.75×10^{-2}	1.1×10^{-2}

---

a) 5×10^{-4} molar concentration.
b) A: concentration is based on the initial concentration of the anhydride stock solution.
B: concentration assayed by infrared spectroscopy.
c) Concentration assayed by infrared spectroscopy
d) Induction period prior to light emission
e) Time required for chemiluminescent intensity to decrease to one-half of its maximum value.
f) Reaction mixture contained approximately 1.5×10^{-3} molar added 2,6-di-t-butyl-4-methylphenol.

Figure III

CHEMILUMINESCENCE FROM TRIPHENYLACETIC ANHYDRIDE IN DIMETHYLPHTHALATE

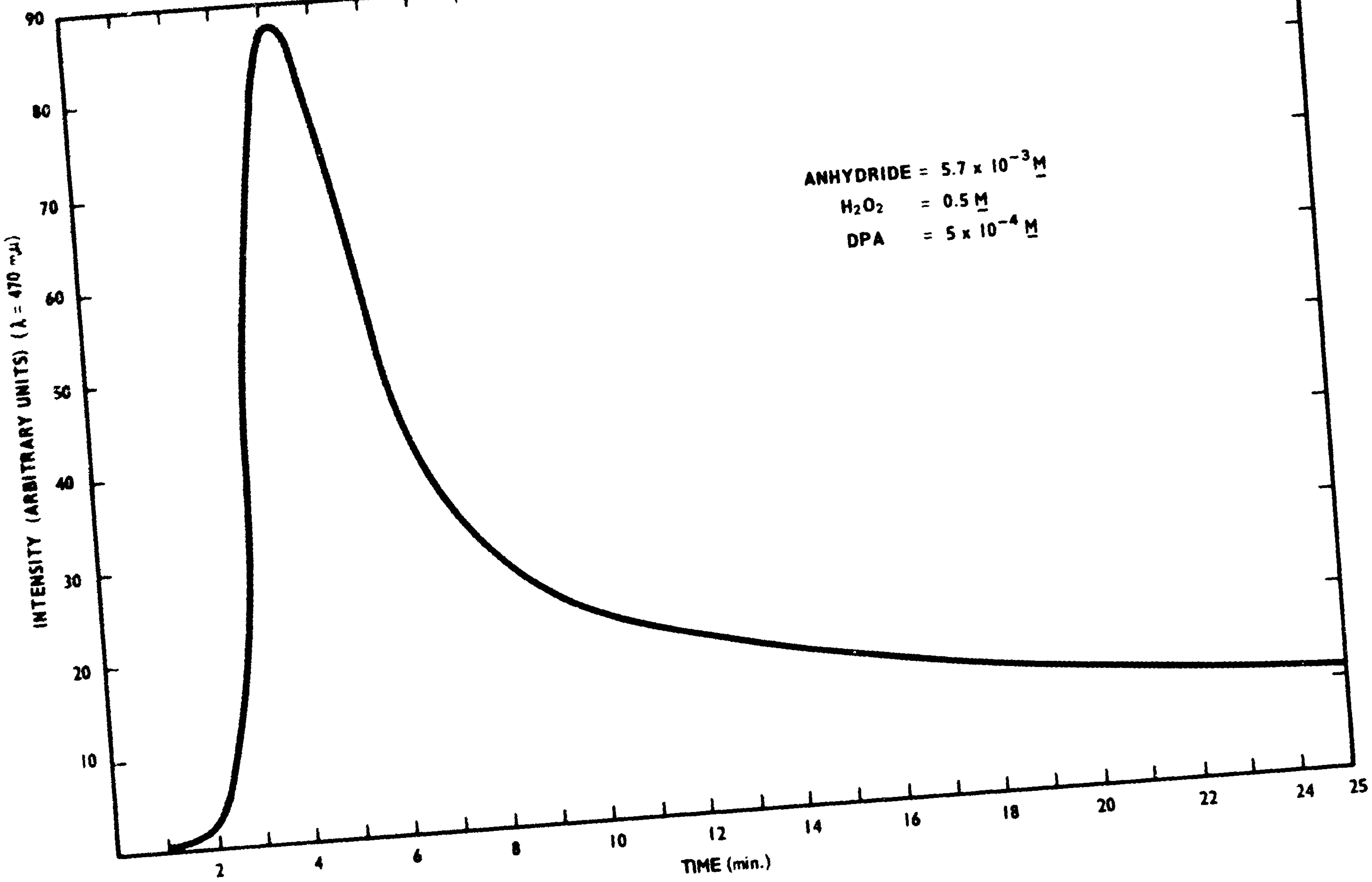


TABLE IV

Quantum Yield of Bistriphenylacetic Oxalic Anhydride Chemiluminescence in Dimethylphthalate Solution Containing 9,10-Diphenylanthracene[a]

$[(C_6H_5)_3C\overset{O}{C}O\overset{O}{C}]_2$[b] mole l.$^{-1}$	H_2O_2 mole l.$^{-1}$	$t_{1/2}I$[c] min.	Quantum Yield Einstein/mole of anhydride
4.53×10^{-3}	0.5	3.0	6.8×10^{-2}
4.53×10^{-3}	0.5	12.0	6.3×10^{-2}
4.53×10^{-3}[d]	0.5	10.0	6.6×10^{-2}
4.53×10^{-3}[e]	0.5	-----	0.00
4.53×10^{-3}[f]	0.5	9.0	6.8×10^{-2}

---

a) 5×10^{-4} molar concentration
b) The concentration is based on the initial concentration of the stock solution.
c) $T_{1/2}I$ represents the time required for the chemiluminescent light intensity to decrease to half of its maximum value.
d) Solution saturated with oxygen
e) Sodium diethyldithiocarbamate present in 10^{-3} molar concentration.
f) Water present in 5×10^{-3} molar concentration.

TABLE V

Quantum Yield of Bistriphenylacetic Oxalic Anhydride Chemiluminescence in Dimethylphthalate Solution

$[(C_6H_5)_3C\overset{O}{\overset{\|}{C}}-O\overset{O}{\overset{\|}{C}}]_2$ mole $l.^{-1}$	H_2O_2 mole $l.^{-1}$	9,10-Diphenylanthracene (DPA) mole $l.^{-1}$	$t_{1/2}I$[a] min.	Quantum Yield Einstein/mole of anhydride
5.67×10^{-3}	0.5	5×10^{-4}	2.0	5.2×10^{-2}
"	0.5	"	2.5	5.6×10^{-2}
"	0.25	"	2.5	6.0×10^{-2}
"	0.25	"	7.5	7.1×10^{-2}
"	0.05	"	7.0	11.8×10^{-2}
5.67×10^{-3}	0.25	1.7×10^{-4}	34.0	4.6×10^{-2}
"	"	5.0×10^{-4}	7.5	7.1×10^{-2}
"	"	5.0×10^{-4}	2.5	6.0×10^{-2}
"	"	1.3×10^{-3}	4.5	8.3×10^{-2}
5.67×10^{-3}	0.5	5×10^{-4}	3.0	6.8×10^{-2}
"	"	"	10.0	6.6×10^{-2}
"	"	"	12.0	6.8×10^{-2}
" b	"	"	9.0	6.8×10^{-2}

---

a) The time required for the chemiluminescent light intensity to decrease to half of its maximum value.
b) Water added to obtain a concentration of 6.73×10^{-3} mole/liter.

TABLE VI

Quantum Yield of Bistriphenylacetic Oxalic Anhydride Chemiluminescence in Dimethylphthalate Solution

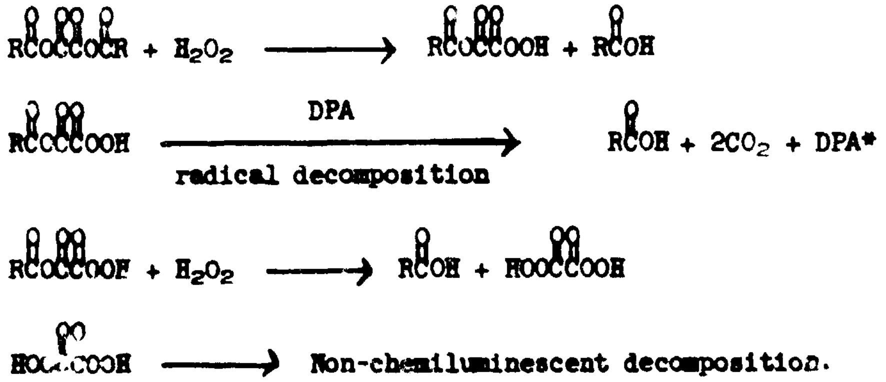
$[(C_6H_5)_3C\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}]_2$ mole l.$^{-1}$	H_2O_2 mole l.$^{-1}$	Rubrene mole l.$^{-1}$	H_2O mole l.$^{-1}$	$t_{1/2}I$[a] mins.	Quantum Yield Einstein/mole of anhydride
4.6 x 10^{-3}	0.25	1.67 x 10^{-4}	zero	3.0	3.6 x 10^{-2}
"	0.25	"	"	3.5	4.0 x 10^{-2}
"	0.41	"	"	3.8	2.3 x 10^{-2}
4.6 x 10^{-3}	0.25	0.33 x 10^{-4}	zero	3.0	4.8 x 10^{-2}
"	"	0.83 x 10^{-4}	"	3.5	4.8 x 10^{-2}
"	"	1.67 x 10^{-4}	"	3.0	3.6 x 10^{-2}
"	"	1.67 x 10^{-4}	"	3.5	4.0 x 10^{-2}
4.6 x 10^{-3}	0.25	1.67 x 10^{-4}	zero	3.5	4.0 x 10^{-2}
"	"	"	3.2 x 10^{-3}	3.0	4.0 x 10^{-2}
"	"	"	6.3 x 10^{-3}	3.8	3.8 x 10^{-2}
1 x 10^{-2}[b]	0.25	1.67 x 10^{-4}	zero	44	3.5 x 10^{-2}
" [c]	"	"	5.1 x 10^{-3}	59	3.2 x 10^{-2}
"	"	"	9.3 x 10^{-1}[d]	5.5	0.6 x 10^{-2}

---

a) The time required for the chemiluminescent light intensity to decrease to half of its maximum value
b) An 18 minute induction period observed.
c) A 16 minute induction period observed.
d) The water added did not dissolve but formed a separate phase.

Experiments summarized in Table IV indicate that oxygen and small amounts of water have negligible effect on the reaction, while the oxidation inhibitor sodium diethyldithiocarbamate extinguishes emission.

As indicated in Table V, increasing hydrogen peroxide concentrations above 5 x 10^{-2} M result in a substantial decrease in quantum yield. This is in sharp contrast to analogous experiments with oxalyl chloride-hydrogen peroxide reactions where the quantum yield was found to increase with increasing hydrogen peroxide in this concentration range. The result tentatively suggests the mechanism indicated below.



1) $\mathrm{R\overset{O}{C}O\overset{O}{C}\overset{O}{C}O\overset{O}{C}R + H_2O_2 \longrightarrow R\overset{O}{C}O\overset{O}{C}\overset{O}{C}OOH + R\overset{O}{C}OH}$

2) $\mathrm{R\overset{O}{C}O\overset{O}{C}\overset{O}{C}OOH \xrightarrow[\text{radical decomposition}]{\text{DPA}} R\overset{O}{C}OH + 2CO_2 + DPA^*}$

3) $\mathrm{R\overset{O}{C}O\overset{O}{C}\overset{O}{C}OOH + H_2O_2 \longrightarrow R\overset{O}{C}OH + HOO\overset{O}{C}\overset{O}{C}OOH}$

4) $\mathrm{HOO\overset{O}{C}\overset{O}{C}OOH \longrightarrow}$ Non-chemiluminescent decomposition.

