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CHEMILUMINESCENT MATERIALS

AMERICAN CYANAMID COMPANY
CENTRAL RESEARCH DIVISION
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SUMMARY

Progress in determing mechanisms of processes fundamental to chemiluminescence is reported with particular reference to (1) studies of oxalyl peroxide chemiluminescence (2) studies of new, potentially useful, chemiluminescent reactions related to oxalyl peroxide decompositions, and (3) synthesis and exploratory studies of new potentially chemiluminescent systems.

Reaction rates and quantum yields were determined as a function of reactant concentrations for the oxalyl chloride, hydrogen peroxide, fluorescer chemiluminescent reaction with the three fluorescers 9,10-diphenylanthracene (DPA), perylene, and rubrene. Quantum yields increased with increasing fluorescer concentration and with increasing hydrogen peroxide concentrations. The relative abilities of the fluorescers to accept excitation energy in the reaction increases in the order DPA $<$ perylene $<$ rubrene. Experiments bearing on the effect of water on the reaction show that the reaction rate and quantum yield increase stantially as the water concentration increases up to a limiting value. Added ethanol also increases the rate but decreases the quantum yield. The mechanistic significance of these results is discussed.

A new chemiluminescent reaction was found in the decomposition of 9-hydroxy-9-carboperoxy-10-methylacridan, prepared in situ from 9-chlorocarbonyl-10-methylacridinium chloride and hydrogen peroxide. A quantum yield of about 1% has been obtained.

Other new chemiluminescent reactions are reported including reactions of mixed oxalic anhydrides with hydrogen peroxide, the reaction of oxalyl chloride with oxalic acid dihydrate, and the reactions of alkaline hydrogen peroxide with trichloroacetyl chloride and with tetracyanoethylene.

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].

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

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

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. Effects of Reactant Concentrations on Reaction Rates and Quantum Yields.

In previous reports[5,6] quantum yields and reaction rates have been reported for a number of oxalyl chloride, hydrogen peroxide, 9,10-diphenylanthracene (DPA) experiments, where the concentrations of reactants were varied over substantial ranges. The conclusions from this study were summarized in the last report[6], where we also reported difficulty in reproducing the absolute magnitude of the quantum yield and rate values. The major source of this difficulty now appears to be the purity of the ether used as solvent for the study. We find that adequate reproducibility can be achieved, however, by using reagent-grade ether, further purified by passage through a neutral alumina column.

A new set of quantum yield and rate data has been obtained for a series of chemiluminescent reactions with DPA. The results are summarized in Table I, and agree well with the results reported for the first experimental set[5].

Quantum yield and reaction rate data have also been determined for chemiluminescence experiments with the fluorescers perylene and rubrene at various fluorescer and hydrogen peroxide concentrations. The results are summarized in Tables II and III. The quantum yield results are qualitatively the same with these fluorescers as for experiments with DPA. Thus the quantum yield increases with increasing fluorescer concentration and with increasing hydrogen peroxide concentration.

Plots of quantum yield versus fluorescer or hydrogen peroxide concentrations are not linear but (as required on mathematical grounds) show that in each case a limiting quantum yield is approached at the higher concentrations. Alternatively, as was reported earlier for DPA[5], plots of the reciprocal of the quantum yield versus the reciprocal of the fluorescer concentration are linear (Figures 1 and 2). As in experiments with DPA[5], the slopes of the lines decrease with increasing hydrogen peroxide concentration.

The relative abilities of the three fluorescers to accept excitation energy in the reaction are shown graphically in Figure 3. It is seen qualitatively that rubrene is substantially better able than perylene to accept excitation energy and that perylene is a more efficient acceptor than DPA. This efficiency order is the same as the order of decreasing singlet excited state energy levels for the three fluorescers suggesting a possible correlation. The efficiency order is the reverse of the order of the fluorescent yields.

Attempts to determine the linearity of plots of the reciprocal of the quantum yield against the reciprocal of the hydrogen peroxide concentration are complicated by the decrease in hydrogen peroxide concentration during a reaction. At low ratios of hydrogen peroxide to oxalyl chloride an appreciable fraction of the hydrogen peroxide is consumed during the reaction so that the over-all quantum yield is not precisely related to the initial hydrogen peroxide concentration. This effect is illustrated by the right hand curve of Figure 4, where it is seen as expected that the greatest deviation from linearity occurs at the lowest hydrogen peroxide concentration. Results reported in the following section, as well as results reported earlier[5], indicate, however, that one equivalent of hydrogen peroxide is consumed rapidly in a reaction with oxalyl chloride which is essentially complete before the light emission process. If this is correct, the relevant hydrogen peroxide concentration for quantum yield correlation should be that concentration remaining following the rapid 1:1 reaction. The center line in Figure 4 shows the result of making this correction. Also shown for purposes of comparison is a plot showing a marked deviation from linearity, which was obtained assuming a rapid 2:1 hydrogen peroxide-oxalyl chloride reaction. Plots corrected for a rapid 1:1 reaction are shown for various fluorescer concentrations of the three fluorescers studied in Figures 5, 6, and 7.

The relationship of quantum yield to fluorescer and hydrogen peroxide concentrations shown in the Figures is that expected for a two-fold branched competitive process. The data is currently being analyzed by computer to permit its comparison with several possible mechanistic models.

TABLE I

Variation of Reaction Rate and Chemiluminescence Quantum Yield with Hydrogen Peroxide $[H_2O_2]$ and 9,10-diphenylanthracene (DPA) Concentrations in Ether Solutions[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		$[H_2O_2] = 1 \times 10^{-1}$ M		$[H_2O_2] = 2 \times 10^{-1}$ M	
	k^1 [b] ($\times 10^2$ sec.$^{-1}$)	Q.Y. [c] ($\times 10^3$)	k^1 [b] ($\times 10^2$ sec.$^{-1}$)	Q.Y. [c] ($\times 10^3$)	k^1 [b] ($\times 10^2$ sec.$^{-1}$)	Q.Y. [c] ($\times 10^3$)	k^1 [b] ($\times 10^2$ sec.$^{-1}$)	Q.Y. [c] ($\times 10^3$)	k^1 [b] ($\times 10^2$ sec.$^{-1}$)	Q.Y. [c] ($\times 10^3$)
0.33	1.38	0.018	1.78	0.042	2.09	0.135	3.07	0.260	[illegible]	0.53
0.67	1.42	[illegible]	1.58	0.072	2.08	0.256	3.14	0.500	7.61	[illegible]
1.33	[illegible]	0.047	1.48	0.123	1.84	0.470	3.10	0.924	7.36	1.65
[illegible]	1.52	[illegible]	1.78	0.389	2.10	1.09	2.97	2.26	5.97	4.17
[illegible]	[illegible]	0.174	1.70	0.478	1.98	1.40	[illegible]	3.32	7.78	6.35
[illegible]	1.62	0.23	1.99	0.53	2.08	2.00	3.04	4.14	5.92	[illegible]
[illegible]	[illegible]	0.37	1.55	0.88	1.98	2.36	2.79	5.27	5.47	[illegible]
[illegible][d]	[illegible]	[illegible]	1.46	0.74	2.00	3.09	3.52	6.09	7.76	11.1

a Reactions were run with [illegible] $\times 10^{-3}$ M oxalyl chloride in ether at 25°C.
b k^1 - pseudo first order rate constant.
c Q.Y. - quantum yield of chemiluminescence based on oxalyl chloride.
d DPA self-absorption occurs at this concentration; Quantum yields are uncorrected.

TABLE II

Variation of Reaction Rate and Chemiluminescence Quantum Yield with Hydrogen Peroxide $[H_2O_2]$ and Perylene Concentrations in Ether Solutions[a]

Perylene Concentration (x 10^{4} Molar)	$[H_2O_2] = 1.1 \times 10^{-2}$ M: K^1 (x 10^2 sec.$^{-1}$)[b]	$[H_2O_2] = 1.1 \times 10^{-2}$ M: Q.Y. (x 10^3)[c]	$[H_2O_2] = 2.2 \times 10^{-2}$ M: K^1 (x 10^2 sec.$^{-1}$)[b]	$[H_2O_2] = 2.2 \times 10^{-2}$ M: Q.Y. (x 10^3)[c]	$[H_2O_2] = 5.5 \times 10^{-2}$ M: K^1 (x 10^2 sec.$^{-1}$)[b]	$[H_2O_2] = 5.5 \times 10^{-2}$ M: Q.Y. (x 10^3)[c]	$[H_2O_2] = 1.08 \times 10^{-1}$ M: K^1 (x 10^2 sec.$^{-1}$)[b]	$[H_2O_2] = 1.08 \times 10^{-1}$ M: Q.Y. (x 10^3)[c]	$[H_2O_2] = 2.16 \times 10^{-1}$ M: K^1 (x 10^2 sec.$^{-1}$)[b]	$[H_2O_2] = 2.16 \times 10^{-1}$ M: Q.Y. (x 10^3)[c]
0.1	1.44	0.037	1.51	0.085	2.20	0.222	2.24	0.458	3.11	0.868
0.2	1.55	0.065	1.80	0.151	2.35	0.435	2.39	0.913	3.42	1.69
0.5	1.33	0.187	1.46	0.399	2.00	1.150	2.03	2.01	3.44	3.91
1.0	2.33	0.298	2.14	0.66	2.36	2.21	2.43	4.31	4.20	7.45
3.3	2.64	0.62	2.74	1.53	2.72	4.53	2.45	10.4	4.20	18.0
5.0[d]	2.41	0.75	2.33	1.82	2.62	5.30	2.53	12.5	4.33	21.9

a Reactions were run 2.40×10^{-3} M oxalyl chloride in ether at 25°C.
b K^1 = pseudo first order rate constant.
c Q.Y. = quantum yield of chemiluminescence based on oxalyl chloride.
d Perylene self-absorption occurs at this concentration; Quantum yields are uncorrected.

TABLE III

Variation of Reaction Rate and Chemiluminescence [Q.Y.] with Hydrogen Peroxide $[H_2O_2]$ and Rubrene Concentrations in Ether Solutions[b]

Rubrene Concentration (x $10^{?}$ Molar)	$[H_2O_2] = 1 \times 10^{-2}M$		$[H_2O_2] = 2 \times 10^{-2}M$		$[H_2O_2] = 5 \times 10^{-2}M$		$[H_2O_2] = 1 \times 10^{-1}M$		$[H_2O_2] = 2 \times 10^{-1}M$		$[H_2O_2] = 3.1 \times 10^{-1}M$[a]	
	K^1 (x 10^2 sec.$^{-1}$)[c]	Q.Y. (x 10^3)[d]	K^1 (x 10^2 sec.$^{-1}$)[c]	Q.Y. (x 10^3)[d]	K^1 (x 10^2 sec.$^{-1}$)[c]	Q.Y. (x 10^3)[d]	K^1 (x 10^2 sec.$^{-1}$)[c]	Q.Y. (x 10^3)[d]	K^1 (x 10^2 sec.$^{-1}$)[c]	Q.Y. (x 10^3)[d]	K^1 (x 10^2 sec.$^{-1}$)[c]	Q.Y. (x 10^3)[d]
[illegible].96	1.59	0.39	1.70	0.75	1.52	2.10	2.65	4.35	4.59	7.60	9.11	9.6
[illegible].17	1.23	0.7[illegible]	1.44	1.56	1.73	4.13	2.80	10.2	5.92	16.5	9.55	16.8
[illegible]	1.21	1.21	1.59	2.58	1.60	6.70	2.92	15.10	6.08	25.9	9.16	27.0
[illegible].74	1.09	1.40	1.61	3.29	2.06	8.90	2.76	18.0	4.93	30.[illegible]	9.28	35.0
10.0	1.53	1.71	1.79	3.52	2.02	9.70	3.18	25.4	5.97	41.1	10.0	47.6
25.[illegible][e]	3.22	1.23	2.92	3.07	2.73	9.30	3.38	23.8	6.2	42.6	—	—

a. Rubrene concentrations for this set were approx. 5% lower than those listed.
b. Reactions were run with 2.?2 x 10^{-3} M. oxalyl chloride in ether at 25°C.
c. K^1 pseudo first order rate constant.
d. Q.Y. = quantum yield at chemiluminescence based on oxalyl chloride.
e. Rubrene self absorption occurs at this concentration; Quantum yields are uncorrected.

