

AD 626295

TECHNICAL REPORT NO. 10

TO THE  
OFFICE OF NAVAL RESEARCH  
AND  
ADVANCED RESEARCH PROJECTS AGENCY  
ARPA ORDER NO. 295, AMEND. 2  
CONTRACT NO. 4200(00)  
TASK NO. 356-452

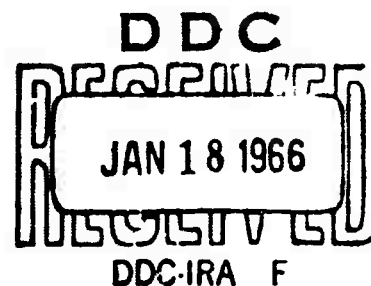
# CHEMILUMINESCENT MATERIALS

AMERICAN CYANAMID COMPANY  
CENTRAL RESEARCH DIVISION  
STAMFORD, CONNECTICUT

CLEARINGHOUSE FOR FEDERAL SCIENTIFIC AND TECHNICAL INFORMATION		
Hardcopy		
\$3.00	0.50	52-a)
REPLINE COPY		

Circle 1

SEPTEMBER 1, 1965 - NOVEMBER 30, 1965



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

## DOCUMENT CONTROL DATA - R&amp;D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) American Cyanamid Company Stamford Research Laboratories Stamford, Connecticut 06904		2a. REPORT SECURITY CLASSIFICATION unclassified	
		2b. GROUP none	
3. REPORT TITLE Chemiluminescent Materials			
4. DESCRIPTIVE NOTES (Type of report and inclusive date) Progress Report No. 10 [September 1, 1965 to November 30, 1965]			
5. AUTHOR(S) (Last name, first name, initial) Rauhut, M. M.; Bollyky, L. J.; Maulding, D. R.; Clarke, R. A.; Roberts, B. G.; Semsel, A. M.; Villanova, A. M.; Whitman, R. H.			
6. REPORT DATE December 31, 1965		7a. TOTAL NO. OF PAGES 51	7b. NO. OF REFS 17
8a. CONTRACT OR GRANT NO. Nonr 4200[00]		9a. ORIGINATOR'S REPORT NUMBER 06-1432-25-Q10	
b. PROJECT NO. ARPA Project No. 299, Amend 3			
c. CONTRACT NO. C... ..		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) None	
d. Task NR 356-452			
10. AVAILABILITY/LIMITATION NOTICES None			
11. SUPPLEMENTARY NOTES None		12. SPONSORING MILITARY ACTIVITY ARPA [monitored by ONR]	
13. ABSTRACT  Progress toward the development of chemiluminescent systems is reported with particular reference to systems encompassing the peroxyoxalate-fluorescent compound mechanism. Synthesis and qualitative evaluation of a number of new chemiluminescent compounds are reported.			

The following scientists made primary contributions  
to the technical effort:

M. M. Rauhut

L. J. Bollyky, R. A. Clarke, D. R. Maulding, B. G. Roberts  
A. M. Samsel, A. M. Villalova, R. H. Whitman.

Microanalyses were carried out under the direction of  
Mr. R. J. Francel; computer analyses under the direction of Dr. D. W. Behnken;  
infrared analyses by Mr. N. B. Colthup; other spectroscopic work was super-  
vised by Dr. R. C. Hirt.

## TABLE OF CONTENTS

Summary	1
Introduction	2
Section I - Oxalic Esters	4
Preparation and Qualitative Evaluation of Oxalic Esters	4
Solubility and Solvent Studies	8
Quantitative Evaluation of Aryloxalate Chemiluminescence	14
Bis[2,4-dinitrophenyl]oxalate [DNPO]	14
Bis[4-cyanophenyl]oxalate [CPO]	27
Bis[4-nitrophenyl]oxalate [NPO]	33
Experimental	35
Section II - Oxalic Amides	36
Experimental	40
Section III - Chemiluminescent Autooxidation	42
Experimental	47
References	48
Distribution	49

SUMMARY

Progress toward the development of chemiluminescent systems is reported with particular reference to systems encompassing the peroxy-oxalate-fluorescent compound mechanism. Synthesis and qualitative evaluation of a number of new chemiluminescent compounds are reported.