The first step of the mechanism is almost certainly the formation of the monoperoxyoxalic acid derivative indicated. Additional hydrogen peroxide would be expected to react with this intermediate as in step 3 to form diperoxyoxalic acid. Results from oxalyl chloride-hydrogen peroxide experiments (Section IA) indicate that under the anhydrous conditions used in these experiments, diperoxyoxalic acid is essentially non-chemiluminescent. So we tentatively suggest that the peroxyoxalic acid derivative, itself may be capable of concerted multiple bond cleavage decomposition (step 2) which provides the excitation energy needed for light emission.

The effect of increasing DPA concentration on quantum yield is indicated in Table V. The observed increase in quantum yield is analogous to the effect of increasing fluorescer concentration in the oxalyl chloride-hydrogen peroxide system (Section IA). However, when rubrene is used as the fluorescer (Table VI) the quantum yield is essentially unchanged with rubrene concentration in the concentration range studied. Additional experiments will be carried out to determine more precisely the effect of fluorescer and fluorescer concentration on quantum yields.

As indicated in Tables IV and V, small quantities of additional water have little effect on the reaction in dimethylphthalate solution. Excess water, however, seriously reduced the quantum yield as indicated in Table VI.

Initial efforts have been made to identify the chemical products from the triphenylacetic-oxalic anhydride reaction with hydrogen peroxide in dimethylphthalate. Infrared analyses of liquid phase products indicate that triphenylacetic acid is the predominant reaction product, although quantitative analyses have not yet been carried out. Results from quantitative manometric and mass spectrometric analyses of gaseous phase products are summarized in Table VII. It is evident from the table that the predominant gaseous product is carbon dioxide along with a substantial amount of carbon monoxide. However, the total gaseous product observed accounts at best for only about 33% of the oxalyl carbon. The quantum yield data summarized in Tables III, IV, and V demonstrates that the triphenylacetic-oxalic anhydride-hydrogen peroxide system is

TABLE VII

Gaseous Products of the Reaction Between IB and H_2O_2 in Dimethylphthalate

Moles Anhydride (x 10^5)	[Anhydride] (x 10^2 moles/l)	[H_2O_2] (x 10^2 moles/l)	[H_2O] (x 10^2 moles/l)	[Rubrene] (x 10^5 moles/l)	Moles CO_2 (x 10^5)	Conv. CO_2 (%)	Moles CO (x 10^5)	Conv. CO^a (%)
71.2764	1.8276	8.7692	-	-	26.9677	37.8	16.7745	23.5
71.2764	1.8276	8.7692	-	-	27.4483	38.5	19.7470	27.7
71.2785	1.7385	8.3415	-	2.4390	19.8709	27.9	12.3293	17.3
71.2782	1.6971	8.5952	9.2857	-	22.4468	31.5	19.8265	27.8

---

a) CO values are subject to some uncertainty.

far superior in efficiency to any previously known non-biological chemiluminescent reaction. Additional work is planned to further define optimum reaction conditions and the effect of reaction variables on quantum yields.

3. Diphenylacetic-oxalic anhydride has been prepared in an admixture with diphenylacetic acid by reaction of diphenylketene with oxalic acid. The reaction proceeded sluggishly, indicative of the relatively low reactivity of diphenyl ketene. The anhydride-acid mixture provided chemiluminescence emission when reacted with hydrogen peroxide in the presence of DPA. Other studies are in progress.

4. Pivalic-oxalic Anhydride. - Attempts to prepare this anhydride from potassium pivalate and oxalyl chloride or from pivalyl chloride and sodium oxalate have provided discouraging results. Mixtures of pivalic acid and pivalic anhydride were cutomarily obtained, with no indication of the formation of the desired mixed anhydride. The formation of substantial quantities of pivalic anhydride in these experiments suggests that pivalic-oxalic anhydride may undergo a decomposition analogous to the decomposition reported for acetic-oxalic anhydride.

SECTION IB

EXPERIMENTAL

Diacetic Oxalic Anhydride (IA)[16,17] - Ketene, prepared by the pyrolysis of acetone[8] at the rate of 0.1 moles ketene per hour, was bubbled through a stirred solution of 4.5 g. (0.05 moles) of anhydrous oxalic acid in 100 ml. anhydrous ether at -50° under argon during 1.25 hours. The reaction solution was then evaporated to dryness under reduced pressure at temperatures below -5°. A white crystalline product was obtained, whose infrared spectrum was in agreement with that expected. Bands characteristic of acetic anhydride or acetic acid were absent from the spectrum. The product was found to be very sensitive to moisture and to decompose at temperatures above -5°.

In a similar experiment, following completion of the reaction at -5°, the reaction mixture was maintained under a ketene atmosphere at 0° for 5.5 hours, and then analyzed by infrared spectroscopy. The resulting solution was found to contain mainly acetic anhydride together with small amounts of diacetic oxalic anhydride and acetic acid.

Bisdiphenylacetic Oxalic Anhydride - A solution of 0.27 g. (0.003 moles) of oxalic acid in 25 ml. of anhydrous ether was added dropwise under argon to a stirred solution of 1.14 g. (0.006 moles) of diphenyl ketene[19] in 30 ml. of petroleum ether. The reaction was stirred 2 hours at 25°; then 2 drops of concentrated sulfuric acid was added, and the reaction mixture was stirred 60 hours at 25°. The reaction mixture was filtered under argon, and the filtrate was evaporated to dryness under reduced pressure to obtain 1 g. of product which was shown to be, by infrared analysis, a mixture of 30% desired product, 60% diphenylacetic acid, and 10% unreacted diphenyl ketene.

The product of the reaction was found to provide chemiluminescence when reacted with hydrogen peroxide and DPA in 1,2-dimethoxyethane.

Potassium Pivalate - Potassium pivalate was prepared by adding 13.2 g. (0.234 moles) of potassium hydroxide to a solution of 20.4 g. (0.2 mole) pivalic acid in 500 ml. of absolute ethanol. The solvent was reduced to 50 ml. and 25 ml. of benzene was added. The volume was further reduced until a solid began to precipitate. The salt was obtained in a yield of 14.8 g. (62%) m.p. > 300°. The infrared spectrum was consistent with that expected for the product.

Attempted Preparation of Dipivalic-Oxalic Anhydride - A suspension of 29 g. (0.2 mole) of potassium pivalate in a mixture of 150 ml. of 1,2-dimethoxyethane and 50 ml. benzene was heated to reflux, and the suspension became gelatinous. The mixture was then cooled to 0° and oxalyl chloride, 16.8 ml. (0.2 mole), was added. There was a substantial evolution of gas as the addition proceeded. The mixture was filtered and the solvents removed, leaving a white, waxy solid. The solid produced a weak, short-lived light when added to 5 ml. of 1,2-dimethoxyethane containing a few mg. rubrene, 4 drops 90% hydrogen peroxide and a pellet of potassium hydroxide. Subsequent infrared analysis indicated that the product was primarily a mixture of pivalic anhydride and pivalic acid with a trace of oxalyl chloride.

Results of similar attempts to prepare the mixed anhydride are summarized in Table VIII. All were marked by a substantial gas evolution as the oxalyl chloride was added.

One attempt was made to prepare the anhydride from 8.04 g. (0.06 mole)of sodium oxalate (which had been dried *in vacuo* at 50°) and 6.03 g. (0.05 mole)of pivalyl chloride in 50 ml. of distilled hexane at 0°. The starting materials were recovered unchanged.

Infrared Study of the Decomposition of Diacetic Oxalic Anhydride - The experiments in Tables Ia and Ib were carried out with solutions of diacetic oxalic anhydride of varying concentrations, prepared under argon in 1,2-dimethoxyethane freshly distilled over $LiAlH_4$. Solutions of reaction components were combined in flasks attached to mercury manifolds and fitted with serum stoppers for the withdrawal of samples. All glassware was thoroughly cleaned, and dried in an oven at 110° for at least 1 hour. The flasks containing the reaction mixtures were placed in a constant temperature bath, and small aliquots of each sample were withdrawn periodically and analyzed by infrared spectroscopy for the disappearance of diacetic oxalic anhydride bands at 1835, 1795, and 1767 cm.$^{-1}$, and for the appearance of an acetic anhydride band at 890 cm.$^{-1}$ and an acetic acid band at 1740 cm.$^{-1}$.

Infrared Study of the Decomposition of Bistriphenylacetic Oxalic Anhydride - For the experiments in Table II, a solution of 2×10^{-2}M bistriphenylacetic oxalic anhydride in 1,2-dimethoxyethane was prepared under argon with freshly distilled solvent. The solution was introduced into a flask attached to a mercury manifold and fitted with a serum stopper for the withdrawal of samples. Other reactants were added when desired. All glassware was thoroughly cleaned, and dried in an oven at 110° for at least 1 hour. The flask containing the sample was placed in a constant

TABLE VIII

Attempts to Prepare Dipivalic oxalic Anhydride

	Reactants (moles)		Solvent	Temp. at Addition	Time (mins.)	Products
	Oxalyl Chloride	Potassium Pivalate				
1.	0.2	0.2	benzene, 50 ml. 1,2-dimethoxyethane, 150 ml.	0°	20	70% Pivalic Anhydride 30% Pivalic Acid
2.	0.03	0.03	ether, 50 ml.	-70°	30	40% Pivalic Anhydride 60% Pivalic Acid
3.	0.08	0.02	benzene, 75 ml.	0°	--	Massive gas evolution blew stoppers off apparatus and reaction mixture foamed out.
4.	0.08	0.02	ether, 50 ml.	-10°	20	Mixture of pivalic anhydride-oxalyl chloride and pivalic acid.
5.	0.08	0.02	hexane, 50 ml.	0°	20	Mixture of above materials
	Sodium Oxalate	Pivalyl Chloride				
6.	0.06	0.05	hexane, 50 ml.	0°	20	Starting material recovered

temperature bath, and small aliquots were withdrawn periodically and analyzed by infrared spectroscopy for the disappearance of the bistriphenylacetic oxalic anhydride band at 1760 cm.$^{-1}$, and for the appearance of a triphenylacetic anhydride band at 1805 cm.$^{-1}$ and a triphenylacetic acid band at 1730 cm.$^{-1}$. The non-catalyzed decomposition was carried out twice.

The absorptivities determined in these experiments were linearly compared to absorptivities determined on standard solutions of triphenylacetic acid and standard solutions of triphenylacetic-oxalic anhydride in 1,2-dimethoxyethane to determine absolute concentrations. The standard absorptivities were: triphenylacetic acid at 1740 cm.$^{-1}$ = 505 l. mole^{-1} cm.$^{-1}$; triphenylacetic anhydride at 1830 cm.$^{-1}$ = 370 l. mole^{-1} cm.$^{-1}$. The data for the experiment in Figure 1 are summarized in Table IX.

Chemiluminescence Quantum Yield and Reaction Rate Determinations for the Reaction of Triphenylacetic Oxalic Anhydride with Hydrogen Peroxide in the Presence of 9,10-diphenylanthracene (DPA) in 1,2-dimethoxyethane Solutions - Dry 1,2-dimethoxyethane was prepared by distillation under argon from lithium aluminum hydride. A stock solution (3×10^{-2} M) of triphenylacetic oxalic anhydride was prepared and transferred under argon to a serum-capped bottle to prevent reaction with atmospheric moisture. Stock solutions of 5×10^{-3} M DPA and 1.5 M H_2O_2 in 1,2-dimethoxyethane were also prepared. Aliquots of the anhydride solution were withdrawn by syringe and combined with aliquots of the DPA solution in the radiometer cuvette[1,2]. The wavelength of the radiometer was set at 430 mμ and the slit opened. The recorder was started and aliquots of hydrogen peroxide were injected from a glass syringe into the magnetically stirred solution in the cuvette.