FIGURE 1
RELATIONSHIP BETWEEN QUANTUM YIELD AND PERYLENE CONCENTRATION

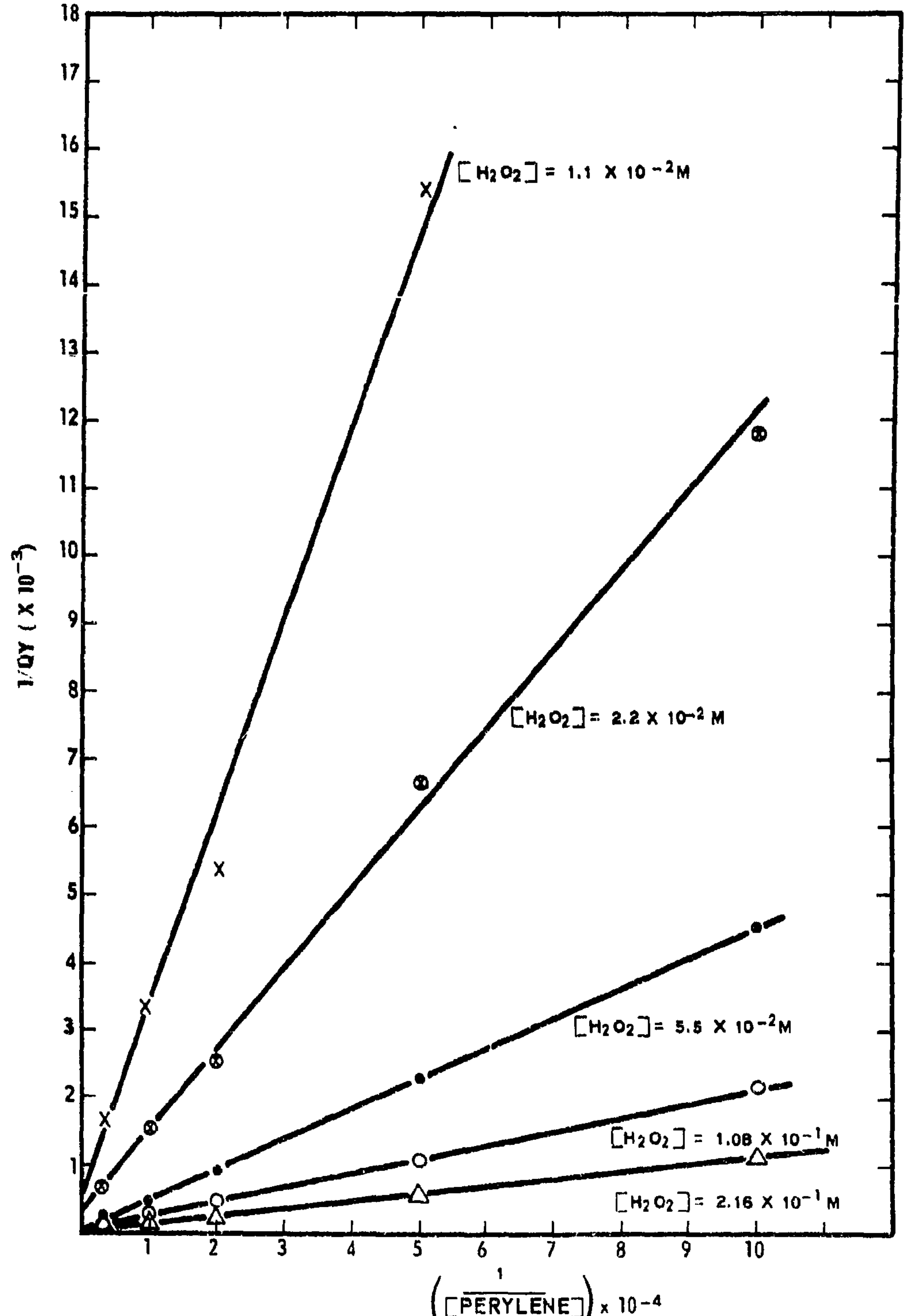


FIGURE 2
RELATIONSHIP BETWEEN QUANTUM YIELD AND RUBRENE CONCENTRATION

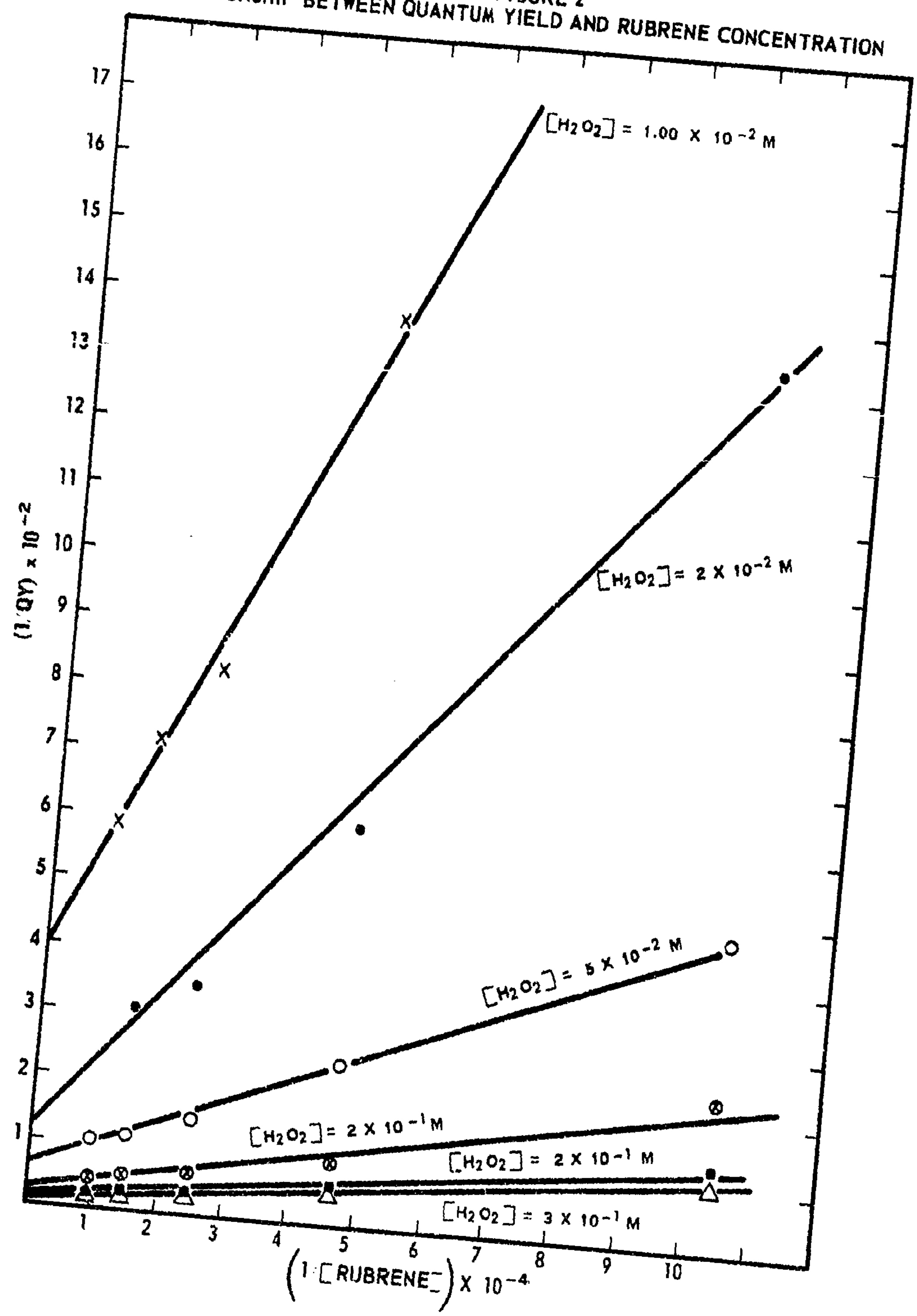


FIGURE 3

RELATIONSHIP BETWEEN QUANTUM YIELDS AND VARIOUS FLUORESCERS

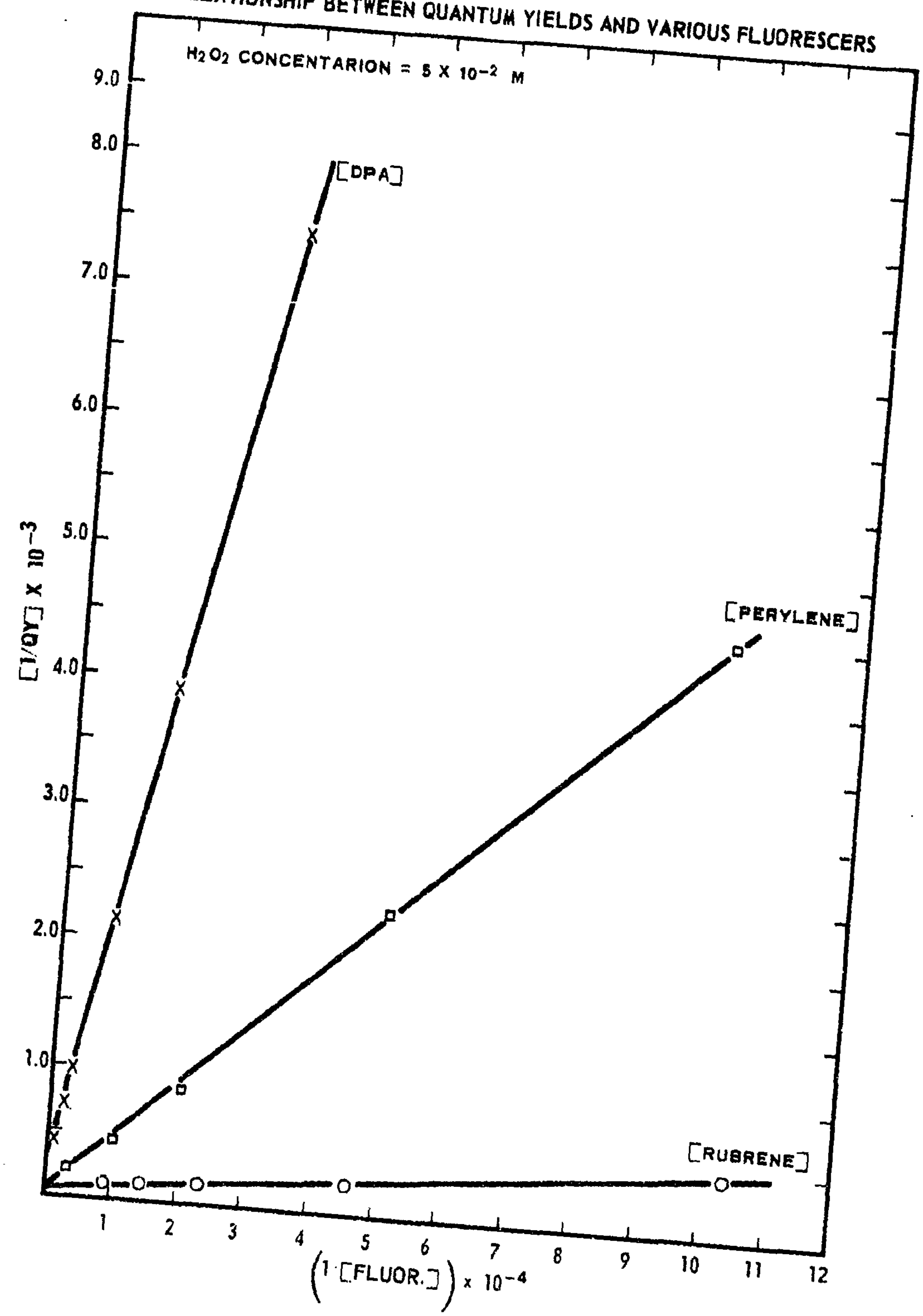


FIGURE 4

EFFECT OF CORRECTING INITIAL HYDROGEN PEROXIDE CONCENTRATION

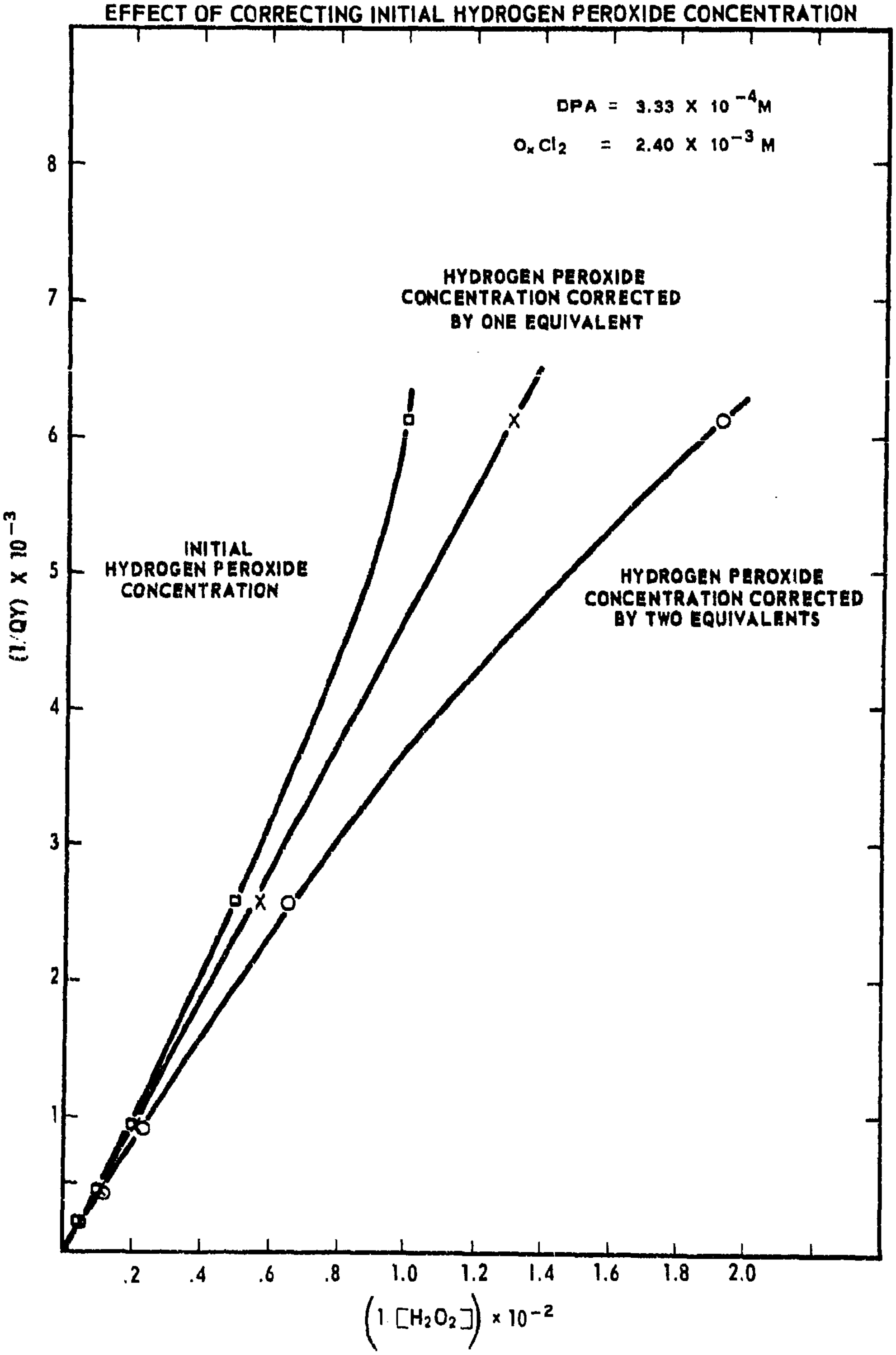


FIGURE 5

RELATIONSHIP BETWEEN QUANTUM YIELD AND H_2O_2 CONCENTRATION FOR DPA REACTIONS

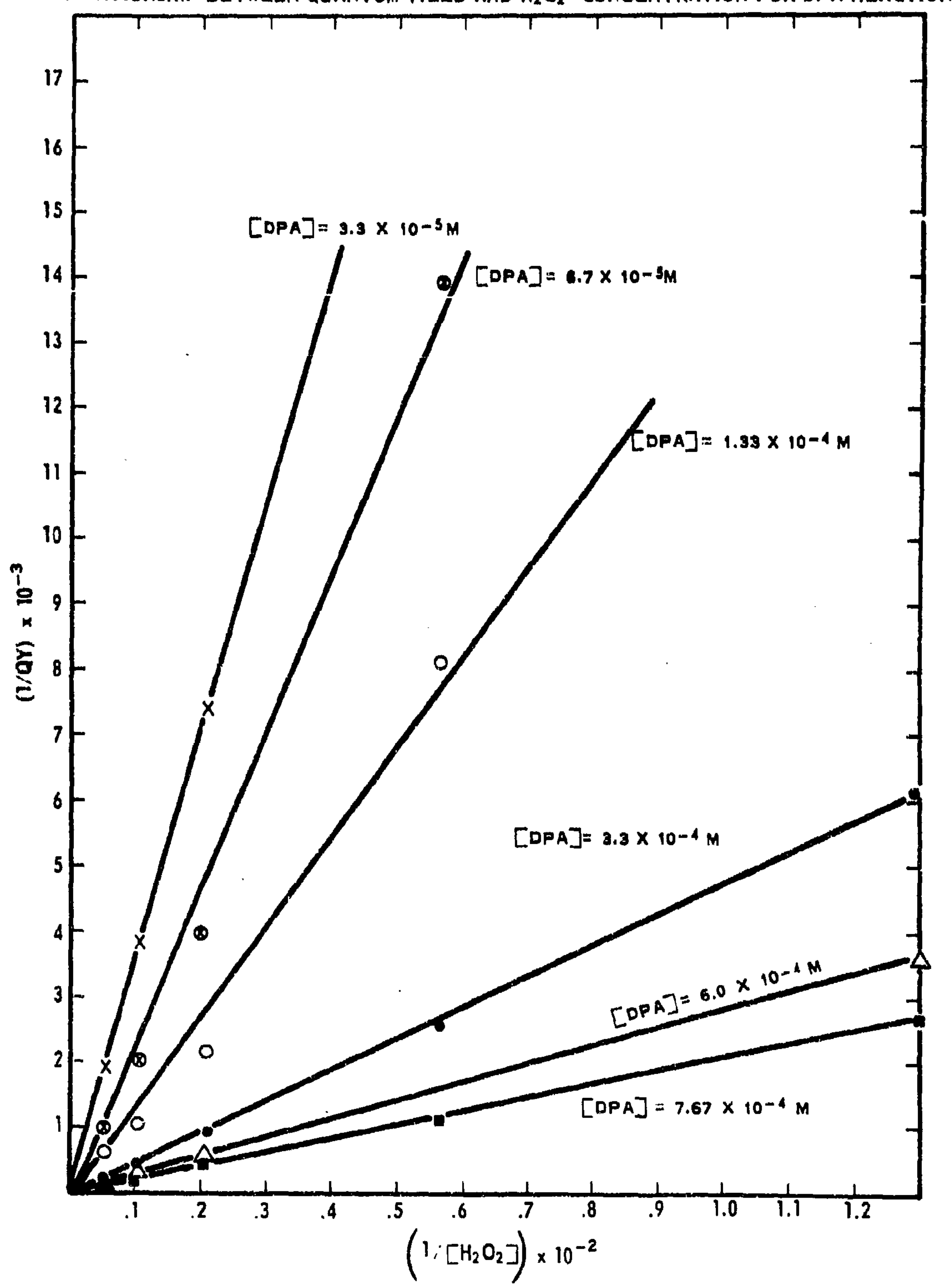


FIGURE 6

RELATIONSHIP BETWEEN QUANTUM YIELD AND H_2O_2 CONCENTRATION FOR PERYLENE EXPERIMENTS

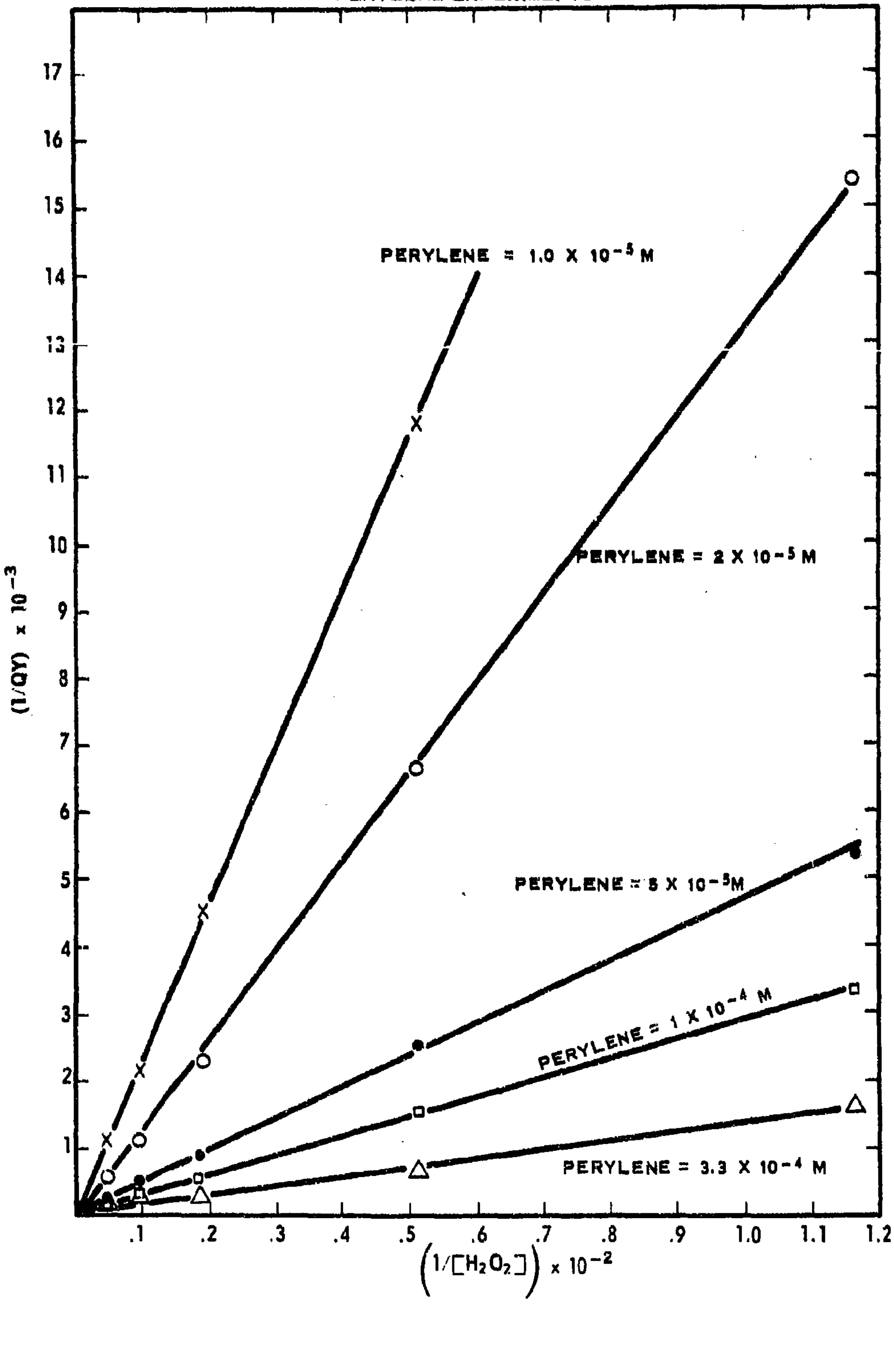
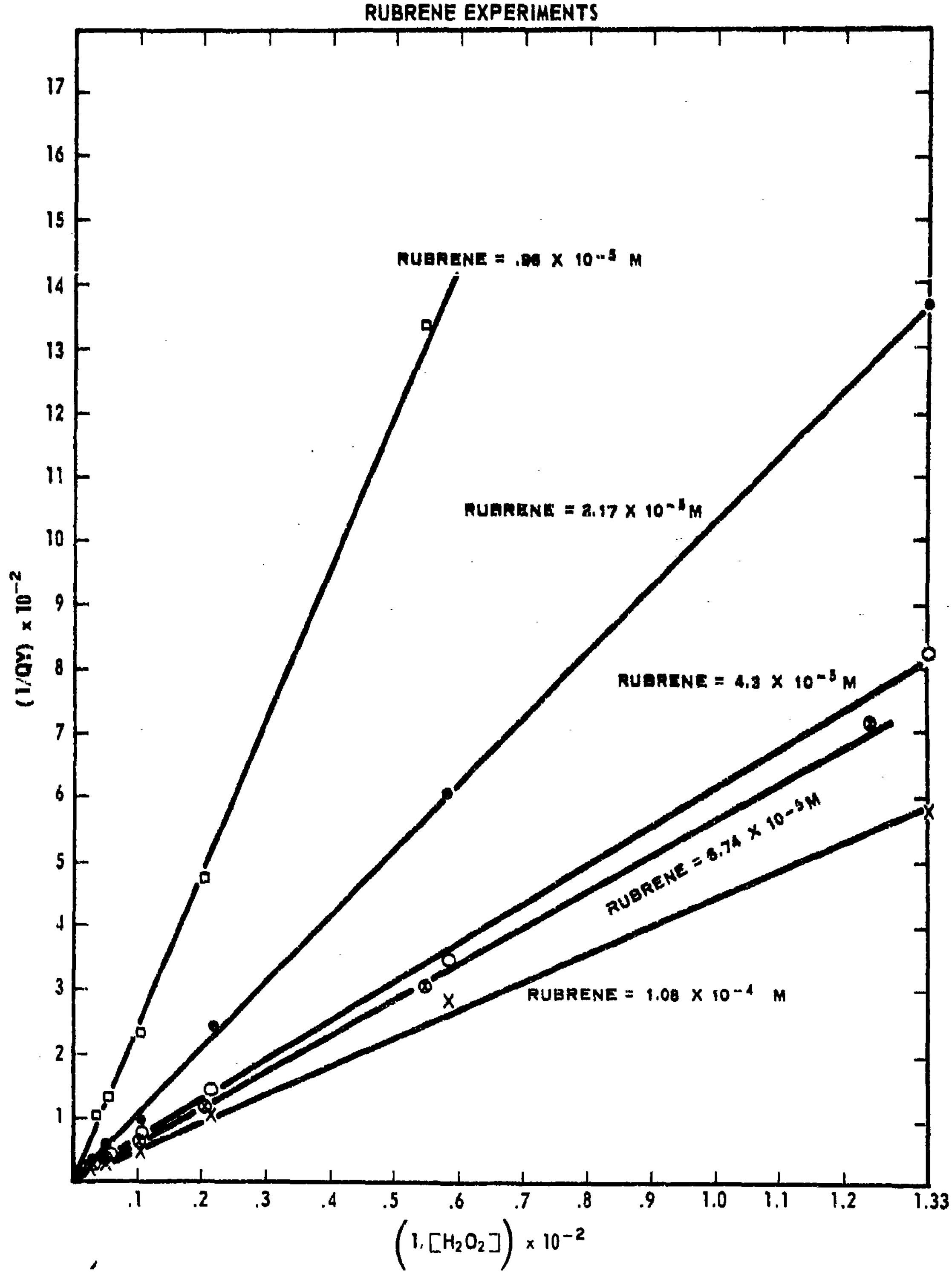


FIGURE 7

RELATIONSHIP BETWEEN QUANTUM YIELD AND H_2O_2 CONCENTRATION FOR RUBRENE EXPERIMENTS



The Effect of Water on the Reaction Rates and Quantum Yields.

The effect of water on the chemiluminescent reaction is shown in Table IV. As seen in the Table small concentrations of water have relatively little effect on the rate or quantum yield. At higher concentrations, however, the rate increases almost linearly with the water concentration, and the quantum yield increases to a maximum value at a water concentration near 0.033 molar under the conditions studied.

High water concentrations present at the start of the reaction might be expected to decrease the quantum yield by a direct non-chemiluminescent reaction between water and oxalyl chloride.[8]

$$\mathrm{Cl{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}Cl + H_2O \longrightarrow \underset{\underset{HCl}{+}}{Cl{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}OH} \xrightarrow{fast} HCl + CO + CO_2}$$

This effect evidently begins to appear at the highest water concentration investigated where the quantum yield begins to decrease. At intermediate water concentrations, however, the increase in quantum yield indicates that water is poorly able to compete with hydrogen peroxide for oxalyl chloride and that most of the oxalyl chloride reacts to form chloroperoxy-oxalic acid.

$$\mathrm{Cl{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}Cl + H_2O_2 \longrightarrow Cl{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}OOH + HCl} \tag{1}$$

This conclusion is consistent with the greater nucleophilic reactivity of hydrogen peroxide relative to water[9].

TABLE IV

The Effect of Water on the Reaction Rate and Chemiluminescence Quantum Yield for the Oxalyl Chloride-Hydrogen Peroxide-Fluorescer Reaction in Ether Solutions[a]

H_2O[b] Conc. ($\times 10^2$ Molar)	Pseudo First Order Rate Constant	Chemiluminescence Quantum Yield
--	2.24×10^{-2}	3.09×10^{-4}
0.167	2.30 "	2.91 "
0.333	2.47 "	3.46 "
1.67	3.82 "	5.08 "
2.5	5.25 "	5.33 "
3.33	6.02 "	6.23 "
5.0	11.10 "	6.09 "