In a series of nine new oxalate esters, seven provided at least medium chemiluminescent intensities in standard qualitative chemiluminescence tests. The active compounds were all electronegatively-substituted aryl esters, thus confirming previous conclusions. Solubilities in several solvents were determined for the more promising compounds as a preliminary to quantitative examination. Bis[2,4-dinitrophenyl]oxalate has been investigated quantitatively in terms of reactant concentration effects and in terms of the effects of accelerators and inhibitors. Triethylamine and 2,4-dinitrophenol strongly accelerate the reaction; 2,6-di-t-butyl-4-methylphenol has little effect on the reaction rate but severely reduces quantum yields. Fluorescer stability was found to increase at low hydrogen peroxide concentrations.

In a series of eight compounds related to oxamide, four were found to be chemiluminescent in qualitative testing. Efforts to develop an air-activated chemiluminescent system based on the peroxyoxalate mechanism have been essentially unsuccessful.

### INTRODUCTION

While the requirements for a practical chemical lighting system necessarily depend on a specific anticipated application, it is clear that for any given use a practical system must deliver light above a minimum specified intensity level for a specified length of time. The intensity and lifetime of a chemiluminescent system are related to the system's light capacity in lumen-hours liter<sup>-1</sup> by equation [1] where L is the light capacity, I is intensity in lumens, T is time in seconds and V is the volume of the system in liters.

$$[1] \quad L = \frac{\int_{T=0}^{T=\infty} IdT}{3600 V}$$

It is clear that L is a fundamental criterion for practical chemiluminescence, since a system where L is below some specified level cannot be made to meet the intensity-lifetime performance demanded by practicality.

While some chemiluminescent systems described in the literature meet certain requirements for practical lighting, all are deficient in terms of light capacity. The design of high light capacity systems is thus the primary goal of research directed toward practical chemical lighting.

Early efforts in this program coupled with a survey of the literature indicated a small probability at best of providing high light capacity systems through empirical modifications of chemical structure or reaction conditions of existing systems. It was also evident that available information on the mechanisms of chemiluminescent processes was inadequate for the deliberate

design of new systems. A program was therefore instituted to determine mechanistic and structural criteria for chemiluminescence so that high light capacity systems could be designed.

Our understanding of these criteria remains incomplete and work aimed at providing mechanistic information is continuing. However, mechanistic work now completed has already provided a substantial insight into the nature of chemiluminescence. The results of this work have been used to design chemiluminescent systems considerably superior in efficiency to those previously known. Thus, a major part of our current effort is being directed toward the discovery of efficient chemiluminescent systems, designed on the basis of newly derived mechanistic hypotheses, and the development of systems now in hand.

In this report, we describe current efforts to improve light capacities, emission lifetimes, and operating characteristics for peroxy-oxalate chemiluminescent systems. Our aims are to: [1] expand the scope of the general class [2] determine the detailed structural requirements for efficient chemiluminescence [3] provide more soluble luminants so that high concentrations can be obtained [4] provide luminants capable of use in water [5] determine the effects of reaction conditions on light capacities and lifetimes [6] modify the systems to accommodate air-activation and [7] to provide efficient, stable fluorescers with high photopic constants.

SECTION I

OXALIC ESTERS

Preparation and Qualitative Evaluation of Oxalic Esters

In the previous report<sup>9</sup>, a number of aryl oxalic esters were shown to produce strong chemiluminescence when reacted with hydrogen peroxide in the presence of a fluorescer. Electron withdrawing substituents improved the intensity significantly while electron releasing substituents diminished the efficiency. We are preparing additional aryl oxalic esters to expand the scope of the system and to provide oxalic esters with still higher chemiluminescent quantum efficiencies and improved solubilities. The evaluation of these compounds is expected to elucidate further the effects of substituents on chemiluminescence and to provide data for the design of a future practical chemiluminescent system.