Quantum yield calculations were made analogously to those described previously for the oxalyl chloride reaction[2]. Results are summarized in Table III.

Chemiluminescence Quantum Yield Measurements for Triphenylacetic-Oxalic Anhydride, Hydrogen Peroxide, Fluorescer Reactions in Dimethyl-Phthalate Solutions - Dimethylphthalate distilled from lithium aluminum hydride was used to prepare stock solutions of the anhydride, hydrogen peroxide and fluorescer. All solutions were prepared and transferred to serum-capped bottles in a dry box to minimize hydrolysis. Aliquots of the reactants were transferred to the magnetically stirred cuvette by syringe, with hydrogen peroxide being the final solution added. The decay curves and spectral distributions were recorded and the quantum yields calculated as described previously[2]. Both 9,10-diphenylanthracene and rubrene were used in different sets of experiments as fluorescent acceptors [See Tables IV, V, and VI].

TABLE IX

Triphenylacetic-Oxalic Anhydride Decomposition in 1,2-Dimethoxyethane Solution as a Function of Time

Time in Hours from Preparation of Solution	Anhydride Concentration[a] (molar)	Triphenylacetic Acid Concentration (molar[b])
0	2.55×10^{-2}	0.89×10^{-2}
5	2.29×10^{-2}	1.41×10^{-2}
20	2.26×10^{-2}	1.55×10^{-2}
26	2.09×10^{-2}	1.60×10^{-2}
30	2.06×10^{-2}	1.75×10^{-2}
48	2.03×10^{-2}	1.75×10^{-2}
94	1.91×10^{-2}	1.98×10^{-2}

---

[a] Measured by I.R. absorbance using 1830 $cm.^{-1}$ for calculation.

[b] Measured by I.R. absorbance using 1740 $cm.^{-1}$ for calculation.

Solubility of Carbon Dioxide in Dimethylphthalate (DMP) - The apparatus (see Figure IV) used consisted of a 300 ml. reaction vessel to which was attached either a 300, 500, or 1000 ml. gas reservoir. A simple differential mercury manometer was included and could be attached to either the reaction vessel or the gas reservoir. Evacuation of the system could be accomplished by means of the oil pump. Agitation was by means of a magnetic stirrer included in the reaction vessel. All volumes in the system were determined by calibration with water.

In a typical determination, 100 ml. of freshly distilled anhydrous dimethylphthalate was placed in the reaction vessel and thoroughly degassed via the oil pump to a pressure of less than 1 mm. Hg. The gas reservoir was evacuated and then charged to a predetermined pressure with carbon dioxide gas. Carbon dioxide was admitted into the reaction vessel and the uptake of the gas followed by the change in pressure indicated by the manometer. When no change in pressure had occurred over a 2 hour period, the system was considered at equilibrium. The Henry's constant was calculated from the known pressures, temperature, and volumes of the system.

Henry's Constant for CO_2/DMP System

Pressure (mm. Hg.)		Free Vol. (ml.)	Temp. °C	Dissolved CO_2 (moles/l. x 10^3)	k.[a] (x 10^{-4})
Initial	Equilibrium				
429.0	338.4	739.1	24.8	3.603	5.75
559.3	476.9	1291.2	25.7	5.678	5.14

---

a) k = P(mm. Hg. at equilibrium)/ mole fraction dissolved CO_2

Gaseous Products from Triphenylacetic-Oxalic Anhydride Reactions with Hydrogen Peroxide in Dimethylphthalate (DMP) - The apparatus used to measure the gaseous products from bistriphenylacetic oxalic anhydride was that of Figure III except that the gas reservoir (B) was replaced by a pressure-equalized dropping funnel which had been calibrated with water. All of the glassware was carefully cleaned in a hot chrome-sulfuric acid wash, rinsed well in distilled water, and dried thoroughly at 110°C in the oven before use.

In a typical determination, aliquots of anhydrous hydrogen peroxide in anhydrous dimethylphthalate (DMP) and, where desired, rubrene or water in DMP, were placed in the reaction vessel and cooled to 0°C by an ice bath. An aliquot of the anhydride solution was placed in the dropping funnel and the entire system flushed with argon and then degassed to less than 1 mm. Hg. via the oil pump. The ice bath was removed from the reaction vessel and the anhydride solution added to the peroxide solution. Gas evolution was followed by the increase in pressure in the reaction vessel. When no pressure increase had been observed for a two hour period, the final pressure was recorded and the gas phase analyzed by mass spectroscopy. The total reaction time was about 18 hours. Results of the gas analysis are summarized in Table X.

TABLE X

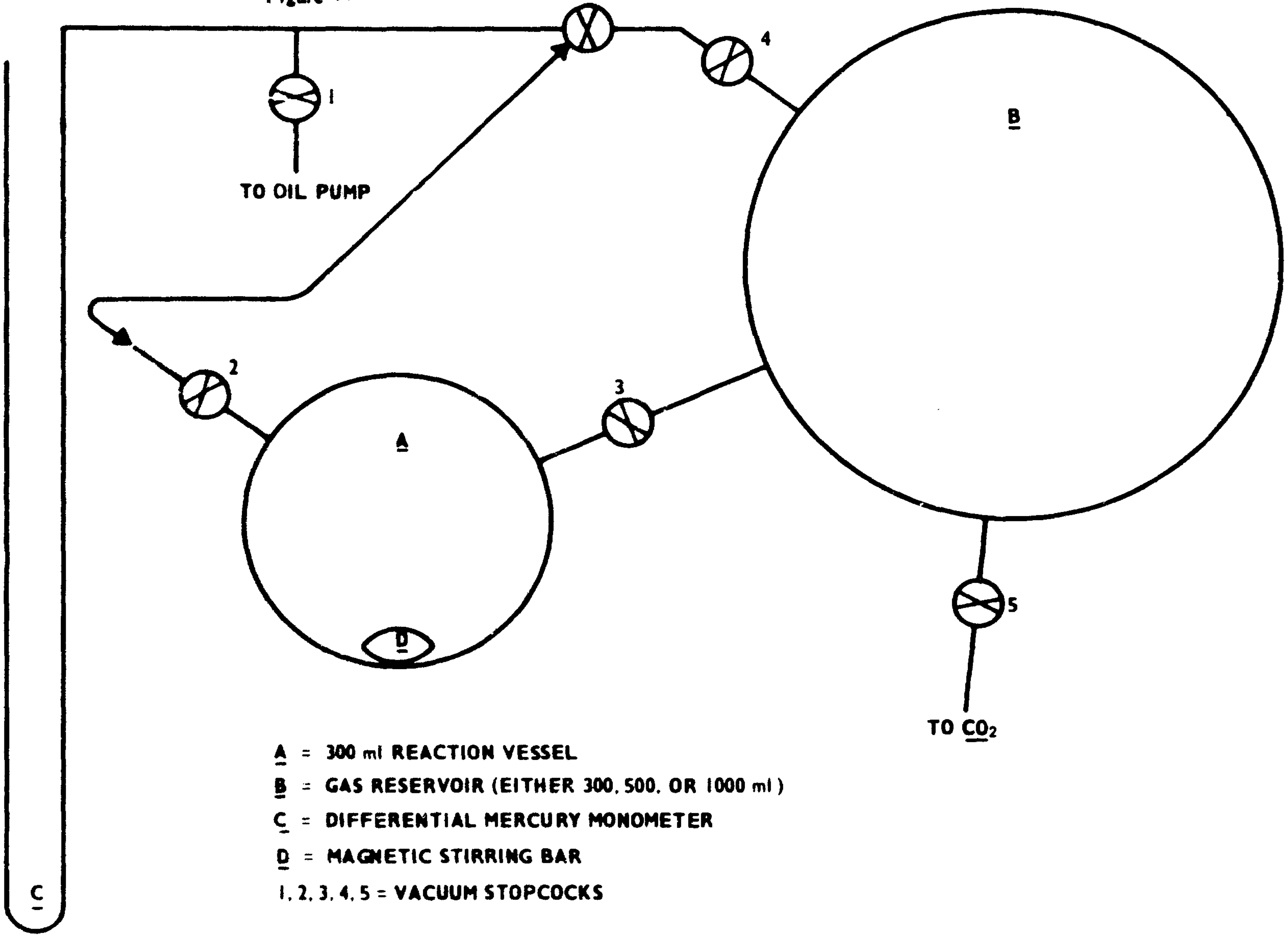
Gaseous Products from the Ib and H_2O_2 Reaction in Dimethylphthalate(1)

[Anhydride] (x 10^2 moles/l.)	[H_2O_2] (x 10^2 moles/l.)	Final Pressure (mm. Hg.)(2)	Temp. (°C)	Mole Per Cent of Product				
				CO_2	CO(3)	H_2O	O_2	A
1.8276	8.7692	23.7	24.8	53.3	36.3	2.1	5.8	2.5
1.8276	8.7692	28.4	24.7	48.5	38.5	1.4	8.5	3.1
1.7385(4)	8.3415	18.9	24.2	50.8	34.8	2.3	6.8	5.3
1.6971(5)	8.5952	25.6	24.8	41.4	40.4	6.8	6.3	5.1

---

(1) Free volume of the system was 342.8 ml.
(2) Initial pressure was between 0-1 mm. Hg.
(3) Values subject to some uncertainty.
(4) Rubrene was present at a concentration of 2.4390 x 10^{-2} moles/l.
(5) Water was present at a concentration of 9.2857 x 10^{-2} moles/l.

Figure 11



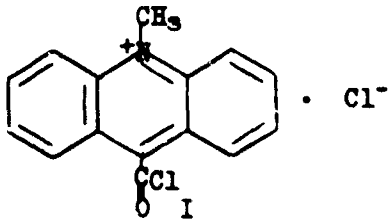
$\underline{A}$ = 300 ml REACTION VESSEL
$\underline{B}$ = GAS RESERVOIR (EITHER 300, 500, OR 1000 ml)
$\underline{C}$ = DIFFERENTIAL MERCURY MONOMETER
$\underline{D}$ = MAGNETIC STIRRING BAR
1, 2, 3, 4, 5 = VACUUM STOPCOCKS

SECTION I

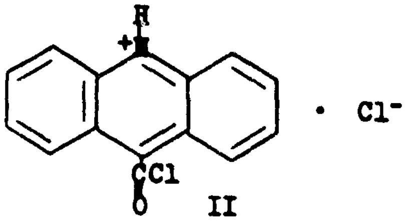
PART C

Chemiluminescence Derived from 9-Carboperoxyacridine Derivatives

Previous reports have described new chemiluminescent systems based on reactions of acridinium salts I[7] and II[6] with aqueous hydrogen peroxide.