a Reactant concentrations: 9,10-diphenylanthracene = 0.75×10^{-4} M; $[H_2O_2] = 0.82 \times 10^{-1}$ M; $[OxCl_2] = 2.35 \times 10^{-3}$ M.

b H_2O added and mixed with reactants prior to $OxCl_2$ injection.

The alternative possibility that chlorooxalic acid is formed from the reaction of oxalyl chloride with water and that it can react with hydrogen peroxide in a step leading to chemiluminescence is improbable under the conditions investigated. Since the reaction of water with chlorooxalic acid is unable to compete with the unimolecular decomposition of chlorooxalic acid[8], hydrogen peroxide could trap chlorooxalic acid only if it is substantially more reactive than water. While this greater reactivity of hydrogen peroxide is almost certainly real under the conditions studied, its acceptance leads to the same conclusion that water is also unable to compete with hydrogen peroxide in the first step and that chlorooxalic acid is not formed at low water concentrations.

Since reaction of water with oxalyl chloride would necessarily decrease the quantum yield, the action of water must occur at a later reaction step. Moreover, this later step would appear to be a rate determining process as indicated by the increase in reaction rate with increasing water concentration. Thus, reaction (1) is apparently not rate-determining and is substantially faster than the over-all reaction rate, a conclusion consistent with earlier results[5]. Confirmatory experiments are being carried out.

The effect of added water must also be reconciled with the observation that substantial light intensities are produced in the absence of added water. This latter result, however, does not necessarily indicate an alternative chemiluminescent pathway operating exclusive of water.

Low but finite water concentrations are probably present in any case in the hydrogen peroxide solutions. Moreover, water is a possible product of the oxalyl chloride-hydrogen peroxide reaction. Indeed the effect of added water on reaction rate and quantum yield is of the same character as the effect of added hydrogen peroxide. The possibility that increasing hydrogen peroxide acts to increase the quantum yield by increasing the steady state concentration of water is being investigated.

The effect of added water at various times after the start of a chemiluminescent reaction is shown in Table V. It is seen that under the conditions studied the ability of water to increase intensity, rate and quantum yield is independent of the time of water addition. This result indicates that the concentration of the key chemiluminescent intermediate decreases with time at the same rate as the intensity decays, and that the intensity is directly proportional to its concentration. A typical intensity decay plot showing the effect of added water is shown in Figure 8.