The new oxalic esters prepared are listed in Table I. Most of these esters were prepared from the reaction of oxalyl chloride with the desired phenol or alcohol in the presence of triethylamine as described earlier.<sup>7,9</sup> A simplified procedure suitable for larger scale preparation has also been devised and used with good results.

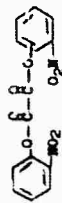
All the newly prepared oxalic esters were subjected to qualitative chemiluminescent tests for preliminary evaluation. The results are summarized in Table II. All of the aryl oxalates prepared were found to be at least moderately chemiluminescent. Although strict comparison is difficult on the basis of qualitative visual observations, the most promising



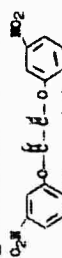
TABLE I

Yield	M.P., °C	Mol. Wt.	Elementary Analysis						Solid in Molal	Infrared: C=O stretching frequencies (cm <sup>-1</sup> )					
			Calcd. Found	Calcd. Found	H	O	F	Solvent		cm <sup>-1</sup> Intensity	cm <sup>-1</sup> Intensity	Intensity			
46%	186.4	332.16	50.61	50.90	2.43	2.61	8.43	8.50	38.53	38.79	1778	1804	0.11	1781	0.20
66%	270-4 (dec)	422.18	39.83	40.27	1.43	1.63	13.27	12.88	45.47	--	1787	1800	0.08	1799 1779	0.12 0.12
54%	186.7- 190	450.3	42.68	42.66	2.24	2.23	12.44	12.64			1777	1812	0.03	1788	0.08
71%	186-9	468.24	41.04	41.65	1.29	1.37	5.98	6.23	27.34	24.35	1779	1801	0.06	1780	0.13
74%	170-2	422.12	39.83	39.93	--	--	--	--	15.16	45.01	1793	1820	0.09	1794	0.27
52%	199-4 (dec.)	522.3	50.58	50.99	1.95	2.18	10.73	10.56			1793	1789	0.09	1763	0.10
76%	238-42 (dec.)	522.26	50.59	50.61	1.93	2.09	10.73	10.29	36.76	--	1784	1788	0.08	1766	0.38
59%	70-71 <sup>a</sup>	202.25	59.39	59.13	8.97	8.81					1762 shoulder 1797	1763	0.30	1736	0.62
44%	B.P. 44-45 at 1.8 mm.	294.1	28.36	28.50	1.58	1.83					1776 liq. 1797	1802	0.25	1774	0.57

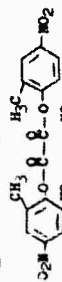
1 Bis(2-nitrophenyl)oxalate



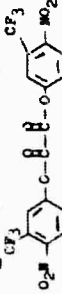
2 Bis(2,5-dinitrophenyl)oxalate



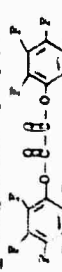
3 Bis(2-methyl-4,6-dinitrophenyl)oxalate



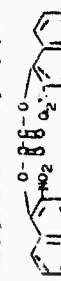
4 Bis(3-trifluoromethyl-5-nitrophenyl)oxalate