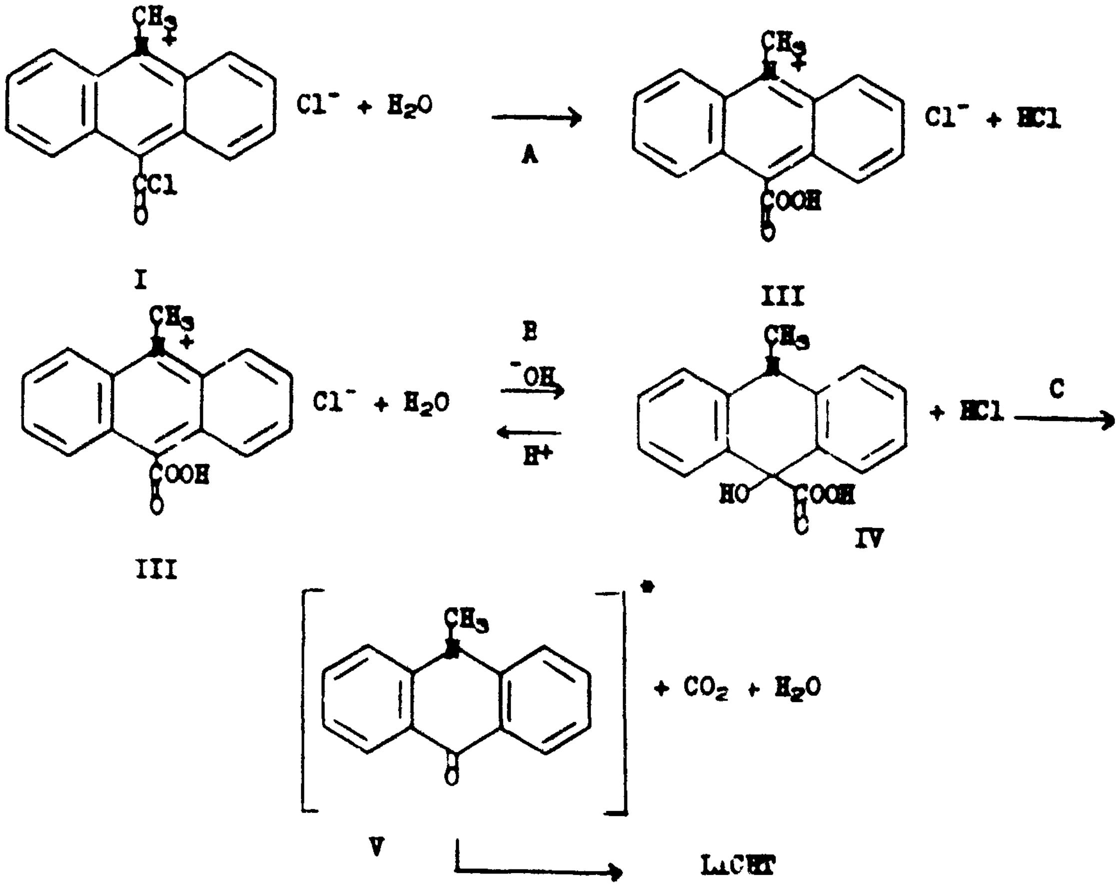


I



II

Evidence was provided in the last report[7] indicating that the chemiluminescent process involves the mechanism diagrammed below.

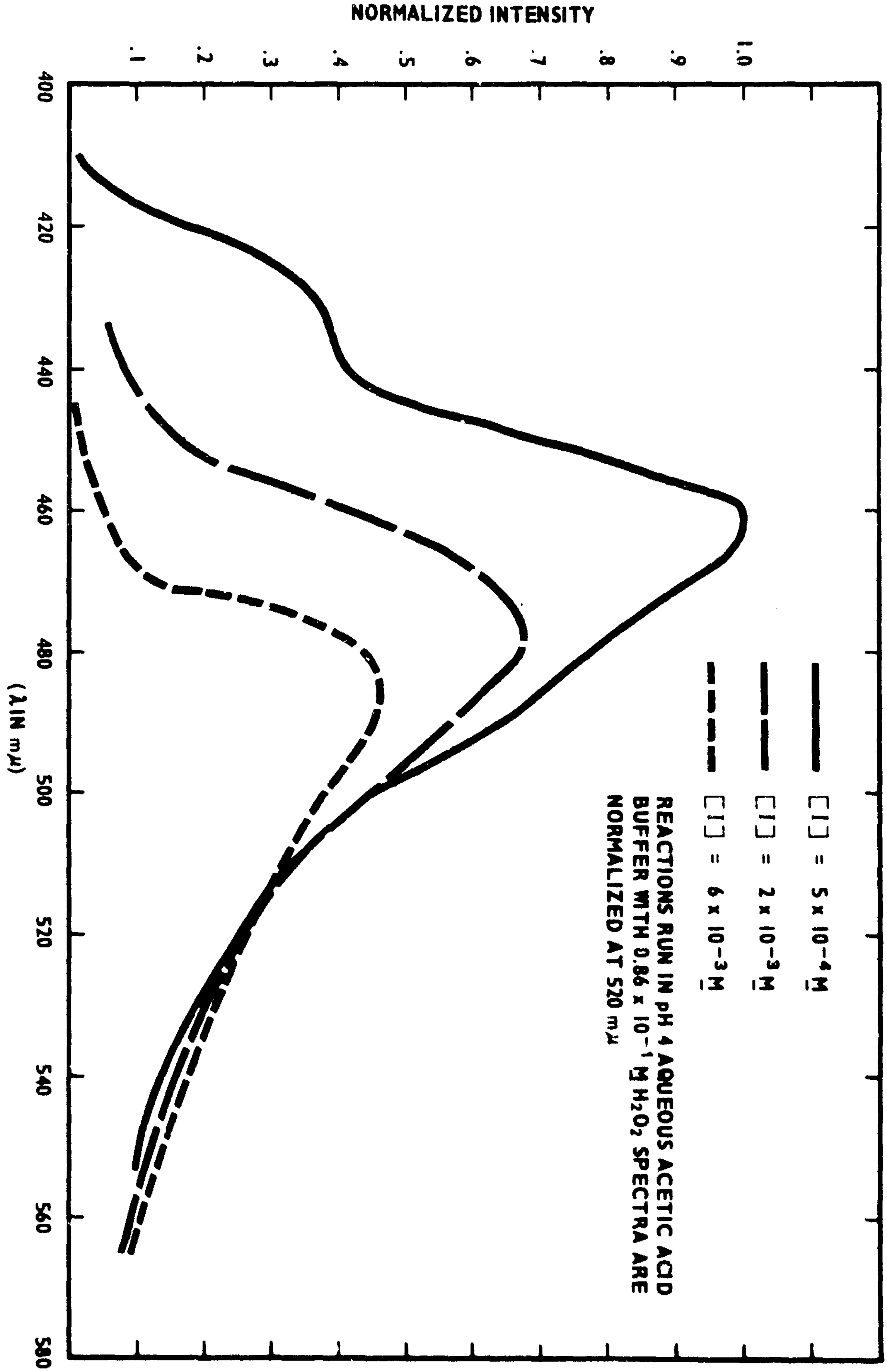


Indeed the reaction was designed on the basis that pseudo base IV might be capable of concerted multiple bond cleavage decomposition and thus provide the substantial energy required to generate excited V as a reaction product.

We have now carried out a series of preliminary quantitative light measurements to further characterize the reaction. The spectral distribution of chemiluminescent emission from reactions of I with aqueous hydrogen peroxide was found to vary substantially with the initial concentrations of I as indicated in Figure I, where the spectra are "normalized" to a common intensity at 520 mμ. The spectral change with increasing concentration is evidently a consequence of reabsorption of emitted light by the acridine derivatives present. The spectral distribution was found, however, to be essentially unchanged with time in a given experiment. The chemiluminescent spectrum obtained at low concentrations of I, where reabsorption (and reemission) would be small, is compared with the fluorescent emission from 10-methylacridone, V, and from reaction by-product 9-carboxy-10-methylacridinium chloride, VI, in Figure II. It is seen that the spectral match with VI is poor, while spectral match of the chemiluminescent light with V fluorescence is fairly good in spite of the different solvents used. (V is poorly soluble in water under the chemiluminescent conditions.) The spectral correspondence of chemiluminescent emission with V fluorescence strongly supports the assignment of excited V as the primary emitting species in

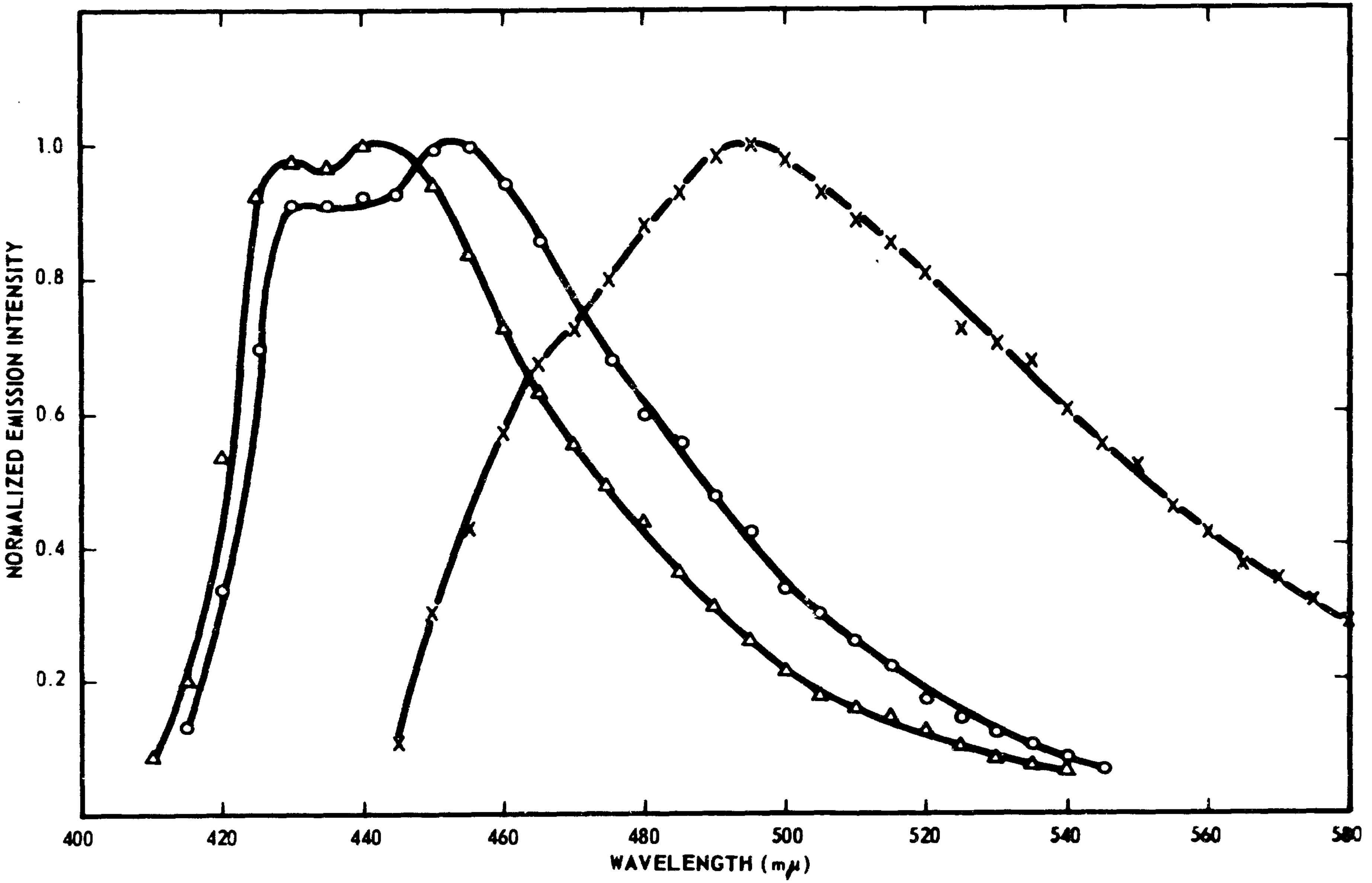
Figure 1

CHEMILUMINESCENCE SPECTRAL EMISSION OF *I*



REACTIONS RUN IN pH 4 AQUEOUS ACETIC ACID BUFFER WITH 0.86 x 10^{-1} M H_2O_2 SPECTRA ARE NORMALIZED AT 520 mμ

FIGURE II
CHEMILUMINESCENCE AND FLUORESCENCE SPECTRA



Notes to Figure II

○ Chemiluminescence emission from 2 x 10^{-4} M V in 1 M H_2O_2.