TABLE V

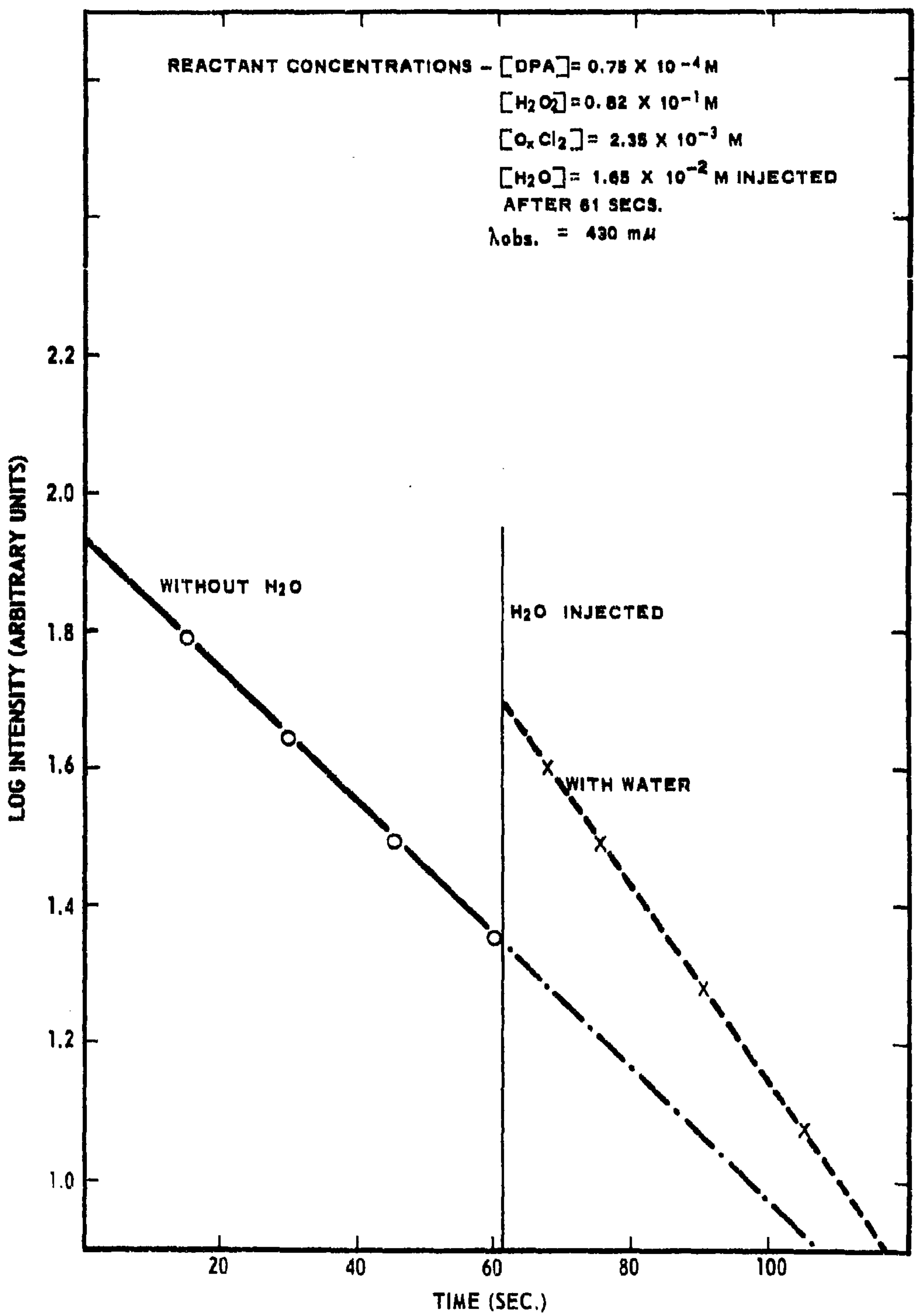
The Effect of Water Added at Various Reaction Times on the Decay Rate and Chemiluminescence Quantum Yields for the Oxalyl Chloride-Hydrogen Peroxide-Fluorescer Reaction in Ether Solutions[a]

H_2O	Time of H_2O Addition sec.	K^1 (sec.$^{-1}$)[d]		Relative Intensity at Time of Addition of H_2O		Quantum Yields[b]	
Moles Liter^{-1}	After reaction Start	Before H_2O Addition	After H_2O Addition	Before Addition	After Addition	without water	with water[c]
0	--	2.24×10^{-2}	--	2.39	--	3.09×10^{-4}	--
3.33×10^{-3}	0	--	2.47×10^{-2}	--	2.81	--	3.46×10^{-4}
3.33×10^{-3}	18	1.93×10^{-2}	2.10×10^{-2}	1.51	1.89	3.33×10^{-4}	3.80×10^{-4}
3.33×10^{-3}	70	2.05×10^{-2}	2.16×10^{-2}	0.49	0.60	3.03×10^{-4}	3.53×10^{-4}
1.67×10^{-2}	0	--	3.82×10^{-2}	--	6.41	--	5.08×10^{-4}
1.67×10^{-2}	20	2.21×10^{-2}	3.14×10^{-2}	1.44	3.27	3.09×10^{-4}	5.02×10^{-4}
1.67×10^{-2}	37	2.21×10^{-2}	3.09×10^{-2}	1.05	2.14	3.15×10^{-4}	4.92×10^{-4}
1.67×10^{-2}	61	2.18×10^{-2}	3.22×10^{-2}	0.66	1.45	3.48×10^{-4}	5.07×10^{-4}
1.67×10^{-2}	93	2.08×10^{-2}	2.90×10^{-2}	0.33	0.68	3.33×10^{-4}	4.93×10^{-4}

a Reactant Concentrations: DPA = 0.75×10^{-4} M; $[H_2O_2] = 8.2 \times 10^{-2}$ M; $[OxCl_2] = 2.35 \times 10^{-3}$ M.
b Based on oxalyl chloride concentration.
c These calculations are described in detail in the experimental section.
d K^1 = pseudo first order rate constant.

FIGURE 8

TYPICAL DECAY CURVE SHOWING THE EFFECT OF WATER ON THE CHEMILUMINESCENCE OF THE "$O_x Cl_2 - H_2O_2$ - FLOURESCER" REACTION



The Effect of Ethyl Alcohol on the Reaction Rate and Quantum Yield

The effect of added ethyl alcohol on the chemiluminescent reaction is shown in Tables VI and VII. It is seen that ethyl alcohol increases the reaction rate but decreases the quantum yield. The result indicates that alcohol reacts analogously with water with a key intermediate in the chemiluminescent reaction to produce a non-chemiluminescent product. The result is consistent with our earlier observation[3] that ethyl peroxyoxalate does not undergo chemiluminescent reaction under the conditions studied.

Effect of Free Radical Inhibitors and Organoperoxides

The effect of added tetralin hydroperoxide on the chemiluminescent reaction is shown in Table VIII. Even at concentrations equivalent to the hydrogen peroxide concentration no effect is detectable. Tetralin hydroperoxide and oxalyl chloride give very little chemiluminescence under these conditions in the absence of hydrogen peroxide.

The effect of the free radical inhibitor 2,6-di-*t*-butyl-4-methylphenol on the chemiluminescent reaction is also indicated in Table VIII. There is no observable effect on the reaction rate, but the quantum yield is drastically reduced. The decrease in quantum yield far exceeds the decrease in quantum yield produced by ethyl alcohol under comparable conditions. This comparison, as well as the absence of a rate effect, substantially eliminates the possibility that the phenol reduces the quantum yield by competing with water or hydrogen peroxide in an ionic process. The phenolic inhibitor was found to have little effect on the fluorescence quantum yield of DPA at the concentrations used showing that the reduction in chemiluminescence quantum yield did not result from fluorescence quenching. The absence of a rate effect indicates that the bulk of the reaction is not a free radical chain process. The decrease in quantum yield, however, suggests that the small fraction of the total reaction (0.5% with rubrene under the conditions studied) that generates light may be a free radical chain process. Additional experiments are planned.

Correction

In Technical Report No. 6[6] on pages 8 and 9, the legend along the left sides of the graphs should be corrected to read: 1/Q.Y. (x 10^{-4}).

TABLE VI

The Effect of Ethyl Alcohol on the Reaction Rate and Chemiluminescence Quantum Yield for the Oxalyl Chloride - Hydrogen Peroxide - Fluorescer Reaction in Ether Solution[a]

Ethyl Alcohol Concentration	Time at Which Ethyl Alcohol was Added	K^1 = Pseudo First Order Rate Constant	Chemiluminescence Yield[b]
--	--	2.11×10^{-2}	3.18×10^{-4}
3.3×10^{-2} M	before start of reaction	2.81×10^{-2}	2.30×10^{-4}
5.0×10^{-2} M	before start of reaction	3.04×10^{-2}	1.85×10^{-4}
6.67×10^{-2} M	before start of reaction	3.36×10^{-2}	1.60×10^{-4}

a Reactant Concentrations: $[DPA] = 0.75 \times 10^{-4}$ M; $[H_2O_2] = 0.82 \times 10^{-1}$ M; $[OxCl_2] = 2.35 \times 10^{-3}$ M.

b Based on oxalyl chloride concentration.

TABLE VII

The Effect of Ethyl Alcohol (added at Various Reaction Times) on the Decay Rate and Chemiluminescence Quantum Yields for the Oxalyl Chloride-Hydrogen Peroxide-Fluorescer Reaction in Ether Solutions[a]

Ethyl Alcohol Moles $Liter^{-1}$	Time of Ethyl Alcohol Addition Secs. after Reaction Start	K^1 ($sec.^{-1}$)[d] Before EtOH Addition	After EtOH Addition	Relative Intensity at Time of Ethanol Addition: Before Addition	After Addition	Quantum Yields[b] Without Water	With Water[c]
0	--	2.11×10^{-2}	--	2.22	--	3.18×10^{-4}	--
3.33×10^{-2}	0	--	2.81×10^{-2}	--	2.12	--	2.30×10^{-4}
3.33×10^{-2}	24	2.04×10^{-2}	2.61×10^{-2}	1.34	1.52	3.30×10^{-4}	2.89×10^{-4}
3.33×10^{-2}	57	2.13×10^{-2}	2.79×10^{-2}	0.66	0.75	3.15×10^{-4}	2.75×10^{-4}

a Reactant Concentrations: DPA = 0.75×10^{-4} M; $[H_2O_2] = 0.82 \times 10^{-1}$ M; $[OxCl_2] = 2.35 \times 10^{-3}$ M.
b Based on oxalyl chloride concentration.
c These calculations are described in detail in the experimental section [for H_2O effect].
d K^1 = pseudo first order rate constant.

TABLE VIII

The Effect of a Free Radical Inhibitor and Accelerators on the Oxalyl Chloride - Hydrogen Peroxide - Fluorescer Reaction in Ether Solutions

Fluorescer and Concentration	Additive	Concentration of Additive	Pseudo First Order Rate Constant	Chemiluminescence Yield[a]	Remarks
[DPA] = 5.3 x 10^{-4} M[b]	--	--	1.77 x 10^{-2}	2.74 x 10^{-3}	--
[DPA] = 5.3 x 10^{-4} M[b]	Tetralin Hydroperoxide	0.6 x 10^{-1} M.	1.31 x 10^{-2}	2.58 x 10^{-3}	(accelerator) initiator
[DPA] = 3.3 x 10^{-4} M[c]	--	--	2.02 x 10^{-2}	3.04 x 10^{-3}	--
[DPA] = 3.3 x 10^{-4} M[c]	2,6-ditertiary butyl-4-methylphenol	2.62 x 10^{-2} M.	2.58 x 10^{-2}	0.76 x 10^{-3}	inhibitor
[Rubrene]$_i$ = 0.7 x 10^{-4} M[d]	--	--	2.77 x 10^{-2}	5.5 x 10^{-3}	--
[Rubrene]$_i$ = 0.7 x 10^{-4} M[d]	2,6-ditertiary butyl-4-methylphenol	2.5 x 10^{-2} M.	2.33 x 10^{-2}	1.48 x 10^{-3}	inhibitor

a. Quantum Yield based on oxalyl chloride concentration.

b. $[H_2O_2]$ = 0.70 x 10^{-1} M, $[OxCl_2]$ = 2.35 x 10^{-3} M.

c. $[H_2O_2]$ = 0.75 x 10^{-1} M, $[OxCl_2]$ = 2.35 x 10^{-3} M.

d. $[H_2O_2]$ = 0.35 x 10^{-1} M, $[OxCl_2]$ = 1.73 x 10^{-3} M.

TABLE IX

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

Fluorescer Conc. Moles/Liter	H_2O_2 Conc. Moles/Liter	Oxalyl Chloride Conc. Moles/Liter	Half-life in Secs.	Chemiluminescence Quantum Yield	Initial Luminosity Lumens/ml.	Brightness Foot Lamberts for 1 cm. thickness	Initial Quantum* Emission Rate [Einsteins sec.$^{-1}$ ml.$^{-1}$]
Rubrene							
0.36×10^{-5}	1×10^{-2}	2.32×10^{-3}	49.3	0.39×10^{-3}	0.14×10^{-2}	0.18	0.13×10^{-10}
[illegible]$.3 \times 10^{-5}$	2×10^{-2}	2.22×10^{-3}	49.8	2.83×10^{-3}	0.97×10^{-2}	1.27	0.88×10^{-10}
6.7×10^{-5}	5×10^{-2}	2.32×10^{-3}	33.6	8.90×10^{-3}	4.67×10^{-2}	6.09	4.26×10^{-10}
$10.$[illegible]$ \times 10^{-5}$	3.1×10^{-1}	2.22×10^{-3}	6.9	47.6×10^{-3}	125.0×10^{-2}	163.7	1.06×10^{-9}
9,10-diphenylanthracene							
$.33 \times 10^{-4}$	1×10^{-2}	2.40×10^{-3}	36.9	0.18×10^{-4}	0.77×10^{-5}	0.001	$.81 \times 10^{-12}$
1.00×10^{-4}	5×10^{-2}	2.35×10^{-3}	37.7	4.70×10^{-4}	0.12×10^{-3}	0.016	2.03×10^{-11}
5.00×10^{-4}	1×10^{-1}	2.35×10^{-3}	19.9	3.32×10^{-3}	1.66×10^{-3}	0.216	2.71×10^{-10}
10.00×10^{-4}	2×10^{-1}	2.35×10^{-3}	8.9	11.1×10^{-3}	1.30×10^{-2}	1.69	2.02×10^{-9}
Perylene							
0.1×10^{-4}	1.1×10^{-2}	2.40×10^{-3}	48.1	0.37×10^{-4}	0.31×10^{-4}	0.004	1.28×10^{-12}
0.5×10^{-4}	2.2×10^{-2}	2.40×10^{-3}	47.4	3.99×10^{-4}	3.22×10^{-4}	0.042	1.40×10^{-11}
3.3×10^{-4}	1.08×10^{-2}	2.40×10^{-3}	28.3	10.40×10^{-3}	1.43×10^{-3}	1.86	6.12×10^{-10}
5.0×10^{-4}	2.16×10^{-2}	2.40×10^{-3}	16.0	21.90×10^{-3}	0.53×10^{-2}	6.97	2.27×10^{-9}

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

SECTION I

EXPERIMENTAL

Quantum yield and rate determinations for oxalyl chloride-hydrogen peroxide-fluorescer experiments were carried out as previously described[5]. Reactant solutions were prepared in reagent grade ether which had been passed through a 2.0 cm. x 33 cm. neutral alumina column.