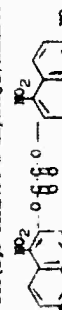
5 Bis(pentafluorophenyl)oxalate



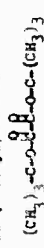
6 Bis(2,4-dinitro-1-naphthyl)oxalate



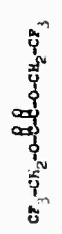
7 Bis(1,6-dinitro-2-naphthyl)oxalate



8 Bis(t-butyl)oxalate

(CH<sub>3</sub>)<sub>3</sub>C-O-C(=O)-O-C(=O)-C(CH<sub>3</sub>)<sub>3</sub>

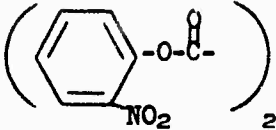
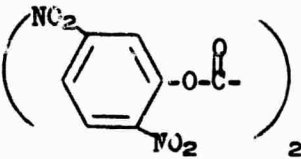
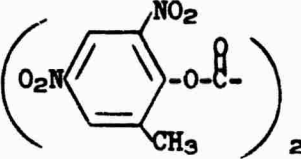
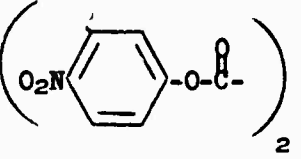
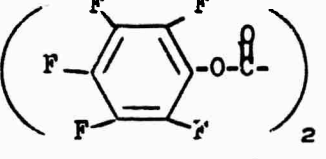
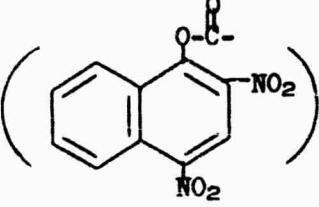
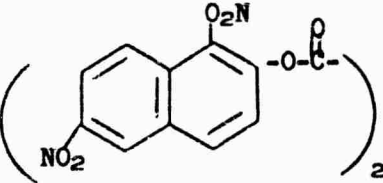
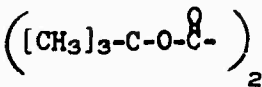
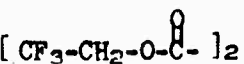
9 Bis(2,4,6-trifluorophenyl)oxalate

CF<sub>3</sub>-CH<sub>2</sub>-O-C(=O)-O-C(=O)-CF<sub>3</sub>

a) Lit. r.p., 69-70, 99c.

**TABLE II**

**Qualitative Chemiluminescent Test of Oxalic Esters**

	Tests <sup>a</sup>			
	A [anhyd. H <sub>2</sub> O <sub>2</sub> ]	B [H <sub>2</sub> O <sub>2</sub> + KOH]	C [H <sub>2</sub> O <sub>2</sub> + H <sub>2</sub> O]	D [H <sub>2</sub> O <sub>2</sub> + H <sub>3</sub> O <sup>+</sup> ]
	M	VS	M	None
	S <sup>b</sup>	S-VS	M	None
	S	S	MW	WV
	S <sup>b</sup>	VS	W-M	None
	S	VS	M	None
	W	M	W	WV
	M-MS	M-MS	VW-W	None
	None	None	None	None
	None	W	None	None

NOTES TO TABLE II

[a] The tests were carried out as follows:

- A. Approximately 3-5 mg. of the compound to be tested is added to a 5 ml. solution of about 1 mg. DPA and 0.2 ml. anhydrous  $H_2O_2$  in anhydrous 1,2-dimethoxyethane maintained at 25°C.
- B. Approximately 3-5 mg. of the compound to be tested is added to a 5 ml. 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 25°C.
- C. As test A except that approximately 0.1 ml. water was added prior to the addition of the compound being tested.
- D. Approximately 3-5 mg. of the compound to be tested is added to a 5 ml. solution of 1 mg. DPA and 0.2 ml.  $CH_3SO_3H$  in 1,2-dimethoxyethane containing 5% water and maintained at 25°C. About 0.5 ml. 30%  $H_2O_2$  is added immediately.

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] A brief induction period was observed.

esters appear to be dinitrophenyl, dinitrocresyl, trifluoromethyl-nitrophenyl and pentafluorophenyl oxalates. The chemiluminescence from these esters is similar to that available from the very efficient bis[2,4-dinitrophenyl]oxalate reported earlier.<sup>9</sup> However, the final evaluation must wait until the planned quantum yield measurements are completed.

The two dinitronaphthyl oxalates shown in Table II are only moderately chemiluminescent probably a result of their poor solubilities. Bis-2,2,2-trifluoroethyl oxalate is weakly chemiluminescent but better than di-t-butyl oxalate which gives chemiluminescence only at 60°C or higher.

#### Solubility and Solvent Studies

Since high light capacity requires high luminant and hydrogen peroxide concentrations [up to  $\sim 10^{-1}$  molar], the more promising esters are being screened for solubility and for solvent effects on chemiluminescence. The results of screening DNPO in 34 solvents are summarized in Table III.

Esters, ketones, ethers and epoxides represent the most promising group of solvents found. The otherwise solubilizing solvents dimethylsulfoxide, hexamethylphosphoramide, and tetramethylurea interfered with the chemiluminescent process.