△ Fluorescence emission from 1 x 10^{-3} M VIII in ethanol containing 0.02 M HCl.

● Fluorescence emission from 1 x 10^{-3} M IV in water.

the chemiluminescent reaction. As noted in previous reports, however, we never regard spectral correspondence between broad emission bands as conclusive proof of the identity of emitting species.

The proposed chemiluminescence mechanism requires the initial formation of peroxyacid III which is followed by a pH-dependent equilibrium with key intermediate IV. In the previous report[7] we showed that formation of III from I and hydrogen peroxide in 1,2-dimethoxyethane is a slow process, essentially complete only after 1 hour. To examine the stability of III and the proposed equilibrium step, a solution was prepared from I and 90% hydrogen peroxide. The solution was essentially non-chemiluminescent under the conditions used, but provided strong chemiluminescent emission on dilution with water. The chemiluminescence yield and light decay rates of the diluted solution were determined under invarient conditions as a function of the "ageing period" of the 90% hydrogen peroxide solution. The decay plots are pictured in Figure III, and the results are summarized in Table I.

As indicated in Table I, the chemiluminescence efficiency increases sharply as the solution of I in 90% hydrogen peroxide stands, reaching maximum yield at about 0.5 hours. Even after short ageing, the quantum yield is higher than that from an equivalent experiment where I was dissolved directly in 1.0 M hydrogen peroxide. This effect is best accounted for in terms of the following competitive processes.

TABLE I

Chemiluminescence Efficiency of Aged Solutions of I in 90% Hydrogen Peroxide[a]

Ageing Period (hrs.)	Half-Intensity Period (sec.)	Quantum Yield ($x 10^2$)	Maximum Brightness (footlamberts from 1.0 cm. thickness)
0.0[b]	35.0	1.3	0.08
0.1	22.5	1.9	0.15
0.5[c]	22.5	3.5	0.24
1.0[c]	25.0	3.4	0.22
1.5	22.5	3.2	0.26
2.0	25.0	2.8	0.21
3.0[d]	35.0	1.9	0.08
3.5	22.5	2.6	0.21
4.25	22.5	2.3	0.19
20	40.0	0.71	0.03
44	58.0	0.23	0.007

(a) A solution of 3.0×10^{-3} M I in 90% H_2O_2 was allowed to stand at 25°. Aliquots (0.1 ml.) were withdrawn periodically and diluted with 2.9 ml. 45% (by volume) aqueous t-butanol to provide chemiluminescent solutions corresponding to 1.0×10^{-4} M I and 1.0 M H_2O_2.

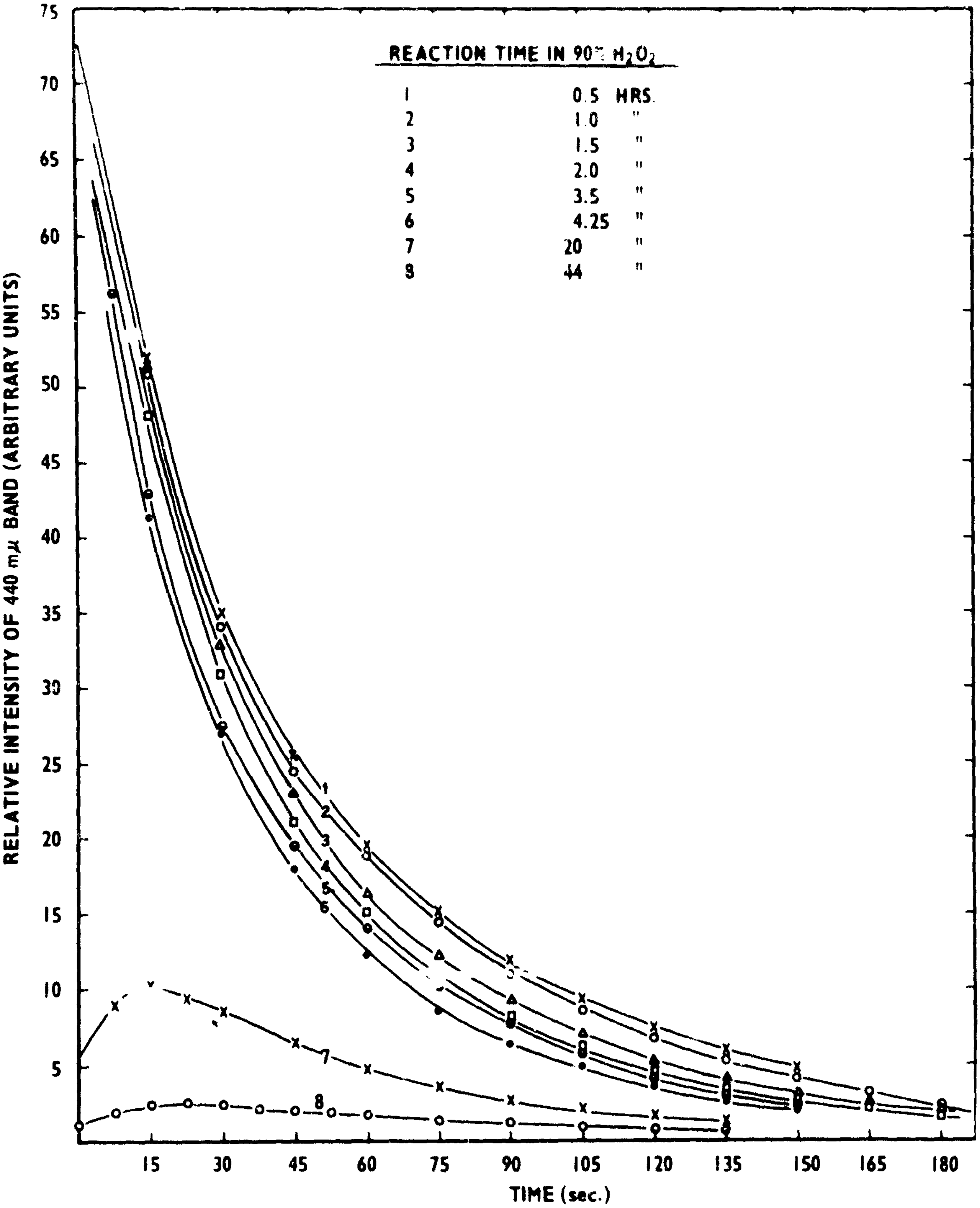
(b) Solution prepared directly by dissolving I in 45% t-butanol containing 1.0 M H_2O_2.

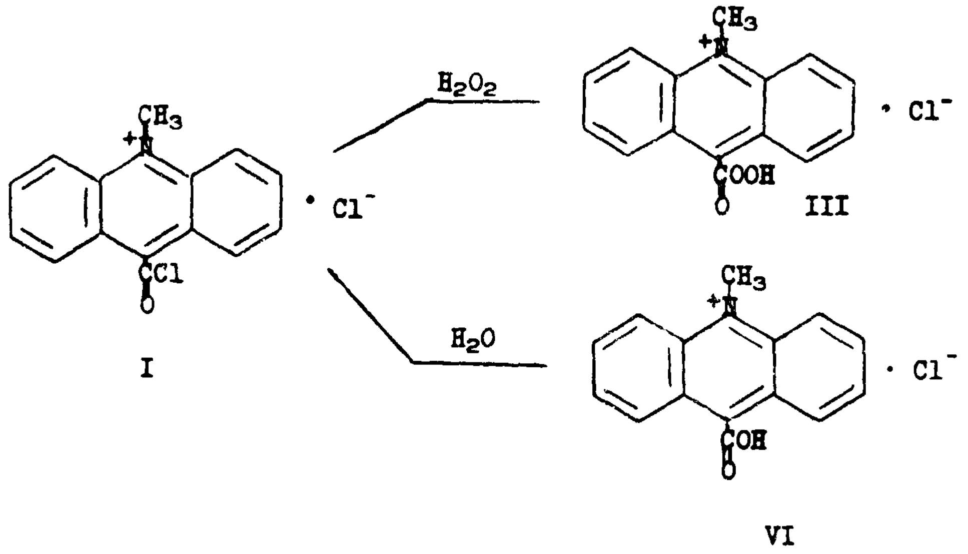
(c) Reaction mixture contained 1.0×10^{-2} M 2,6-di-t-butyl-4-methylphenol.

(d) Diluted with water.

Figure

REACTIONS OF SOLUTIONS OF IN 90% H_2O_2 AFTER DILUTION WITH 45% AQUEOUS t-BUTANOL





Thus, in 90% hydrogen peroxide, I is converted predominantly to III provided sufficient time is allowed for the relatively slow process. But in the presence of excess water an appreciable fraction of I is converted to non-chemiluminescent VI, reducing the chemiluminescence efficiency.

As indicated in Table I, the chemiluminescence efficiency decreases only slowly with time beyond 0.5 hours, presumably the result of a slow non-chemiluminescent decomposition of III. Even after 3.5 hours the efficiency was still 74% of that observed after 30 minutes, and an appreciable emission was still observed approximately two days later.

The highest quantum yield observed in the experiments was 3.5%. This efficiency is of comparable magnitude to that obtained in oxalyl chloride-hydrogen peroxide-rubrene chemiluminescence[6] and is substantially higher than the 1% quantum yields reported for 3-aminophthalhydrazide (luminol) chemiluminescence[2]. It is also evident from the Table that higher chemiluminescence yields were obtained in aqueous t-butyl alcohol than in water.

Several attempts to inhibit the reaction with the free radical inhibitor 2,6-di-t-butyl-4-methylphenol are reported in Table I. It is evident from the results that no appreciable inhibition or yield loss was observed; thus, the reaction does not appear to involve a free radical chain mechanism. This result is in sharp contrast to free radical inhibition experiments with the oxalyl chloride-hydrogen peroxide reaction (Section I A) where 2,6-di-t-butyl-4-methylphenol produced a marked reduction in efficiency.

A second series of preliminary experiments was carried out to determine the effects of reaction conditions on the quantum yield and light decay rate. In these experiments I was treated with aqueous hydrogen peroxide under a variety of conditions and the absolute emission intensity was determined as a function of time. The results are summarized in Table II.

Plots of log I vs. time were linear for three of the experiments, which were carried out under pseudo first order reaction conditions with an excess of hydrogen peroxide in an acetic acid-sodium acetate buffer at pH 4. In all of the experiments, however, except at the highest concentration of I, the plots closely approximated straight lines. Typical plots are shown in Figure IV. A comparison of the quantum yield values in Table II indicates that (1) the quantum yield increases substantially with increasing hydrogen

TABLE II

Reactions of I with Aqueous Hydrogen Peroxide(a)

[I] (moles $l.^{-1}$)	[H_2O_2] (moles $l.^{-1}$)	k^1 (sec.$^{-1}$)	Quantum Yield (x 10^4)	Half-life (sec.)
5×10^{-4}	8.6×10^{-2}	1.21×10^{-2}	9.8	57
2×10^{-3}	8.6×10^{-3}	1.1×10^{-2b}	0.53	64
2×10^{-3}	8.6×10^{-2}	1.23×10^{-2}	4.2	55
2×10^{-3c}	8.6×10^{-2}	8.9×10^{-4}	1.0	780
2×10^{-3}	8.6×10^{-1}	2.44×10^{-2}	10.6	28
6×10^{-3}	8.6×10^{-2}	1.0×10^{-2d}	1.5	70

(a) Reactions run in acetic acid-sodium acetate buffer at pH 4 except where noted. Reaction temperature = 25°C.