New Technique for Handling Fast Reactions

It is necessary to thoroughly mix the reactants in any chemiluminescent system to produce homogeneous emission of light for quantitative measurement. We have until now mixed the solutions prior to placing them in the spectrometric apparatus, but this time consuming process prevented the recording of the first 8 seconds of the reaction. In very fast reactions this time can amount to one half-life or more and therefore the technique described below was developed for fast mixing of the reactants and recording of their emission from the start of the reaction. The ability to continue mixing throughout a run without interfering with the recording of the data is also useful where gas evolution occurs or where precipitates form.

The cell dimensions are 3 cm. diameter by 1 cm. thickness and it was found possible to use a micro-magnetic stirrer in conjunction with a stirrer-hot plate placed vertically behind the cell to get excellent mixing. The magnet kept the stirrer away from the front surface of the cell and thereby eliminated any interference to the measurements.

Experiments carried out by this technique have given essentially identical results to those obtained by the earlier method.

Effect of Water on the Oxalyl Chloride, Hydrogen Peroxide and Fluorescer Reaction in Ether Solutions

Two sets of reactions involving water were carried out: (1) where known, varying quantities of water were added prior to the addition of oxalyl chloride and (2) where a constant concentration of water was added at varying times after the start of the reaction.

The technique involved the use of the magnetic stirrer described above to enable rapid mixing where the water was added during the emission.

1. Appropriate aliquots of the stock solution of water in ether were pipetted into the cuvette after the aliquots containing DPA and H_2O_2 had been added. After mixing, the cuvette was placed in position and the magnetic stirrer started. Oxalyl chloride was injected and the data recorded. Table IV summarizes the results.

2. DPA and H_2O_2 solutions and ether were pipetted into the cuvette. The magnetic stirrer was started and, with the recorder running, oxalyl chloride was injected. After 20 seconds, an ethere. water solution was injected and the decay curve was completed. This experiment was repeated with identical concentrations with the water injection occurring at varying times. The results are summarized in Table V.

The quantum yield measurements headed "without water" in Table V were calculated in each experiment from the observed initial intensity and the observed pseudo first order rate constant obtained prior to water injection.

The quantum yield values in Table V for water addition were calculated from the following equation:

$$Q_W^t = \left(\frac{Q_W^{ob}}{Q^{ob}} \right) Q^t$$

where Q_W^t is the calculated overall quantum yield in the presence of water, Q^{ob} is the portion of the total quantum yield observed following the time of water addition but in the absence of water, Q_W^{ob} is the portion of the total quantum yield observed following actual water addition, and Q^t is the total quantum yield in the absence of water. This formula assumes that the quantum yield is directly proportional to the amount of a key chemiluminescent intermediate present at any given time. The constancy of the quantum yield values reported in Table V verifies this assumption.

SECTION II

STRUCTURAL CRITERIA FOR CHEMILUMINESCENT COMPOUNDS

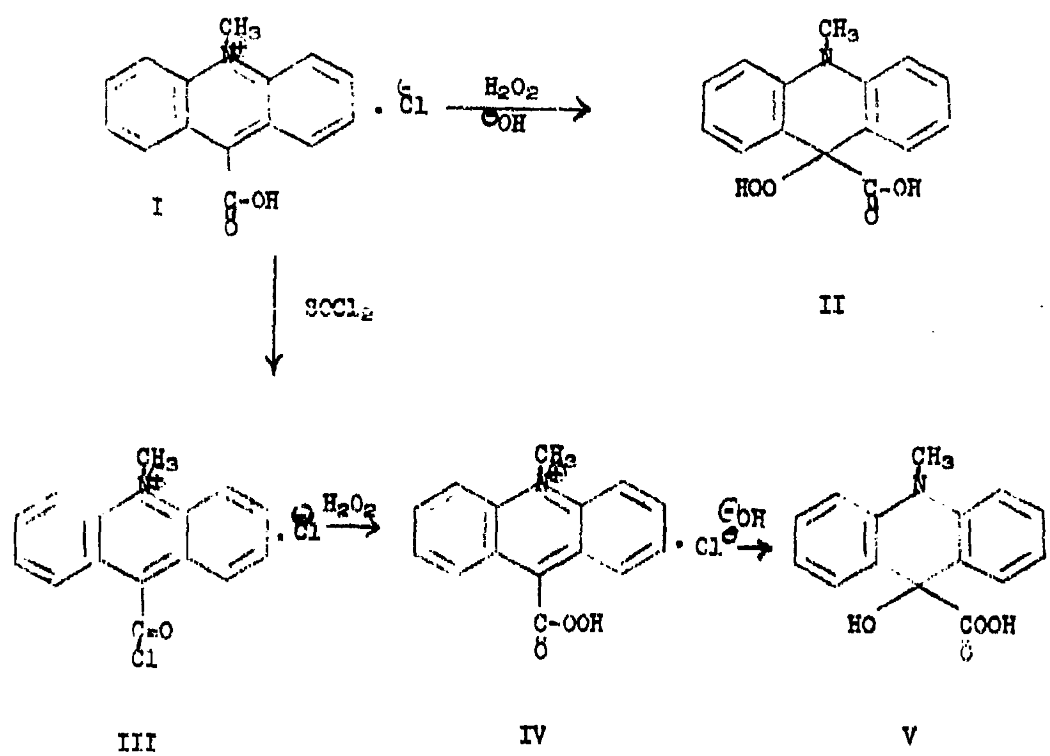
PART A

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[4,5] appreciable emission has been observed principally 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 intermediates[1]. Preceding reports[5] 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.

1. Peroxides Based on the Acridine System

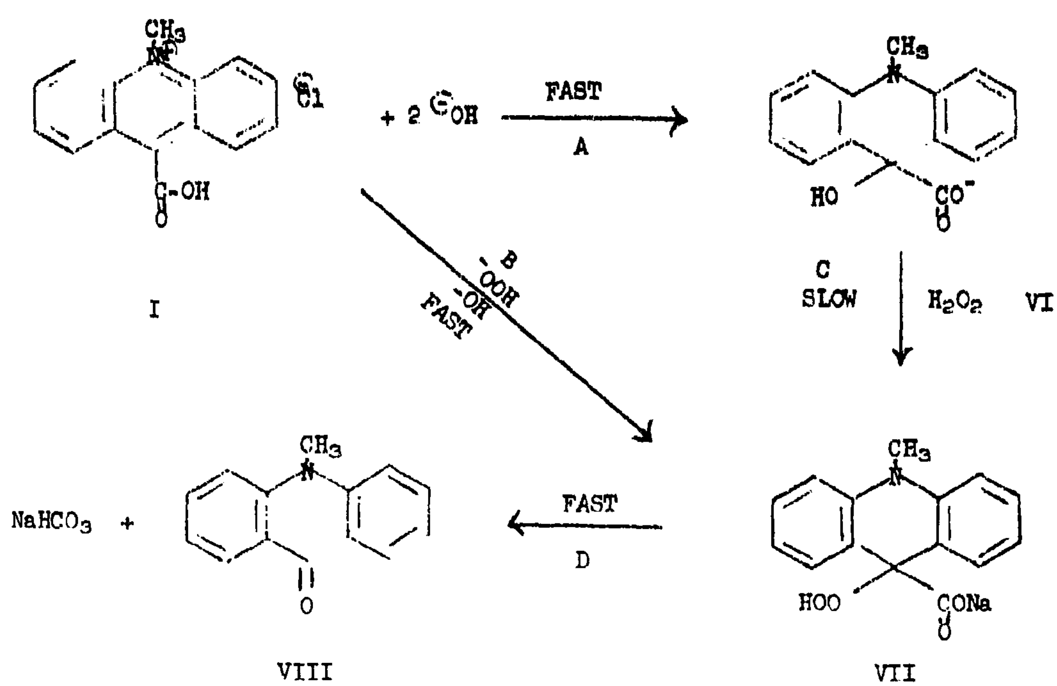
Previous reports[4,5,6] have described efforts to prepare 9-carboxy-10-methylacridinium chloride (I) and 9-chlorocarbonyl-10-methylacridinium chloride (III), wanted as precursors to 9-carboxy-9-hydroperoxy-10-methylacridan (II) and 9-carboperoxy-9-hydroxy-10-methylacridan (V). While the structures of peroxides II and V differ substantially it was considered possible that both might generate chemiluminescence on decomposition by a concerted multiple bond cleavage mechanism.



Preparation of I was described in the preceding report[6]. A satisfactory analysis has now been obtained. Reaction of I with thionyl chloride has now provided III in quantitative yield. We find that reaction of I with alkaline hydrogen peroxide is not chemiluminescent, but that reaction of III with aqueous hydrogen peroxide provides a moderately strong chemiluminescent emission. The chemistry of acridines I and III is now under investigation. The currently available information is summarized below.

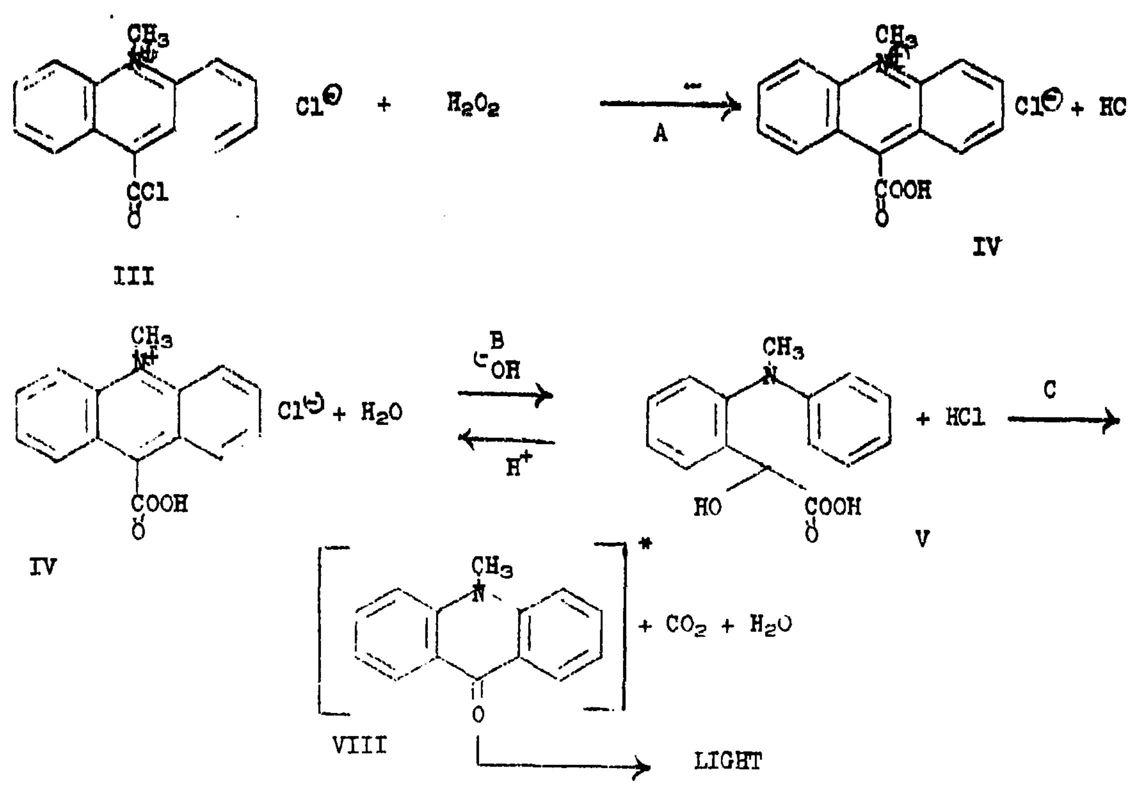
9-Carboxy-10-methylacridinium Chloride (I)

Acridinium salt I is readily soluble in water giving a yellow solution. Addition of dilute aqueous sodium hydroxide rapidly (30 seconds) decolorizes the solution indicating the formation of the pseudobase VI. Addition of aqueous hydrogen peroxide has no immediate effect, but after about 5 minutes, a yellow precipitate of 10-methylacridone (VIII) begins to appear. Alternatively, addition of dilute aqueous sodium hydroxide to an aqueous solution of I and hydrogen peroxide results in the immediate separation of VIII. Even at a pH of 5.2, reaction of I with hydrogen peroxide gives VIII quantitatively within a two hour period. Reactions A, B, and D are evidently fast while reaction C is relatively slow. Light emission from I was not observed in any of the experiments.



9-Chlorocarbonyl-10-methylacridinium Chloride (III)

Reaction of acridinium salt III with hydrogen peroxide in water or aqueous 1,2-dimethoxyethane provides chemiluminescent emission. The overall reaction is strongly pH dependent with the intensity of emission and the reaction rate increasing with increasing alkalinity. In solutions of pH 1-2 the intensity is weak, but lifetimes can exceed one hour; in solutions of pH 3-4 the intensity is medium to strong with lifetimes on the order of 10 to 20 minutes. In neutral or alkaline solutions the emission is seen as a bright flash. In very dilute, acid solutions, quantum yields near 1% have been obtained, but other preliminary results indicate that the efficiency decreases as the concentration of III increases. The results are consistent with the following processes.



Step A is evidently slow as indicated by a reaction of 0.16 molar III and 1.3 molar hydrogen peroxide in anhydrous 1,2-dimethoxyethane where the rate of disappearance of III was followed by infra-red analysis at 1780 and 1770 $cm.^{-1}$. About 20 minutes was required at room temperature for the concentration of III to decrease by one-half. (The kinetics were complicated by the appearance of a significant amount of water and by a change of pH as the reaction proceeded. A good first order plot was not obtained.) Step A, however, may proceed by an Sn1 mechanism, as does the hydrolysis of mesitoyl chloride[10], since added sodium chloride reduces the rate (and chemiluminescence intensity) while added sodium sulfate has little effect.[11]

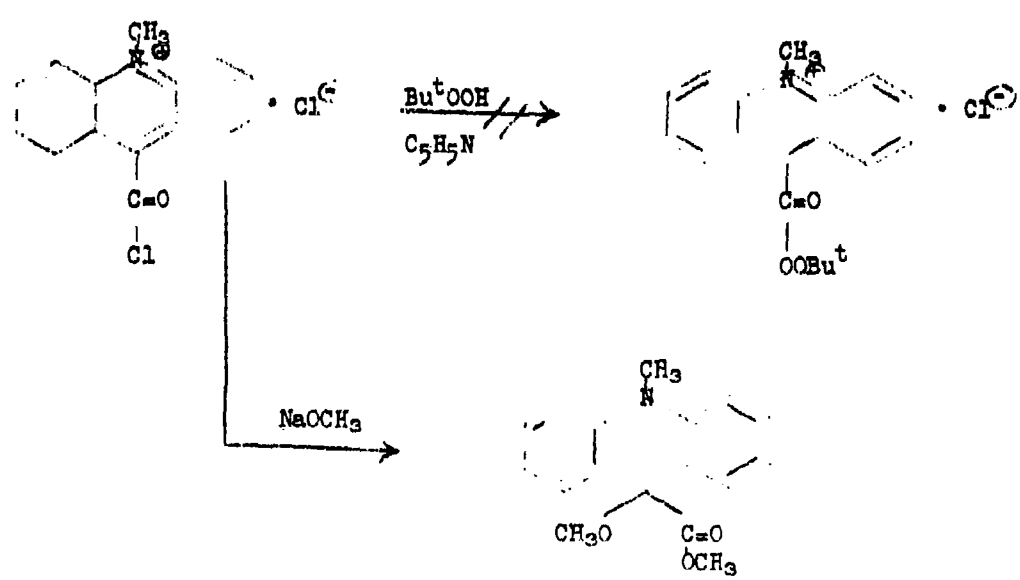
Equilibrium B is indicated by the following observations:

(a) Water (or hydroxide ion) is required for appreciable chemiluminescence. Moreover, solutions prepared from III and hydrogen peroxide in tetrahydrofuran or 1,2-dimethoxyethane can be stored up to several hours before generation of chemiluminescence by the addition of water.