A series of chemiluminescence tests carried out in various mixtures of water and 1,2-dimethoxyethane, are summarized in Table IV. The chemiluminescence was found to decrease with increasing water concentration; chemiluminescence was not observed in water alone. It is not known at present if the effect of water is due to decreased solubility of the reactants or to interference with the chemiluminescent reaction.

TABLE III

Test of bis[2,4-dinitrophenyl]oxalate [DNPO] for  
Chemiluminescence in Various Solvents<sup>a</sup>

	Solubility of DNPO [moles l <sup>-1</sup> ]	Solubility of H <sub>2</sub> O <sub>2</sub> [moles l <sup>-1</sup> ]	Tests <sup>b</sup>	
			A	B
Acetone	> 2 x 10 <sup>-2</sup>	> 1.0	S	S
1,2-Propylene oxide	> 2 x 10 <sup>-2</sup>	> 1.0	VS	VS
1,2-Dimethoxyethane	> 2 x 10 <sup>-2</sup>	> 1.0	S	S
Dimethylcarbonate	> 2 x 10 <sup>-2</sup>	> 1.0	S[long]	S[long]
Propylene Carbonate	> 2 x 10 <sup>-2</sup>	> 1.0	S[long]	S[long]
Dimethylphthalate	> 2 x 10 <sup>-2</sup>	> 1.0	S[long]	S[long]
Tetrahydrofuran	> 2 x 10 <sup>-2</sup>	> 1.0	MS	MS
Nitromethane	> 2 x 10 <sup>-2</sup>	> 0.1	MW	MS
Ether	< 2 x 10 <sup>-2</sup>	> 0.1	S	S
Triethylphosphate	< 2 x 10 <sup>-2</sup>	> 0.1	S	
Perfluorohexane	< 2 x 10 <sup>-2</sup>	> 0.1	None	None
Methyl perfluorooctanoate	< 2 x 10 <sup>-2</sup>	> 0.1	None	VW
Anisole		Not Soluble		
Benzene	< 2 x 10 <sup>-2</sup>	Not Soluble		
o-Dichlorobenzene	< 2 x 10 <sup>-2</sup>	Poorly Soluble	MS[long]	
Tetralin	< 1 x 10 <sup>-2</sup>	~ 0.03	W	
Nitrobenzene <sup>c</sup>	< 2 x 10 <sup>-2</sup>	< 1.0	MW	MW
Sulfolane <sup>c</sup>	< 2 x 10 <sup>-2</sup>	> 1.0	MS	
Dimethylformamide <sup>d</sup>	> 2 x 10 <sup>-2</sup>	> 1.0	S[very short]	S[very short]
Dimethylsulfoxide	> 2 x 10 <sup>-2</sup>	> 1.0	None	
Hexamethylphosphoramide	> 2 x 10 <sup>-2</sup>	> 1.0	None	
Tetramethylurea	> 2 x 10 <sup>-2</sup>	> 1.0	None	
Chloroform	< 2 x 10 <sup>-2</sup>	> 1.0	V	M[long]
Methylene Chloride	< 2 x 10 <sup>-2</sup>	< 1.0	W	M[long]
Carbontetrachloride		Not Soluble		
Acetonitrile	< 2 x 10 <sup>-2</sup>	> 1.0	M	M
t-Butyl alcohol	< 2 x 10 <sup>-2</sup>	> 1.0	VW	W[long]
Glycerine	< 2 x 10 <sup>-2</sup> [deep yellow color present]	> 1.0	None	None
Ethylacetate	< 2 x 10 <sup>-2</sup>	> 0.1	S[short]	S[short]
Diethyloxalate	< 2 x 10 <sup>-2</sup>	> 1.0	MS[long]	
Cyclohexane	< 2 x 10 <sup>-2</sup>	< 1.0	VW	W[long]
Chlorobenzene	< 2 x 10 <sup>-2</sup>	< 1.0	S	VS
Pyridine	reacts with DNPO	> 1.0	None	None
Acetic Acid	< 2 x 10 <sup>-2</sup>	> 1.0	M	S[long]