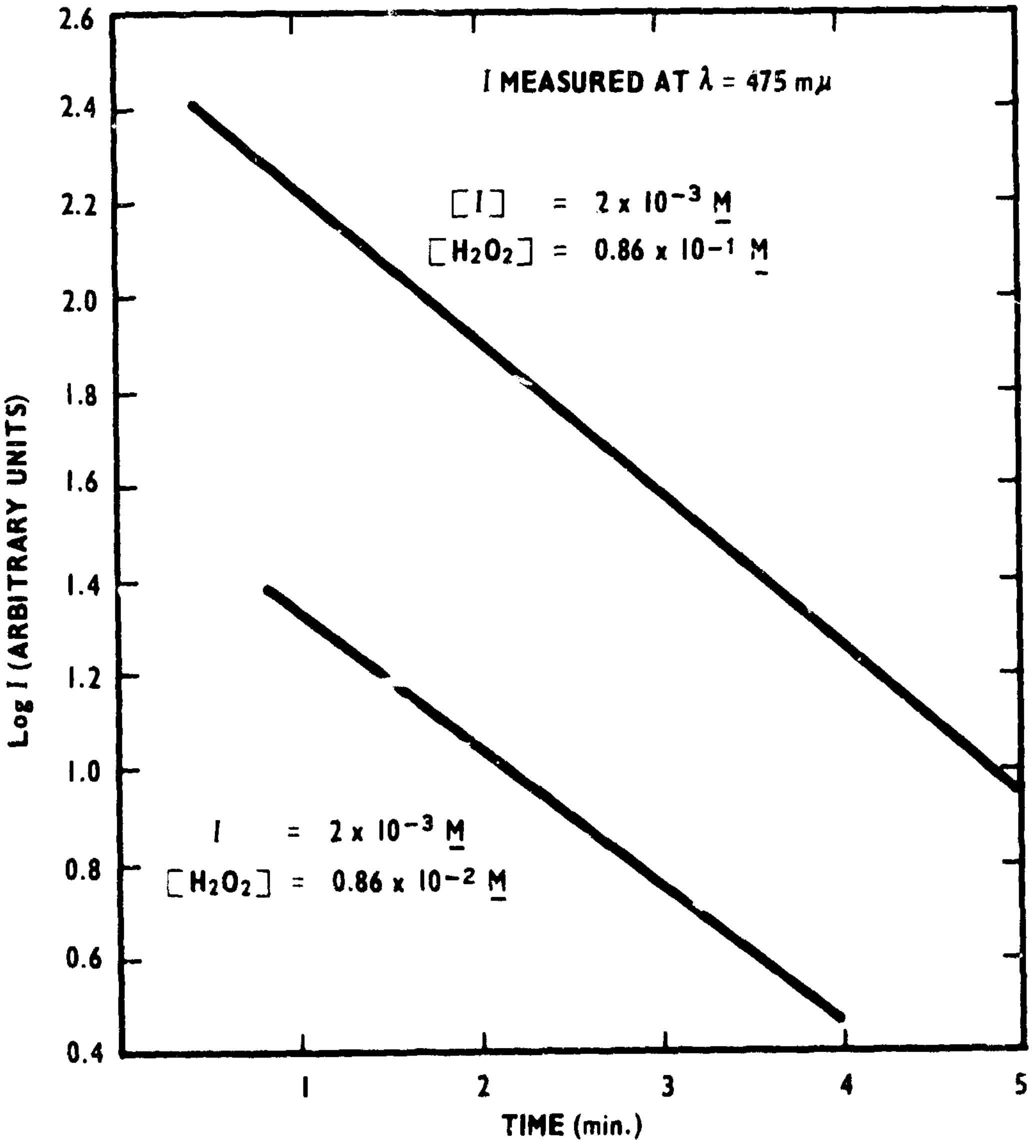
(b) Linear Log I vs. T plot after 90 sec.

(c) Reaction medium was unbuffered water.

(d) Linear Log I vs. T plot only after 120 sec.

Figure IV

REACTIONS OF I WITH HYDROGEN PEROXIDE IN AN AQUEOUS ACETATE BUFFER AT pH 4



peroxide concentrations (2) the quantum yield decreases substantially with increasing concentrations of I and (3) that higher quantum yields are obtained in buffered solutions at pH 4 than in unbuffered solutions where the limiting pH is 2.4.

The effect of hydrogen peroxide on quantum yield is easily understood in terms of the competition between hydrogen peroxide and water for I as discussed earlier.

Moreover, the increase in reaction rate that is observed only at the highest hydrogen peroxide concentration studied suggests that at lower hydrogen peroxide concentration at pH 4 the rate is determined primarily by the rate of the side reaction discussed earlier between I and water and that at the highest hydrogen peroxide concentration, hydrogen peroxide competes successfully with water so that a substantial fraction of I is converted to III. Thus, with increasing hydrogen peroxide the rate of disappearance of I increases and the steady state concentration of III and IV increases causing the overall rate increase with higher intensity and quantum yield.

The decreasing quantum yield with increasing concentration of I results in part from serious reabsorption of primary emission at the higher concentrations (See Figure I). However, reabsorption does not account for the entire yield loss. The quantum yield for the experiment in Table II with 6×10^{-3} $\underline{M}$ I was approximately corrected for reabsorption by recalculation in terms of the spectral distribution obtained in the experiment with 5 x 10^{-4} *M* I. This approximation does not take into account fluorescent emission by the reabsorbed light at the higher concentration and thus gives an erroneously *high* quantum yield. In spite of the *high* bias of the correction, the corrected quantum yield for the 6 x 10^{-3} *M* experiment was substantially *lower* than the actual quantum yield obtained at 5 x 10^{-4} *M* I. The quantum yield values were: measured yield at 6 x 10^{-3} *M* I = 1.54 x 10^{-4}; corrected yield at 6 x 10^{-3} *M* I = 4.5 x 10^{-4}; measured quantum yield at 5 x 10^{-4} *M* I = 9.8 x 10^{-4}. Thus fluorescence quenching of the emitting species or non-chemiluminescent side reactions involving intermediates derived from I reduce the quantum yield by a factor of at least two at the higher concentration of I.

As indicated in Table II, buffered reactions at pH 4 were substantially more rapid than corresponding non-buffered experiments. This is in agreement with previously reported qualitative observations[7] and is in agreement with the proposed equilibrium between III and IV.

SECTION I - PART C

EXPERIMENTAL

The instrumentation, its calibration, and its use for determining fluorescence and chemiluminescence quantum yields have been described in earlier reports[1,2,6].

Experiments with Solutions of I in 90% Hydrogen Peroxide

A stock solution containing 0.0438 gms. of I (3×10^{-3} M) in 90% H_2O_2 was prepared. At appropriate intervals of time, 0.10 ml. of this solution was injected into the magnetically stirred cuvette containing 2.9 ml. of a 45% (V/V) tertiary butanol solution in water. The decay of the 440 mμ band and a spectral distribution were recorded. The results are summarized in Table I and Figure III. For the experiments with inhibitor present 2.9 ml. of a 45% (V/V) aqueous tertiary butanol solution containing 1.0×10^{-2} M. 2,6-di-t-butyl-4-methylphenol was used as the diluent.

Reactions of I with Hydrogen Peroxide in Aqueous Buffer Solution of pH 4

A pH 4 buffer was prepared containing 1.7×10^{-1} M sodium acetate and 1.0 M acetic acid. Appropriate quantities of I were weighed into 25 ml. volumetric flasks so as to provide after dilution the concentrations reported in Table II. Aliquots of 30% H_2O_2 were added to the flask and the solution immediately diluted to 25 ml. with the buffer. After mixing, a 3 ml. portion was transfered to the cuvette and placed in the radiometer. Spectral and decay plots were recorded as described previously[2].

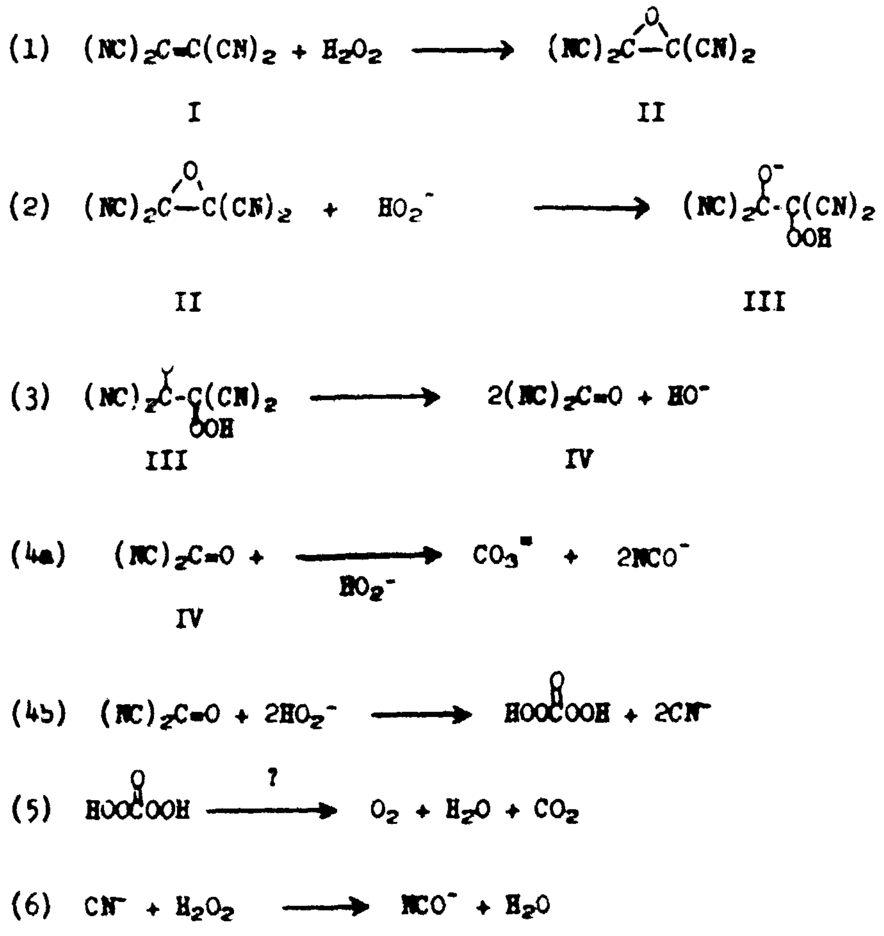
Figure I shows the effect of reabsorption upon the emitted light and Figure IV shows typical decay plots of the 475 mμ band with time. Table II summarizes the quantitative data obtained for this set of experiments.