(b) The overall reaction rate and chemiluminescence intensity is strongly pH dependent. A brightly glowing reaction at pH 3 in aqueous solutions can be essentially extinguished by the addition of dilute sulfuric acid. With the addition of base, chemiluminescence reappears.

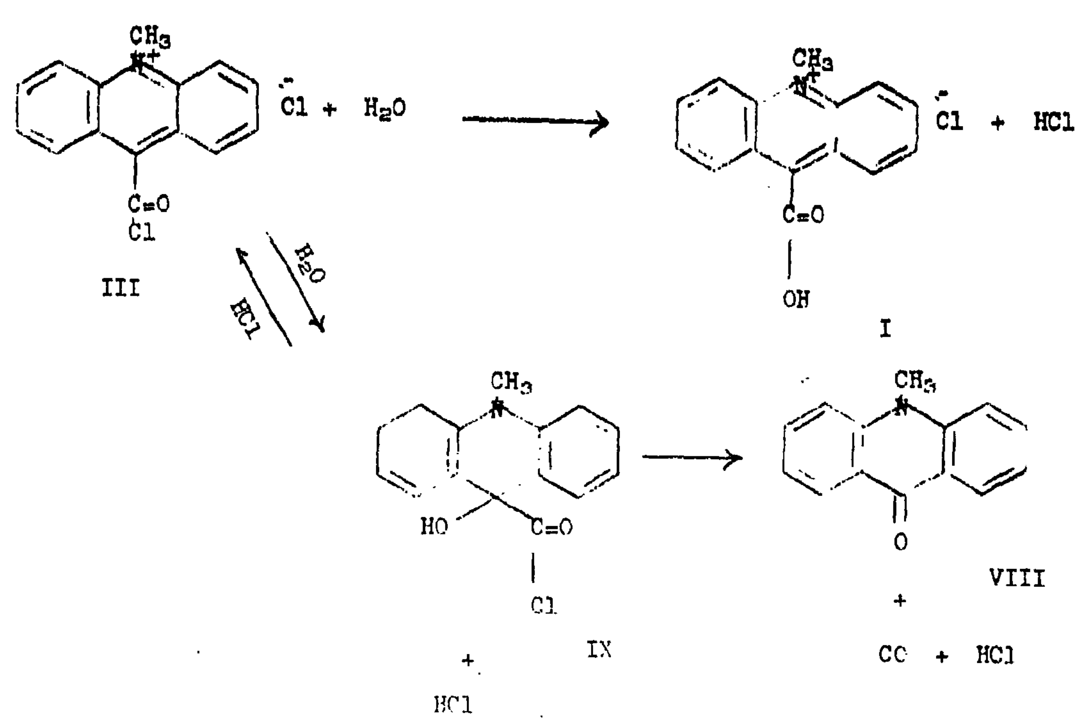
(c) Replacement of hydrogen peroxide with t-butylhydroperoxide does not interfere with chemiluminescent emission under alkaline conditions. Thus ionization of peracid IV is not required for chemiluminescence.

Step C is indicated by the formation of 10-methylacridone which has been obtained in 52% yield from the chemiluminescent reaction. Attempts to prepare stable analogs of IV and V have thus far been unsuccessful. Two attempts to prepare the t-butyl ester of IV gave only 10-methylacridone (VIII). An attempt to prepare the t-butyl ester of 9-carboperoxy-9-methoxy-10-methylacridone by combining III with t-butyl hydroperoxide followed, after 30 minutes, by reaction with sodium methoxide and methanol gave 9-carbomethoxy-9-methoxy-10-methylacridan in 55% yield.



In other chemiluminescence experiments it was found that a reasonably stable solid mixture of III and sodium perborate can be prepared and that this can be used to generate chemiluminescence on demand by addition to water. It was also found that a solution of III and 5 molar hydrogen peroxide in dimethylphthalate when combined with water generated chemiluminescence at the interface, and that extended lifetimes could be obtained depending on the degree of agitation.

Hydrolysis of III, like the reaction with hydrogen peroxide, occurs only slowly in acidic solutions. A solution of 2.8×10^{-2} molar III in water after standing one hour still generated strong emission on treatment with hydrogen peroxide. After 90 minutes the emission was weak. Moreover, hydrolysis does not proceed straightforwardly to acid I, but rather gives a mixture of I and 10-methylacridone (VIII) along with carbon monoxide.



Carbon monoxide has been obtained in 37% yield along with a 57% yield of VIII. Since I is stable (as the pseudobase VI) in alkaline solution, the formation of VIII and carbon monoxide from hydrolysis of III is best accounted for in terms of the intermediate pseudobase IX. Indeed, the formation of VIII from hydrolysis of III supports the concept of pseudobase V as an intermediate in the chemiluminescent reaction of III with aqueous peroxide.

The chemistry and chemiluminescent properties of III are being studied further.

9-Cyano-9-hydroxy-10-methylacridan. - In the previous report[6] we described isolation of a compound from reaction of 9-cyano-10-methylacridinium bisulfate with sodium hydroxide in ethanol, and, pending analysis, tentatively described the product as the expected hydroxy acridan. Analyses of the material, now in hand, make this assignment highly dubious. The structure of the material must, for the present, be considered unknown.

SECTION IIA

EXPERIMENTAL

10-Methylacridinium-9-carboxylate

The preparation of this compound was reported previously[6]. After drying the solid *in vacuo* for 72 hours at 100° in an Abderhalden pistol with KOH, an analysis was obtained for the zwitterionic form of the product.

Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90.

Found: C, 76.28; H, 4.79; N, 6.14.

Reactions of 9-Carboxy-10-methylacridinium Chloride with Hydrogen Peroxide

The compound does not produce light when treated with alkaline hydrogen peroxide. A yellow solution of 10 mg. of 9-carboxy-10-methylacridinium chloride in 1 ml. of 30% hydrogen peroxide was treated with 1 ml. of 5% sodium hydroxide. A yellow solid separated immediately, followed by extensive gas evolution. Water was added to facilitate centrifuging the mixture. The solid was collected, washed with water, and dried. An infrared spectrum identified the product as 10-methylacridone.

In a second experiment the yellow solution of 10 mg. of 9-carboxy-10-methylacridinium chloride in 1 ml. of water was treated with 1 ml. of 5% sodium hydroxide. After 10-20 seconds the solution became colorless. When there was no precipitate after 10 minutes, 2 ml. of 30% hydrogen peroxide were added to the solution. There was no chemiluminescence and no precipitate. After 5 minutes, a precipitate began to form and gas evolution was observed.

In a third experiment, a solution of 0.27 g. (1 millimole) of 9-carboxy-10-methylacridinium chloride in 100 ml. of a pH 5.2 potassium acid phthalate buffer containing ten weight per cent hydrogen peroxide was prepared. After standing 2 to 3 minutes a precipitate began to form. The reaction was allowed to continue for two hours after which time the precipitate was collected, dried and weighed to obtain: 0.19 g. (91%) of 10-methyl-9-acridanone as identified by comparison of its IR spectrum with that of an authentic sample.

9-Chlorocarbonyl-10-methylacridinium Chloride

In a 100 ml. flask, 5.0 g. (0.0183 mole) of 9-carboxy-10-methylacridinium chloride was refluxed with 30 ml. of thionyl chloride for a 6 hour period. The crude product was obtained by adding boiling hexane to the refluxing solution until the solution became cloudy. The yellow product precipitated rapidly on cooling. This yellow solid was then dissolved in 30 ml. of boiling thionyl chloride and again boiling hexane was added to the cloud point to precipitate the product. Infra-red spectral analysis indicated that the product at this stage was obtained as the $SO_2Cl^{\ominus}$ salt. The compound was therefore heated for 24 hours at 100°C in the Abderhalden drying pistol over KOH to yield the chloride salt.

Obtained 5.3 g. (100% based on starting acid)

Anal. Calcd. for $C_{15}H_{11}NOCl$: C, 61.66; H, 3.80; N, 4.80; Cl, 24.27.

Found: C, 62.14; H, 3.93; N, 4.66; Cl, 24.08.

The infra-red spectrum after drying was in agreement with the assigned structure.

Chemiluminescent Reactions of 9-Chlorocarbonyl-10-methylacridinium Chloride

A. Effect of Water Dilution - A solution of 0.1 g. of 9-chlorocarbonyl-10-methylacridinium chloride (III) in 10 ml. of 30% aqueous hydrogen peroxide emitted a weak green light. This solution was then diluted, in the dark, with tap water until the emission was estimated to be at its maximum. The maximum emission occurred after 3 liters of water had been added. Additional water decreased the intensity. During this dilution the color of the emission changed from green to blue, becoming a brilliant blue at the maximum.

B. Reaction with Solid Perhydrates - A mixture of 50 mg. of 9-chlorocarbonyl-10-methylacridinium chloride (III) and 50 mg. of sodium perborate (or sodium pyrophosphate peroxide) produced strong light emission when added to 1 liter of water.

C. pH Effect - A Beckman pH meter was used to study the course of the chemiluminescent reaction of 9-chlorocarbonyl-10-methylacridinium chloride, 30% aqueous hydrogen peroxide and water (tap and distilled).

1. The addition of about 0.05 g. of III to 5 ml. of 30% hydrogen peroxide dropped the pH to 1.9. Distilled water (pH 6.6) was added slowly to a maximum emission at pH 2.9. Excess water raised the pH to 3.4 but decreased the intensity. The addition of pH 6.86 buffer solution (prepared from Beckman Buffer #22331) brightened the emission to a new maximum at pH 5.3.

2. On the addition of about 0.05 g. of III to 5 ml. of 30% peroxide (pH 2.5) the pH fell to 1.5. Tap water, pH 7.4, was added until pH was 2.85. As the chemiluminescent reaction progressed, the pH dropped gradually, then steadied after 20 minutes at pH 2.45. Additional water brightened the emission to a maximum at pH 4.7. Excess water caused the light to fade at pH 5.1.

D. Effect of Acid on Reaction - A solution of about 0.05 g. of III in 5 ml. of 30% hydrogen peroxide was diluted with 25 ml. 0.1 N hydrochloric acid. There was no detectable light emission. The addition of 25 ml. 0.1 N sodium hydroxide gave a rapid, intense diffused emission.

A similar experiment using 0.001 N hydrochloric acid resulted in a weak emission of light. A pH 4.01 buffer solution then produced a steady bright emission. The addition of pH 6.86 buffer solution gave a very bright, relatively brief light.

The chemiluminescent reaction was also quenched by the addition of 6N sulfuric acid and revived with 50% sodium hydroxide.

E. Salt Effect - Three simultaneous chemiluminescent reactions were run by diluting a solution of 0.15 g. of 9-chlorocarbonyl-10-methylacridinium chloride (III) in 3 ml. of 30% hydrogen peroxide with 500 ml. of pH 4.01 buffer (prepared from Beckman Buffer #14054) solution. One of the buffer solutions also contained 29.2 g. (0.5 mole) of sodium chloride (ionic strength: 1 μ); the second buffer solution contained 47.3 g. (0.33 mole) sodium sulfate (ionic strength: 1 μ); the third solution contained only the buffer. The reaction with buffer alone was the brightest and longest. The sodium sulfate reaction was substantially brighter and longer lived than the sodium chloride.

F. Other Reactions - A solution of III in 5 M hydrogen peroxide-dimethylphthalate was allowed to stand for 30 minutes. Water was then added and light was observed at the interface.

The addition of methanol or tetrahydrofuran quenches the chemiluminescent reaction. Light emission recurs, however, when water is added to the darkened reaction.

Chemiluminescence Quantum Yield for the Reaction of 9-Chlorocarbonyl-10-methylacridinium Chloride (III) with Aqueous Hydrogen Peroxide. - A 2.00×10^{-4} molar solution of acridinium salt III was prepared by rapidly dissolving 0.00292 g. in 50.0 ml. of 0.86 molar aqueous hydrogen peroxide. A 3 ml. aliquot was transferred to the cuvette of the radiometer-fluorimeter[1,2]. The intensity decay rate, spectral distribution, and quantum yield were determined as previously described[2]: Q.Y. = 9.6×10^{-3}; half-life = 210 sec.; λ max. = 450 mμ.

G. Infra-red Analysis of Reaction of Hydrogen Peroxide and 9-Chlorocarbonyl-10-methylacridinium Chloride - A 5% (0.16 M) solution of 9-chlorocarbonyl-10-methylacridinium chloride was made by dissolving 70 mg. (0.25 mole) of the acridinium salt in 1.26 g. 1,2-dimethoxy ethane to which 10 drops of 98% hydrogen peroxide had been added. An aliquot was then used to fill a 0.09 mm. infra-red cell. A series of spectra were run in the region between 2000 cm.$^{-1}$ and 1600 cm.$^{-1}$, using reference cell containing the glyme/peroxide mixture. The data obtained is summarized in the following table.

Time	Absorption 1780 cm.$^{-1}$ [a]	Absorption 1700 cm.$^{-1}$ [a]	Absorption 1720 cm.$^{-1}$ [b]	% Acridinium Acid Chloride
0 min.	est. .75	est. .65		100
5	.67	.57	.06	89
10	.61	.51	.09	82
15	.57	.47	.15	76
25	.34	.28	~ 40	45-48
45	.07	.05	~60	9
60	.04	.03		5

a These bands were used to measure the disappearance of the 9-chlorocarbonyl-10-methylacridinium chloride.

b This band seems to be due to the acid derivative of the acridinium salt rather than a peracid. The formation of water during the reaction interfered with measurements of the appearance of N-methylacridone.

Reactions of 9-Chlorocarbonyl-10-methylacridinium Chloride (III) with t-Butyl Hydroperoxide and with Perlauric Acid - A mixture of 0.05 g. of III in 5 ml. of t-butyl hydroperoxide did not yield any observable light when diluted with water. A brief light emission was produced when 1 ml. of 20% sodium hydroxide was added. Further dilution with water produced a weak, steady emission. The addition of a few drops of 50% sodium hydroxide to this solution then yielded a bright, short-lived light.

The addition of about 0.05 g. of III to 10 ml. of a tetrahydrofuran solution of about 0.05 g. perlauric acid did not produce an observable light emission. The dilution of the mixture with water yielded a medium emission.

Attempted Preparation of the Tertiary Butyl Peroxy Ester of 9-Carboxy-10-methylacridinium Chloride. - Method A - A solution of 0.5 g. (1.71 millimoles) of 10-methyl-9-chlorocarbonyl acridinium chloride in 10 ml. of anhydrous tertiary butyl hydroperoxide was heated at 40°C and 50 mm. pressure for 30 minutes. The excess tertiary butyl hydroperoxide was then removed under reduced pressure provided by the oil pump. The solid residue was washed out of the reaction flask and onto a Buchner funnel with hexane, washed well with hexane, dried and weighed to obtain 0.35 g. (98%) of 10-methyl-9-acridanone, m.p. 198-200° (Lit. m.p. 201-203°C) also identified by comparing its infra-red spectrum with that of an authentic sample.

Method B - A solution of 0.135 g. (1.71 millimoles) of freshly distilled pyridine in 5 ml. of freshly distilled anhydrous glyme was added to 0.50 g. (1.71 millimoles) of 10-methyl-9-chlorocarbonyl acridinium chloride in 5 ml. of anhydrous tertiary butyl hydroperoxide in the dark. Only the weakest perceptible chemiluminescence was observed. The reaction was then stirred for 30 minutes at room temperature. The clear solution was separated from an oil which had settled out by decantation. This oil was identified as pyridine hydrochloride by comparison of its infra-red spectrum with that of an authentic sample. Addition of 50 ml. of hexane to the clear solution precipitated a solid which was collected, washed with hexane, then dried and weighed to obtain 0.34 g. (95%) of 10-methyl-9-acridanone as identified by comparison of its infra-red spectrum with that of an authentic sample.

Attempted Preparation of 9-Methoxy-9 Tertiary Butyl Peroxy Carbonyl-10-Methylacridan. - A solution of 0.5 g. (1.71 millimoles) of 9-chlorocarbonyl-10-methylacridinium chloride in 5 ml. of anhydrous tertiary butyl hydroperoxide containing 0.14 g. (1.71 millimoles) of freshly distilled pyridine was allowed to stand at room temperature for 30 minutes and then was decanted from the pyridine hydrochloride which had formed. Addition of 5.3 ml. (3.42 millimoles) of 0.65 N sodium methoxide in methanol produced a color change from orange to colorless. Removal of by-product sodium chloride by filtration and evaporation of the methanol solution gave an off-white solid which was crystallized from hexane to give 0.21 g. (55%) of 9-methoxy-9-methoxycarbonyl-10-methylacridan, m.p. 150-151°C. A second crystallization from hexane gave an analytical sample, m.p. 150-151°C.

Anal. Calcd. for $C_{17}H_{17}NO_3$: C, 72.06; H, 6.05; N, 4.94.

Found: C, 71.82; H, 6.12; N, 5.06.

The infra-red spectrum is in agreement with the assigned structure.

Hydrolysis of 9-Chlorocarbonyl-10-methylacridinium Chloride (III) - 1. Aliquots of a solution of 0.21 g. of III in 25 ml. of water were tested for chemiluminescent activity with hydrogen peroxide and water at intervals over a three hour period. The light emission was still bright after 90 minutes. After 120 minutes the emission was weaker. The chemiluminescent activity was completely gone after 180 minutes.

2. The products of the hydrolysis of III were determined by dissolving 0.4953 g. of III in 100 ml. of water. After twelve hours the precipitate was collected, dried, and weighed to obtain 0.2058 g. (57%) of 10-methylacridone, m.p. 201-203°. Lit. m.p. 201-203°. The infra-red spectrum was identical to that of an authentic sample.

The filtrate was evaporated to dryness, and the solid was dissolved in ethanol. Addition of ether caused the precipitation of 0.097 g. (20%) of 9-carboxy-10-methylacridinium chloride, identified by comparison of its infra-red spectrum with that of an authentic sample.

Carbon Monoxide from Reaction of 9-Chlorocarbonyl-9-methylacridinium Chloride (III) with water. - Evolved gas from reaction of 22 mg. of III with excess water was swept by nitrogen into a 200 ml. syringe until reaction was complete. The contents of the syringe were ejected into a Liston Becker Gas Analyzer Model 15 for carbon monoxide analysis. The yield of carbon monoxide was 34.8 mole % of the III charged.

In a second experiment 35 mg. of III was reacted with 1 N aqueous sodium hydroxide. The carbon monoxide yield was 32 mole %.

In both experiments, the CO yield is probably too low. It was observed that some of the evolved gas was trapped in a foam at the surface of the liquid phase.

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 of oxalyl chloride with hydrogen peroxide in the presence of a fluorescer (see Section I) has clearly implicated a peroxy-oxalic acid as a key intermediate. Indeed a number of peroxyoxalate derivatives have been found to provide chemiluminescence on decomposition[2,3,4,5,6]. To further expand our understanding of this general chemiluminescent process, we are continuing to study the structural requirements bearing on chemi-luminescent efficiency.

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.

The short lifetime of the oxalyl chloride-hydrogen peroxide-fluorescent compound reaction stems from the rapid reaction between oxalyl chloride and hydrogen peroxide as well as from the rapid decomposition rate of monoperoxyoxalic acid, the key chemiluminescent intermediate. A process which provides monoperoxyoxalic acid by a slow reaction would necessarily have a slow overall rate and a long lifetime.

A general reaction class which might provide slow and perhaps adjustable reaction rates leading in the presence of a fluorescer to long-lived chemiluminescence is shown in the following equation.

$$\underset{\text{I}}{\mathrm{A\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}B}} \xrightarrow{H_2O_2} \underset{\text{II}}{\mathrm{A\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOH}} \xrightarrow{H_2O} \mathrm{HO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOH}$$

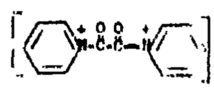
$$\underset{\text{I}}{\mathrm{A\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}B}} \xrightarrow{H_2O} \underset{\text{III}}{\mathrm{HO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}B}} \xrightarrow{H_2O_2} \mathrm{HO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOH}$$

Thus, in formula I the groups A and B might be selected so as to provide slow reactions with hydrogen peroxide and with water. The preparation of chemiluminescent compounds corresponding to formulae II and III is also a possibility.

A preliminary search for such reactions was described in the last report[6]. Recent exploratory experiments are summarized in Table I. Several oxalic anhydrides, Lewis base complexes, esters, amides, and oxalic acid itself were screened for chemiluminescence in the presence of a fluorescer under seven standard chemiluminescence test conditions. As indicated in the table, promising initial results were obtained from the anhydrides and Lewis base complexes studied as well as from diphenyloxalate. These results are discussed in more detail below. Aliphatic esters and oxalic amides were poorly reactive as expected. Weak chemiluminescence was observed when anhydrous oxalic acid or potassium oxalate was reacted

TABLE I

Oxalic Acid Derivatives Tested for Chemiluminescence

	TEST CONDITIONS (a)						
	A (Δ)	B ($R\cdot$)	C ($H_2O \cdot Na_2O_2$)	D ($H_3O^+ \cdot H_2O_2$)	E ($R\cdot + O_2 + \phi_2CH_2$)	F (H_2O_2)	G (Na_2O_2)
Anhydrides:							
$(C_6H_5)_3C-\overset{O}{C}-O-\overset{O}{C}-\overset{O}{C}-O-\overset{O}{C}-C(C_6H_5)_3$ (IV)	VW	W	MW	VS	VW	VS	VS
$C_6H_5-\overset{O}{C}-O-\overset{O}{C}-\overset{O}{C}-O-\overset{O}{C}-C_6H_5$ (V)	None	None	None	VW	VW	VW	M
Lewis base-oxalyl chloride complexes:							
 $2Cl^-$	W	S			VS	S	
$\left[(n\text{-}Bu)_3-\overset{+}{P}-\overset{O}{C}-\overset{O}{C}-\overset{+}{P}-(n\text{-}Bu)_3\right]$ $2Cl^-$						MS	
$\left[(C_6H_5)_3-\overset{+}{P}-\overset{O}{C}-\overset{O}{C}-Cl\right]$ Cl^-						MS	
Esters:							
$C_6H_5-O-\overset{O}{C}-\overset{O}{C}-O-C_6H_5$	None	None	W	VW	None	WM	MS
$C_6H_5-S-\overset{O}{C}-\overset{O}{C}-S-C_6H_5$	None	None	None	None	None	VW	W
$CH_3-O-\overset{O}{C}-\overset{O}{C}-O-CH_3$	None	None	None	None	None	None	None
$CH_3CH_2-O-\overset{O}{C}-\overset{O}{C}-O-CH_2-CH_3$	None	None	VW	None	None	None	VW
$(CH_3)_2CH-O-\overset{O}{C}-\overset{O}{C}-O-CH(CH_3)_2$	None	None	VW	None	None	None	W
$C_6H_5-\overset{O}{C}-\overset{O}{C}-O-CH_2-CH_3$	None	None	None	None	None	None	VW
$(C_6H_5)_2CH-O-\overset{O}{C}-\overset{O}{C}-O-CH-(C_6H_5)_2$	None	None	None	None	None	None	None
Amides:							
$H_2N-\overset{O}{C}-\overset{O}{C}-NH_2$	None	None	None	None	None	None	None
$H_2N-\overset{S}{C}-\overset{S}{C}-NH_2$	None	None	None	None	None	None	None
$C_6H_5-NH-\overset{O}{C}-\overset{O}{C}-NH-C_6H_5$	None	None	None	None	None	None	None
$HN-\overset{O}{C}-\overset{O}{C}-NH$ (ring closed by $\overset{}{C}=O$)	None	None	None	None	None	None	None
$H_2N-\overset{O}{C}-\overset{O}{C}-OH$	None	None	None	None	None	None	None
$H_2N-NH-\overset{O}{C}-\overset{O}{C}-NH-NH_2$	None	None	None	VW	None	None	None
Acid and Salts:							
$HO-\overset{O}{C}-\overset{O}{C}-OH$ (anhydrous)	None	None	None	None	None	None	[illegible]
$HO-\overset{O}{C}-\overset{O}{C}-OH \cdot 2H_2O$	None	None	None	None	None	None	None
$KO-\overset{O}{C}-\overset{O}{C}-OK$	None	None	None	None	None	None	VW
[illegible]	None	None		[illegible]	None	[illegible]	[illegible]

(See following page for footnotes.)

FOOTNOTES FOR TABLE I

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.

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, ~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.

with sodium peroxide in glyme (test G). This observation probably represents the detection of the following reaction.

$$\mathrm{K O\overset{O}{C}\overset{O}{C}O^-} + \mathrm{NaOO^-} \longrightarrow [\mathrm{KO\text{-}\overset{O}{\underset{}{C}}\text{-}\overset{O^-}{C}\text{-}OONa}] \longrightarrow \mathrm{{}^-O\overset{O}{C}\text{-}\overset{O}{C}OONa}$$

The known oxygen exchange of oxalic acid is believed to occur by a similar mechanism[12].

Anhydrides of Oxalic Acid

The two mixed anhydrides of oxalic acid prepared and tested so far show a large difference in chemiluminescence properties (Table I). Compound IV undergoes weak chemiluminescent reactions on thermal decomposition and in the presence of oxygen and a free radical initiator. Strong chemiluminescence is obtained in reactions with peroxides at various conditions. Benzoic oxalic anhydride (V) alternatively produces significantly weaker chemiluminescence and only in reactions with peroxides. The preparation of other oxalic anhydrides is in progress.

$$(\mathrm{C_6H_5})_3\mathrm{C\text{-}\overset{O}{C}\text{-}O\text{-}\overset{O}{C}\text{-}\overset{O}{C}\text{-}O\text{-}\overset{O}{C}\text{-}C}(\mathrm{C_6H_5})_3$$

IV

$$\mathrm{C_6H_5\overset{O}{C}O\text{-}\overset{O}{C}\text{-}\overset{O}{C}\text{-}O\overset{O}{C}C_6H_5}$$

V

The reaction of triphenylacetic acid oxalic acid anhydride IV with hydrogen peroxide produces a very bright chemiluminescent light for 20-30 minutes in the presence of either 9,10-diphenylanthracene or rubrene. Quantum yield measurements are in progress. The presence of water appears to be essential for chemiluminescence at least when traces of acid are present. Both acid and base catalysis improve the intensity of the emitted light.

Organic hydroperoxides and peroxycarboxylic acids as well as hydrogen peroxide give chemiluminescence on reaction with anhydride IV. Peroxides tested successfully include perbenzoic acid, benzoyl peroxide, perlauric acid and t-butylhydroperoxide. Di-t-butyl peroxide, as expected, failed to produce chemiluminescence.

A program is currently under way for the detailed study of the above reactions of triphenylacetic-oxalic anhydride IV and the accompanying chemiluminescence.

Lewis Base-Oxalyl Chloride Complexes

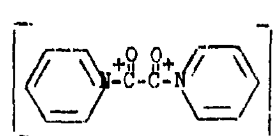
Various chemiluminescent reactions of the pyridine complex of oxalyl chloride have been reported earlier[6] including its thermochemiluminescence, oxygen promoted chemiluminescence and its chemiluminescent reaction with several peroxides. Reaction of the pyridine complex with hydrogen peroxide and a fluorescer provides a bright flash. Attempts to measure the quantum yield in 1,2-dimethoxyethane have failed because of the short lifetime. Other solvents like dimethylphthalate may slow down the reaction enough to permit the measurement.

To broaden the scope of the chemiluminescent reaction of the pyridine complex, attempts were made to prepare complexes of oxalyl chloride with other Lewis bases. Preparation of a 2:1 complex from tributylphosphine and a 1:1 complex from triphenylphosphine have been successful. Attempts to prepare and isolate pure complexes from triethylamine, hexamethylphosphoramide, and heptamethylisobiguanide have not been successful. The oxalyl chloride-phosphine complexes were found to provide chemiluminescence on reactions with a variety of peroxides (Table II), although only reactions with hydrogen peroxide have provided strong intensities. The reaction lifetimes are short.