SECTION I

PART D

Tetracyanoethylene Chemiluminescence

As described in the previous report[7], the reaction of tetracyanoethylene I with alkaline, anhydrous hydrogen peroxide in the presence of a fluorescer such as rubrene provides a moderately strong chemiluminescent emission. Cyanates, carbonates, and bicarbonates were identified as the principle products. It seemed possible that the chemiluminescent emission might be derived from one of the steps in the following sequence:



$$(1)\quad \underset{\text{I}}{(NC)_2C{=}C(CN)_2} + H_2O_2 \longrightarrow \underset{\text{II}}{(NC)_2\overset{O}{C{-}C}(CN)_2}$$

$$(2)\quad \underset{\text{II}}{(NC)_2\overset{O}{C{-}C}(CN)_2} + HO_2^- \longrightarrow \underset{\text{III}}{(NC)_2\overset{O^-}{C}{-}\underset{OOH}{C}(CN)_2}$$

$$(3)\quad \underset{\text{III}}{(NC)_2\overset{O^-}{C}{-}\underset{OOH}{C}(CN)_2} \longrightarrow 2\underset{\text{IV}}{(NC)_2C{=}O} + HO^-$$

$$(4a)\quad \underset{\text{IV}}{(NC)_2C{=}O} + \xrightarrow[HO_2^-]{} CO_3^{=} + 2NCO^-$$

$$(4b)\quad (NC)_2C{=}O + 2HO_2^- \longrightarrow HOO\overset{O}{C}OOH + 2CN^-$$

$$(5)\quad HOO\overset{O}{C}OOH \xrightarrow{?} O_2 + H_2O + CO_2$$

$$(6)\quad CN^- + H_2O_2 \longrightarrow NCO^- + H_2O$$

Thus the reaction of I with hydrogen peroxide is known to produce epoxide II under certain conditions[20]; and the reaction of II with the hydrogen peroxide anion to give hydroperoxide III is typical of epoxide-nucleophilic reactions[21]. Moreover, the decomposition of III to give carbonyl cyanide (IV) would be typical of concerted bond cleavage peroxide decomposition[7]. IV might then be oxidized by hydrogen peroxide directly to cyanate by a process probably involving concerted multiple bond cleavage[7] as in step 4a, or nucleophilic displacement by the hydrogen peroxide anion might occur as in step 4b. Step 5 is hypothetical but it is known that the reaction of phosgene with hydrogen peroxide in the presence of a fluorescer gives carbon dioxide, and is not chemiluminescent[4]. Cyanate would be an expected product in any case, since it is a known product of the reaction of cyanide ion with hydrogen peroxide[22].

Accordingly, the possible intermediates II, IV, and CN^- were each tested for chemiluminescence under the conditions where chemiluminescence was observed from I. In reactions with hydrogen peroxide and potassium *t*-butoxide or potassium hydroxide in 1,2-dimethoxyethane containing rubrene moderately strong chemiluminescence lasting approximately ten minutes was observed from both II and IV, but not from potassium cyanide. The chemiluminescent reactions were remarkably similar in intensity and lifetime to the analogous reaction with I.

The observed chemiluminescence from II and IV does not, of course, establish that chemiluminescence from I is derived by the process indicated above, since there is no evidence that the three chemiluminescent reactions do not proceed by independent mechanisms. However, the proposed mechanism is reasonable in terms of the known chemistry and the chemiluminescent results.

The chemiluminescent emission derived from the reaction of IV with hydrogen peroxide suggests that direct oxidation of IV (step 4a) occurs rather than displacement of cyanide by peroxide (step 4b). Step 4b is analogous to the reaction of phosgene with hydrogen peroxide, and the latter is not appreciably chemiluminescent in the presence of a fluorescer. The mechanism by which IV is oxidized by hydrogen peroxide, however, can only be speculative at present.

SECTION I - PART D

Experimental

Tetracyanoethylene oxide (II) was prepared by the method of Reiche and Dietrich[20].

Carbonyl cyanide (IV) was prepared using a modification of the method described by W. J. Linn[23]. A mixture of 7.2 g. (0.05 mole) of tetracyanoethylene oxide and 9.3 g. (0.05 mole) of diphenyl sulfide in 75 ml. of freshly distilled glyme was heated for three hours at 80°. The product, ca. 2 ml. of a yellow liquid, was distilled from the black reaction mixture at 27°/18 mm.

An aliquot of the product was characterized by treatment with dimethylaniline in acetic acid to provide the known derivative, bis(p-dimethylaminophenyl)dicyanomethane. The crystalline solid isolated from this reaction had an infrared spectrum consistent with that expected for the derivative and the m.p., 195-197°, was in agreement with the lit. m.p., 194-196°.[23]

Chemiluminescence Tests

Tetracyanoethylene oxide (II). - About 5 mg. of II were dissolved in 10 ml. of 1,2-dimethoxyethane containing a few mgs. of rubrene, and 5 mg. of potassium t-butoxide was added. The addition of several drops of 90% hydrogen peroxide produced a medium intensity light emission with a duration of about 10 minutes. Potassium hydroxide gave similar results.

Carbonyl Cyanide (IV). - One drop of carbonyl cyanide was added to 5 ml. of 1,2-dimethoxyethane containing a pellet of potassium hydroxide, a few mgs. of rubrene and several drops of 90% hydrogen peroxide. The yellow light produced had a medium intensity lasting for several minutes.

SECTION II

Exploratory Tests for Chemiluminescent Reactions

Tests established[7] for the screening of oxalic acid derivatives were used to evaluate a number of other compounds, selected primarily in terms of their availability, but also selected to establish new guide-lines for the design of chemiluminescent systems. The test results are compiled in Table I.

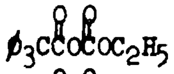
TABLE I

Exploratory Chemiluminescence Tests

	Chemiluminescence Tests[a]						
	A	B	C	D	E	F	G
1. Trichloroacetic acid		-	-		-	-	-
2. Trifluoroacetic acid		-	-		-	-	VW
3. Trifluoroacetic anhydride		-	-	-	-	-	-
4. Glycolic acid, calicium salt			-	-	-		
5. Chloral		-	VW	-	-	-	W
6. d-Tartaric acid	-	-	-	-	-	-	-
7. d-Mannose			-	-	-	-	-
8. Itaconic anhydride			-	-	-	-	-
9. Tetrahydroxysuccinic acid, disodium salt			-	-	-	-	-
10. Malonitrile			-	-	-	-	VW
11. Benzenehexol			-	-	-	-	-
12. 1,3-Dihydroxy-2-propanone			-	-	-	-	-
13. Methylaminomethyltartronic acid			-	-	-	-	-
14. Dimethyl acetylenedicarboxylate			-	-	-	-	-
15. Chloroacetylchloride			-	-	-	-	MW
16. Dichloroacetylchloride			-	-	-	-	MW
17. Cyclohexylphenylglycolic acid			-	-	-	-	-
18. Diketene			-	-	-	-	W

Table continued

TABLE I (continued)

	Chemiluminescence Tests						
	A	B	C	D	E	F	G
19.  $\phi_3C\overset{O}{C}O\overset{O}{C}OC_2H_5$						-	-
20.  $\phi_3C\overset{O}{C}O\overset{O}{C}OC\phi_3$						-	-
21. Lactic acid[b]						-	-
22. α-Hydroxy isobutyric acid[b]						-	-
23. dl-Mandelic acid[b]						-	-
24. Benzilic acid[b]						-	-
25. Benzilide						-	-
26. Ethylene oxide			-			-	-
27. Tetramethylethylene oxide						-	-
28. Octamethyloxamidimium chloride[b]						-	-
29. Tetraphenylethylene oxide[c]							-

FOOTNOTES FOR TABLE I

a) Tests:

A) Approximately 3-5 mg. of the compound to be tested is added to 5 ml. of a solution of about 1 mg. 9,10-diphenylanthracene (DPA) in paraffin (ESSO household wax) maintained at 160-170°C.

B) Approximately 3-5 mg. of the compound to be tested is added to 5 ml. of a solution of about 1 mg. DPA and ~5 mg. AIBN in paraffin maintained at 85-90° under argon atmosphere.

C) Approximately 3-5 mg. of the compound to be tested is added to 5 ml. of a solution of about 1 mg. DPA in 1,2-dimethoxyethane containing 5% water at 60-65°C. About 5 mg. Na_2O_2 is added immediately.

D) Approximately 3-5 mg. of the compound to be tested is added to 5 ml. of a solution of 1 mg. DPA and 0.2 ml. CH_3SO_3H in 1,2-dimethoxyethane containing 5% water and maintained at 60-65°C. About 0.5 ml. 30% H_2O_2 is added immediately.

E) Approximately 3-5 mg. of the compound to be tested is added to 5 ml. of a solution of 1 mg. DPA, and 5-10 mg. AIBN in diphenylmethane maintained at 85-90° under an oxygen atmosphere.

Footnotes continued

FOOTNOTES FOR TABLE I (continued)

F) Approximately 3-5 mg. of the compound to be tested is added to 5 ml. of a solution of about 1 mg. DPA and 0.2 ml. anhydrous H_2O_2 in anhydrous 1,2-dimethoxyethane maintained at 60-65°C.

G) Approximately 3-5 mg. of the compound to be tested is added to 5 ml. of a slurry of 1 mg. DPA, $\sim$0.2 g. KOH (1 pellet) and 0.2 ml. anhydrous H_2O_2 in anhydrous 1,2-dimethoxyethane maintained at 60-65°C.

Qualitative intensities are based on the oxalyl chloride, hydrogen peroxide reaction taken as strong (S). Other designations are M = medium; W = weak; VW = very weak, barely visible.

b) In an additional test, a solution of 10-15 mg. of the compound in 10 ml. 0.1 M K_2CO_3 containing 1-2 mg. of fluorescein was treated with 1 ml. of 30% H_2O_2 and 10 ml. of 6×10^{-2} M $K_2S_2O_8$. No chemiluminescence was observed.

c) In an additional test, a solution of 10 mg. of the compound in dimethyl sulfoxide containing 1-2 mg. rubrene was treated with 0.5 ml. of 50% aqueous potassium hydroxide and 2 ml. 30% hydrogen peroxide. No chemiluminescence was observed.

SECTION II

EXPERIMENTAL

Tetraphenylethylene Oxide (TPEO)

TPEO was prepared by the method of Schmidlen[24] as cited by Wang and Cohen[25], m.p. 205-6°, lit.[25], m.p., 204-5°.

Anal. Calcd. $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.25; H, 6.02.

Bistriphenylacetic Carbonic Anhydride - A slurry of 1.63 g. (0.005 moles) of potassium triphenylacetate in 50 ml. of 1:1 (V:V) benzene-glyme was prepared at 25° under argon, and then 0.25 g (0.0025 moles) of phosgene in 4 ml. of benzene was added slowly to the stirred slurry. The reaction mixture was stirred 2 hours at 25° under argon, then filtered to remove insoluble material. The reaction filtrate was evaporated to dryness under vacuum at 20-25° to obtain 1.2 g. of material, m.p. 179-192°, soften 134°, whose infrared spectrum is in agreement with that expected for the desired product.

α-Chloroacetylchloride - The procedure of Bickel[26] was used to obtain 10.9 g. (82%) of product, m.p. 48.5-50.0° (lit.[26] m.p. 50°).

Mixed Anhydride of Triphenylacetic Acid and Carbonic Acid, Monoethyl Ester - A solution of 2.9 g. (0.01 moles) of triphenylacetic acid and 0.8 g. (0.01 moles) of pyridine in 75 ml. of anhydrous ether was prepared. The stirred solution was cooled to 0° under argon, and then 1.1 g. (0.01 moles) of ethyl chlorocarbonate in 25 ml. of anhydrous ether was added dropwise during 15 mins. The reaction mixture was stirred 0.5 hours at 0°, then filtered to remove insoluble material. The reaction filtrate was evaporated to dryness under reduced pressure to obtain 1.5 g. (41%) of white solid product, whose infrared spectrum strongly indicated mostly the desired product together with small amounts of contaminants. The product of the reaction was found to be non-chemiluminescent, and further purification was not undertaken.

Other Materials - Benzilide[27], tetramethylethylene oxide[28], and octamethyloxamidinium dichloride[29], were prepared according to literature recipes.

SECTION III

Toxicity and Thermal Stability Data

As a guide to possible hazards in the use of chemiluminescent systems, data on toxicity and exothermic decomposition as measured by differential thermal analysis will be published as they are obtained.

When it is contemplated that systems of interest will be stored and used as dilute solutions, the hazards involved would be those of the solutions, not the pure chemiluminescent constituents. It is apparent, then, that toxicity or other hazards due to solvents should be considered, especially for storage in poorly ventilated spaces, or areas exposed to high temperatures.

For systems requiring non-aqueous solvents (i.e., the oxalyl derivatives) those solvents used in the experimental work were selected without regard to potential hazard. Since some latitude is available in the choice of solvent, it seems unlikely that solvent hazard need be a serious consideration. Two useful and relatively non-volatile solvents which have been used extensively in studying oxalyl derivatives show very low levels of acute oral toxicity. Acute oral LD_{50} in rats has been measured for dimethylphthalate (6.9 gms./kgm)[30] and ethylene glycol dimethylether (4.39 gms./kgm)[31].

Toxicity of chemiluminescent components is generally not known. However, the toxicity of 3-aminophthalhydrazide (luminol) was examined in the Environmental Health Laboratory of the American Cyanamid Company. As indicated in the attached report, the pure material has an

LD_{50} greater than 10 gms./kgm. Concentrated hydrogen peroxide (90%) is considered to have high acute local toxicity[31], although dilute aqueous solutions are used as a skin antiseptic. Its behavior in non-aqueous solutions is not known. Of the various oxalyl derivatives used in this program, only oxalyl chloride is well known. No literature information on oxalyl chloride could be found beyond the general observation that pure acid chlorides hydrolyze rapidly to the corresponding carboxylic acid and HCl and possess the toxicity of their components. Oxalyl chloride, however, hydrolyzes to CO, CO_2 and HCl rather than to oxalic acid and HCl. In concentrated form, oxalyl chloride should probably be considered highly toxic and is certainly very irritating; however, its behavior in dilute solutions as used in this program (10^{-2} M maximum) is unknown.

No information on exothermic decomposition is yet available.

SOP '46 REV. 4-64 [illegible] 4-64

TOXICITY DATA

ENVIRONMENTAL HEALTH LABORATORY

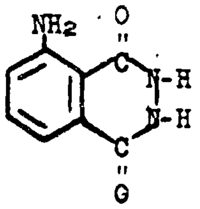
CENTRAL MEDICAL DEPARTMENT

CYANAMID

AMERICAN CYANAMID COMPANY
WAYNE, NEW JERSEY 07470

REPORT 64-96 **DATE** 17 Jul 1964 **PAGE** 367

PRODUCT 5-AMINO-2,3-DIHYDRO-1,4-PETHALAZINE DIONE; LUMINOL



EHL NO. 62-125 **CL NO.** 3825 **DISTRIBUTION** 63S1

SINGLE ORAL DOSE
BOOK 1 **PAGE** 830

SEX Male **SPECIES** Albino Rat (CF Nelson) **LD$_{50}$** Greater than 10 g/kg

CONDITIONS Dosed with a 20% aqueous dispersion.

DOSAGE	ONSET OF (S) SIGNS, (D) DEATH, HOURS AND DAYS									DIED	MEAN WT.		TIME OF (R) RECOVERY, DAYS						
	0-6	6-24	2	3	4	5	6	7	8-14	DOSED	I	T	1	2	3	4	5	6	7-14
1. 10.0 g/kg										0/5	77	152							
2. 5.0										0/5	104	194							
3.																			
4.																			

SIGNS OF INTOXICATION None observed.

GROSS AUTOPSY Normal.

SINGLE PARENTERAL DOSE
BOOK **PAGE**

SEX **SPECIES** **LD$_{50}$**

CONDITIONS

DOSAGE	ONSET OF (S) SIGNS, (D) DEATH, HOURS AND DAYS									DIED	MEAN WT.		TIME OF (R) RECOVERY, DAYS						
	0-6	6-24	2	3	4	5	6	7	8-14	DOSED	I	T	1	2	3	4	5	6	7-14
1.																			
2.																			
3.																			
4.																			

SIGNS OF INTOXICATION

GROSS AUTOPSY

SINGLE DERMAL DOSE
BOOK **PAGE**

SEX **SPECIES** **LD$_{50}$**

CONDITIONS

DOSAGE	ONSET OF (S) SIGNS, (D) DEATH, HOURS AND DAYS									DIED	MEAN WT.		TIME OF (R) RECOVERY, DAYS						
	0-6	6-24	2	3	4	5	6	7	8-14	DOSED	I	T	1	2	3	4	5	6	7-14
1.																			
2.																			
3.																			
4.																			

SIGNS OF INTOXICATION

SKIN IRRITATION

GROSS AUTOPSY

SINGLE INHALATION SEX SPECIES LC_{50}

BOOK PAGE CONDITIONS

CHAMBER CONCENTRATION	ONSET OF (S) SIGNS, (D) DEATH, MIN. AND HOURS										DIED DOSED	MEAN WT.		DAYS TO DEATH OR RECOVERY						
	0-15	15-30	30-60	2	3	4	5	6	7	8		I	T	0	1	2	3	4	5	6-14
1.																				
2.																				
3.																				
4.																				

SIGNS OF INTOXICATION

GROSS AUTOPSY

RABBIT SKIN IRRITATION

BOOK 5 PAGE 116

CONDITIONS 0.5 ml of a 5% solution of the compound applied under an impermeable patch.

REACTION	RABBIT NUMBER, VALUE						MEAN VALUE
	1	2	3	4	5	6	
RYTHEMA							
INTACT	0	0	0	0	0	0	0
INTACT	0	0	0	0	0	0	0
ABRADED	0	0	0	0	0	0	0
ABRADED	0	0	0	0	0	0	0
MA							
ACT	0	0	0	0	0	0	0
ACT	0	0	0	0	0	0	0
ABRADED	0	0	0	0	0	0	0
ABRADED	0	0	0	0	0	0	0

WAS STRUCTURE OF THE TISSUE AT THE SITE OF CONTACT DESTROYED OR CHANGED IRREVERSIBLY IN 24 HOURS OR LESS? YES ☐ NO ☑

THE SCORING SYSTEM USED HEREIN FOR SKIN AND EYE IRRITATION REACTIONS IS THAT OF DRAIZE, J. H., WOODWARD, G., AND CALVERY, H. O.: J. PHARMACOL. EXPTL. THERAP., 82:377, 1944. THE MAXIMUM POSSIBLE VALUE FOR A SKIN REACTION (EXCLUDING NECROSIS) IS 4. THE "PRIMARY IRRITATION SCORE" IS THE SUM OF THE MEAN VALUES DIVIDED BY 4. THE MAXIMUM POSSIBLE SCORES FOR EYE IRRITATION REACTIONS (AGAIN EXCLUDING NECROSIS) ARE: CORNEA, 80; IRIS, 10; CONJUNCTIVAE, 20.

PRIMARY IRRITATION SCORE ____________

RABBIT EYE IRRITATION

BOOK 19 PAGE 467

CONDITIONS Dosed with 0.1 ml of a 5% suspension in H_2O.

TIME, HOURS	STRUCTURE	RABIT NUMBER, VALUE						MEAN VALUE
		1	2	3	4	5	6	
24	CORNEA	0	0	0	0	0	0	0
	IRIS	0	0	0	0	0	0	0
	CONJUNCTIVAE	0	0	0	0	0	0	0
48	CORNEA	0	0	0	0	0	0	0
	IRIS	0	0	0	0	0	0	0
	CONJUNCTIVAE	0	0	0	0	0	0	0
72	CORNEA	0	0	0	0	0	0	0
	IRIS	0	0	0	0	0	0	0
	CONJUNCTIVAE	0	0	0	0	0	0	0

AT ANY OF THE READINGS MADE AT 24, 48 AND 72 HOURS, WAS THERE:

- DISCERNIBLE OPACITY OR ULCERATION OF THE CORNEA OTHER THAN A SLIGHT DULLING OF THE NORMAL LUSTER? YES ☐ NO ☑
- INFLAMMATION OF THE IRIS OTHER THAN SLIGHT DEEPENING OF THE FOLDS, OR SLIGHT CIRCUMCORNEAL INJECTION? YES ☐ NO ☑
- A DIFFUSE, DEEP-CRIMSON RED APPEARANCE OF THE CONJUNCTIVAE, WITH INDIVIDUAL VESSELS NOT EASILY DISCERNIBLE? YES ☐ NO ☑
- AN OBVIOUS SWELLING OF THE CONJUNCTIVAE, EXCLUDING CORNEA AND IRIS, WITH PARTIAL EVERSION OF THE LIDS? YES ☐ NO ☑

WAS THERE DESTRUCTION OR IRREVERSIBLE CHANGE OF ANY TISSUE IN 24 HRS. OR LESS? YES ☐ NO ☑

COMMENT

This compound is considered to be practically non-toxic by ingestion in single doses. It is not expected to present any significant hazards to health in ordinary industrial handling.

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. American Cyanamid Company, "Chemiluminescent Materials," Technical Report No. 4, Contract Nonr 4200(00).
5. American Cyanamid Company, "Chemiluminescent Materials," Technical Report No. 5, Contract Nonr 4200(00).
6. American Cyanamid Company, "Chemiluminescent Materials," Technical Report No. 6, Contract Nonr 4200(00).
7. American Cyanamid Company, "Chemiluminescent Materials," Technical Report No. 7, Contract Nonr 4200(00).
8. E. A. Chandross, Tetrahedron Letters, No. 12, 761 (1963).
9. W. Dasler and C. D. Bauer, Ind. Eng. Chem., 18, 52 (1946).
10. J. Mitchel and D. Smith, Aquametry, Interscience, New York, 1948.
11. H. Staudinger, Ber., 41, 3558 (1908).
12. F. D. Greene and G. Kazan, J. Org. Chem., 28, 2168 (1963).
13. I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, The MacMillan Co., New York, 1945, p. 630.
14. G. Wittig and R. W. Hoffman, Ber., 95, 2718 (1962).
15. C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, J. Am. Chem. Soc., 77, 3233 (1955).
16. W. R. Edwards and W. M. Henley, J. Am. Chem. Soc., 75, 3587 (1953).
17. C. D. Hurd and M. F. Dull, J. Am. Chem. Soc., 54, 3427 (1932).
18. J. W. Williams and C. D. Hurd, J. Org. Chem., 5, 122 (1940).
19. H. Staudinger, Ber., 38, 1735 (1905).
20. A. Reiche and P. Dietrich, Ber., 96, 3044 (1961).
21. R. E. Parker, Chem. Revs., 59, 737 (1959).

22. O. Masson, J. Chem. Soc., 91, 1449 (1907).

23. W. J. Linn, U. S. Pat. 3,115,517.

24. J. Schmidlen, Ber., 43, 1157 (1910).

25. C. H. Wang and S. G. Cohen, J. Org. Chem., 26, 3301 (1961).

26. H. Bickel, Ber., 22, 1537 (1989).

27. R. T. Arnold, W. E. Parham, and R. M. Dodson, J. Am. Chem. Soc., 71, 2439 (1949).

28. E. L. Eliel and M. N. Rerick, J. Am. Chem. Soc., 82, 1362 (1960).

29. W. H. Urry and J. Sheeto, Paper presented at "Symposium on Chemiluminescence" at U. S. Army Research Office, Durham, N. C., April 1, 1965. (Preprints, pg. 223).

30. Industrial Hygiene and Toxicology, F. A. Patty, Ed., Interscience Pub., New York, 1962.

31. Dangerous Properties of Industrial Materials, N. Irving Sax, Reinhold Pub. Co., New York, 1957.

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