TABLE II

Chemiluminescence of the Lewis Base-Oxalyl Chloride System

Order of Addition to Solvent	COMPLEX A: Petroleum ether	COMPLEX A: Glyme	COMPLEX B: Glyme	COMPLEX C: Petroleum ether	COMPLEX C: Glyme
1. Water 2. Complex	None				None
1. Anhydrous H_2O_2 2. Complex	S	S	MS	MS	MS
1. 90% H_2O_2 2. Complex	S	S	MS	MS	MS
1. Peroxybenzoic acid 2. Complex	None				
1. Benzoyl peroxide 2. Complex	None				
1. Peroxylauric acid 2. Complex	VW	VW	VW	W	VW
1. t-Butyl hydroperoxide 2. Complex	None	VW	VW	VW	None
1. di-t-Butyl peroxide 2. Complex	None		None		
1. Na_2O_2 2. Complex	VW	W	None	W	
1. Complex 2. Anhydrous H_2O_2	S				

Complex A:  $2Cl^-$

Complex B: $\left[(n\text{-Butyl})_3\overset{+}{P}-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{+}{P}(n\text{-Butyl})_3\right]\ 2Cl^-$

Complex C: $\left[\phi_3\overset{+}{P}-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Cl\right]\ Cl^-$

Note: Tests were carried out in the following manner. To 5 ml. of the test solvent containing 1 mg. 9,10-diphenylanthracene was added approximately 15 mg. peroxide and approximately 3 mg. of complex.

Esters of Oxalic Acid

As indicated in Table I, the chemiluminescence of the tested oxalic esters-hydrogen peroxide reactions is substantially weaker than that of the anhydrides or Lewis base complexes. Diphenyloxalate proved to be more strongly chemiluminescent than primary, secondary or tertiary alkyl oxalates. Therefore, the thiophenol ester of oxalic acid was prepared and was expected to yield the peroxyoxalic acid intermediate even more readily than diphenyloxalate. However, the chemiluminescence of the thio compound was proved to be inferior possibly because the produced thiophenol may act as a radical inhibitor for the decomposition of the peroxalate chemiluminescence intermediate.

Co-ordinated Oxalates

Although large percentages of water may be tolerated in certain cases, most of the oxalic acid based chemiluminescence systems function best in organic solvents. A possible way to achieve an aqueous system might be the use of water soluble co-ordinated oxalates. These oxalates are known to exchange oxygen-18 rapidly using both basic and acidic conditions[12], indicating the possibility that reaction with hydrogen peroxide might give monoperoxyoxalic acid and chemiluminescence.

Two co-ordinated oxalates were prepared: potassium trioxalato chromium trihydrate $(K_3Cr(C_2O_4)_3 \cdot 3H_2O$ and potassium trioxalato-aluminum trihydrate $K_3Al(C_2O_4)_3 \cdot 3H_2O$. Both of these compounds reacted with hydrogen peroxide in water, or aqueous glyme under acidic conditions and formed gaseous products, but chemiluminescence was not observed. The fluorescer in these experiments was a mixture of sodium fluorescein and 9,10-diphenylanthracene.

Polyoxalic Acid

To examine the possibility that polyoxalic acid might decompose by a concentrated multiple bond cleavage mechanism and thereby provide chemiluminescent emission in the presence of a fluorescer, several reactions were carried out between oxalic acid and oxalyl chloride.

$$\mathrm{Cl\overset{O}{C}\overset{O}{C}Cl + HO\overset{O}{C}\overset{O}{C}OH \longrightarrow H\{O\overset{O}{C}\overset{O}{C}\}OH}$$

$$\mathrm{H\{O\overset{O}{C}\overset{O}{C}\}OH \xrightarrow{F} H_2O + CO_2 + CO + F^*}$$

When freshly sublimed anhydrous oxalic acid was reacted with oxalyl chloride in tetrahydrofuran in the presence of rubrene, a weak emission was observed. The use of oxalic acid dihydrate under the same conditions, however, produced a substantial chemiluminescent emission accompanied by extensive gas evolution. This increase in emission, accompanied by gas evolution, also occurred when water was added one minute after a tetrahydrofuran solution of anhydrous oxalic acid and oxalyl chloride were mixed. This brightened emission was not observed when 5 minutes elapsed between the initial mixing and the addition of water. A neat mixture of the two reactants showed no sign of reaction, even after heating to reflux, until tetrahydrofuran was added; whereon the acid dissolved and a substantial amount of gas was evolved.

This new chemiluminescent reaction between oxalyl chloride, oxalic acid, and water in the presence of a fluorescer is of substantial interest in that a peroxide is not involved. While the effect of water is not yet understood, the results are in preliminary agreement with the original concept of concentrated multiple bond cleavage decomposition of a polyoxalic acid. Additional studies are planned.

SECTION IIB

EXPERIMENTAL

Bistriphenylacetic acid oxalic acid anhydride

Triphenylacetic acid (2.889 g., 0.01 mole), and potassium hydroxide (0.6 g., 0.01 mole) were added to 300 ml. absolute ethyl alcohol in a 500 ml. one neck flask and dissolved by boiling. The solution was cooled, and concentrated to a volume of 30 ml. in vacuo. A white precipitate appeared and was filtered and dried in a nitrogen atmosphere to obtain 3.0 g. white potassium triphenylacetate. Three grams of the acetate was slurried in 100 ml. dry benzene in a 200 ml. round bottom flask. Approximately 50 ml. benzene was distilled and the condensate was checked to assure the complete removal of water from the system. The remaining slurry was cooled to room temperature under an argon atmosphere. Oxalyl chloride (1.48 ml., 0.015 mole) was added and the mixture was stirred 15 minutes. The mixture was filtered to remove 0.9 g. solid, mostly potassium chloride (by IR), under an argon atmosphere using an oil pump. The filtrate was evaporated to dryness with the use of a vacuum pump. The white residue (1.9 g, 60% yield) was identified by infra-red analysis as the desired anhydride and was subjected to microanalysis after repeated washings with anhydrous ether. The material melted at 167-168°.

Anal. Calcd. for $C_{42}H_{30}O_6$: C, 79.98; H, 4.79; O, 15.22

Found: C, 78.55; H, 4.92; O, 15.37.

Dibenzoic-Oxalic Anhydride

Solid sodium benzoate (7.2 g, 0.05 mole) was added to a solution of 12.7 g. (0.1 mole) of oxalyl chloride in 100 ml. of anhydrous ethyl acetate during 45 minutes. The reaction was heated at 70-73°C for 3 hours and filtered to obtain 2.9 g. (100%) of NaCl. Evaporation of the filtrate gave a white solid which appeared to be a mixture by infra-red spectroscopy. The solid was extracted with boiling hexane to give a hexane insoluble solid which had an infra-red spectrum which was in agreement with that for the expected product. Benzoic acid, 2.0 g. (33%) (m.p. 119-121°; lit. m.p. 122°) was obtained from the hexane extract. The hexane insoluble material was crystallized from ethyl acetate-hexane to obtain 2.2 g. (30%) of material of m.p. 98-99°C.

Anal. Calcd. for $C_{16}H_{10}O_6$: C, 64.43; H, 3.38; O, 32.19.

Found: C, 64.19; H, 3.35; O, 32.38.

On dissolving a portion of the material in hot water gas was evolved and benzoic acid (m.p. 121-122°, lit. m.p. 122°) was deposited from the solution on cooling.

Diphenylmethyl oxalate

To a solution of 1.84 g. (0.01 mole) diphenyl carbinol and 0.01 mole pyridine in 200 ml. freshly distilled 1,2-dimethoxyethane in a 300 ml. round bottom flask, 0.46 ml. (0.005 mole) oxayl chloride was added while the solution was strongly agitated. After 20 minutes the precipitate was filtered and washed repeatedly with water and dried to obtain 1.7 g. (81% yield) of the product. The product was recrystallized from benzene to obtain material, m.p. 142-143°.

Dithiophenol ester of oxalic acid

A procedure identical to that above for diphenylmethyl oxalate was used to give an 80% yield of the desired product, m.p. 122-123°.

Anal. Calcd. for $C_{14}H_{10}S_2O_2$: C, 61.28; H, 3.68; S, 23.38; O, 11.66.

Found: C, 61.87; H, 3.90; S, 22.88; O, 11.12.

2:1 Tributylphosphine-Oxalyl chloride Complex. - A solution of 1.0 g. (0.005 moles) of tributylphosphine in 25 ml. dry petroleum ether was added during 10 minutes to a stirred solution of 0.3 g. (0.0025 moles) of oxalyl chloride in 25 ml. dry petroleum ether at 0° under argon. The reaction mixture was stirred 1/2 hour, then the solvent was removed under vacuum (without applying external heat) to obtain approximately 1.0 g. (77%) of yellow, semi-solid product whose infra-red spectrum is in agreement with that expected for the desired prodect.

1:1 Triphenylphosphine-Oxalyl chloride Complex. - A solution of 0.3 g. (0.0025 moles) of oxalyl chloride in 50 ml. dry petroleum ether was added during 15 minutes to a stirred solution of 1.3 g. (0.005 moles) of triphenylphosphine in 100 ml. dry petroleum ether at 0° under argon. The reaction mixture was stirred 1 hour, then the precipitated material was collected by filtration to obtain 0.7 g. (43.7%) of product, whose infra-red spectrum is in agreement with that expected for the 1:1 complex of triphenylphosphine and oxalyl chloride.

Attempted Synthesis of Oxalyl chloride Complexes. - Attempted preparations of complexes of oxalyl chloride with hexamethyl-phosphoramide, triethylamine, and heptamethylisobiguanide according to the general procedure above used for the preparation of the phosphine complexes did not yield products in any appreciable amount.

Potassium trisoxalatochromium trihydrate- and potassium trisoxalatoaluminum trihydrate- were prepared according to literature procedures.[12,13]

Oxalic Acid and Oxalic Chloride Reactions

1. The addition of 25 ml. of a 1M solution of oxalyl chloride in tetrahydrofuran to 25 ml. of 1M solution of anhydrous oxalic acid in tetrahydrofuran, in the presence of rubrene, produced a weak light emission.

2. This experiment was repeated using oxalic acid dihydrate instead of the anhydrous acid. A bright emission resulted followed by vigorous gas evolution. This experiment was repeated using 9,10-diphenylanthracene as the fluorescer with similar results.

3. Addition of sublimed anhydrous oxalic acid to pure oxalyl chloride produced no indication of reaction even after heating to reflux. The addition of tetrahydrofuran to the mixed caused the acid to dissolve. A substantial amount of gas was also evolved.

4. When 2.5 ml. aliquots of the 1M tetrahydrofuran solutions of anhydrous oxalic acid and oxalyl chloride were mixed in the presence of 9,10-diphenylanthracene a weak emission was observed. Within one minute of the initial mixing water was added, causing a rapid evolution of gas and a strong blue emission. This experiment was repeated with a 5 minute lapse between mixing and water dilution. There was no second, brighter emission.

Phenyl Oxalate

A solution of 25.4 g. (0.2 mole) of oxalyl chloride in 50 ml. of ether was added during 30 minutes to a solution of 37.6 g. (0.4 mole) of phenol in 200 ml. of ether containing 60 ml. (0.44 mole) of triethyl amine. After standing overnight, the reaction mixture was filtered. The collected solid was washed thoroughly with water and dried over P_2O_5 under reduced pressure to obtain 25.6 g. (53%) of phenyl oxalate, m.p. 133-134° (Lit m.p. 134°).

SECTION II

PART C

Exploratory Tests for New Chemiluminescent Reactions

The chemiluminescence tests originally established for the screening of oxalic acid derivatives were used to evaluate other readily available compounds. Over sixty per cent of the compounds selected for test have provided visible chemiluminescence. The results are summarized in Table I. Two new systems were found to provide high enough intensities and long enough lifetimes to justify further study.

Tetracyanoethylene (TCNE) Chemiluminescence

A moderately strong long lived chemiluminescence is produced on mixing TCNE, anhydrous hydrogen peroxide and a strong base in presence of a fluorescer in glyme solution. Little is known about this reaction as yet. The main products include cyanates, carbonates and bicarbonates, and small amounts of cyanide.

Chemiluminescent light is emitted by any order of mixing of the reagents. Either 9,10-diphenylanthracene or rubrene may be used as a fluorescer. The intensity of the chemiluminescent light increases with time to a maximum in about 5-7 minutes and diminishes slowly afterward.

Trichloroacetyl Chloride Chemiluminescence

A medium strong chemiluminescent light is produced for 5-10 minutes on mixing trichloroacetyl chloride with anhydrous hydrogen peroxide in the presence of 9,10-diphenylanthracene in 1,2-dimethoxyethane. The chemiluminescence is significantly improved by the addition potassium hydroxide or potassium-*t*-butoxide. The reaction is presently being investigated.

TABLE I

Exploratory Chemiluminescence Testing

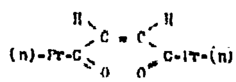
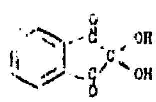
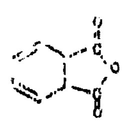
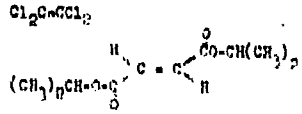
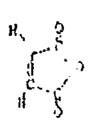
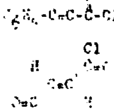
	Chemiluminescence Tests (a)						
	A	B	C	D	E	F	G
$(CN)_2C=C(CN)_2$	None	None	None	VW	None	VW	[illegible]
$Cl_3C-\overset{O}{C}-CCl_3$	None	None	W	VW	None	None	[illegible]
$(CH_3)_2C(OH)-C(OH)(CH_3)_2$	None	None	VW	None	None	None	W
	None	None	VW	None	None	None	VW
	None	None	None	None	None	None	[illegible]
	None	None	None	None	None		
$CH_3-\overset{O}{C}-\overset{O}{C}-CH_3$						None	None
$(C_6H_5)_2C=C(C_6H_5)_2$	None	None	None	None	None	None	[illegible]
$Cl_2C=CCl_2$	None	None	None	None	None	None	VW
	None	None	None	None	None	None	None
$C_6H_5-\overset{O}{C}-\overset{O}{C}-C_6H_5$	None	None	None	None	None	None	VW
$CH_3O-\overset{O}{C}-OCH_3$	None	None	W	None	None	None	None
	None	None	None	None	None	None	None
$C_6H_5-C\equiv C-\overset{O}{C}-Cl$	None	None	None	None	None	None	VW
	None	None	None	None	None	None	[illegible]
$\overset{OH}{CH_2}-\overset{OH}{CH_2}$	None	None	None	None	None	None	None
$CH_2-CH-CH_2$	None	None	None	None	None	None	
[illegible]			None	None	None	[illegible]	[illegible]
[illegible]			[illegible]	None	[illegible]	[illegible]	

TABLE I (continued)

	Chemiluminescence Tests (a)						
	A	B	C	D	E	F	G
$CH_3-C(-O-CH_2-CH_3)_3$			VW	None	None	VW	W
$Cl_3C-C(=O)OH$				None			
$F_3C-C(=O)OH$				None			
$(HO-CH_2-C(=O)-O)_2Ca$						None	None
$(C_6H_5)_3C-C(=O)-OH$				None		None	None
$(CH_3-CH_2O)_3CH$	None	None	None	None	None	None	None
$Cl_3C-CH(OH)-OC_2H_5$	None	None	VW	None	None	None	None
$Cl_3C-C(=O)-H$						None	None

(See following page for footnotes.)

FOOTNOTES FOR TABLE I

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_2H 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.

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, ~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, barely visible.

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