NOTES TO TABLE III

- [a] The bis[2,4-dinitrophenyl]oxalate [DNPO]-hydrogen peroxide-9,10-diphenylanthracene chemiluminescent system was tested in various solvents to obtain a qualitative evaluation of the chemiluminescent light intensity emitted as well as of the approximate solubility of reagents. The visually observed chemiluminescent intensities are based on the oxalyl chloride-hydrogen peroxide reaction in ether taken as strong [S]. Other designations are M = medium; W = weak; VW = very weak, barely visible.
- [b] A 50 mg. DNPO was added to 5 ml. magnetically stirred solvent in a test tube. After 15 minutes the solubility of DNPO was observed. Approximately 1 mg. 9,10-diphenylanthracene was added and then sufficient 98% hydrogen peroxide was added to give either 1 mole l<sup>-1</sup> or 0.1 mole l<sup>-1</sup> concentration as noted. Chemiluminescence was observed in the dark, and then the solubility of hydrogen peroxide was noted.
- B As test A except prior to the addition of hydrogen peroxide, approximately 0.2 g. KOH was added.
- [c] Solvent is colored.
- [d] DNPO reacted with the solvent.

TABLE IV

The Chemiluminescence of DNPO in Water-1,2-Dimethoxyethane  
Mixed Solvent

---

	<u>Test<sup>a</sup></u>
100% water	None
95% water - 5% 1,2-dimethoxyethane	VW
75% water - 25% 1,2-dimethoxyethane	W
50% water - 25% 1,2-dimethoxyethane	W
25% water - 75% 1,2-dimethoxyethane	W
0% water - 100% 1,2-dimethoxyethane	S

---

[a] Approximately 3-5 mg. bis[2,4-dinitrophenyl]oxalate [DNPO] was added to a 5 ml. solution of about 1 mg. 9,10-diphenylanthracene and 1 mg. disodium fluorescein and 0.2 ml. anhydrous hydrogen peroxide maintained at 25°C.

Qualitative chemiluminescent 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.

The more promising esters in Table II were tested for solubility in a series of solvents as indicated in Table V.

All solvents used dissolve at least 0.1 mole liter<sup>-1</sup> hydrogen peroxide and do not appear to seriously interfere with the chemiluminescent reaction. Solubilities were highest in propylene carbonate and 1,2-dimethoxyethane for most oxalic esters.



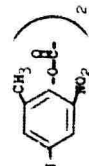


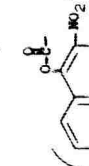


As indicated in Table V, 3-trifluoromethyl-4-nitrophenyl oxalate showed particularly high solubilities among the compounds tested. Compounds with moderate solubilities included pentafluorophenyl and 2-methyl-4,6-dinitrophenyl oxalate. Naphthyl oxalates in general were poorly soluble.

In another approach toward achieving high luminant concentrations, liquid oxalic esters were tested for chemiluminescence in the absence of solvent. Diethyl oxalate, which is only weakly chemiluminescent in 1,2-dimethoxyethane solvent when reacted with hydrogen peroxide in the presence of a fluorescer was found equally chemiluminescent without solvent present. This observation suggests the feasibility of using a very high concentration of liquid moderately efficient oxalic ester for chemiluminescence.



TABLE V

Approximate Solubilities of Oxalic Esters<sup>a</sup> (mole l<sup>-1</sup>)

Solvents	Approximate Solubilities of Oxalic Esters <sup>a</sup> (mole l <sup>-1</sup> )										
	Diethylphthalate	Propylene Carbonate	1,2-Dioxane	Dimethylacetone	Dimethyladipate	Diethylphthalate	Diethyl Oxalate	Tetrahydrofuran	Dimethyl Carbonate	1,2-Propylene Oxide	Acetone
1 	< 3.1 x 10 <sup>-3</sup>	1.5 x 10 <sup>-2b</sup>	2.8 x 10 <sup>-2</sup>	< 1.1 x 10 <sup>-2</sup>	< 1.4 x 10 <sup>-2</sup>	< 8 x 10 <sup>-3</sup>	< 6.8 x 10 <sup>-3</sup>	< 4 x 10 <sup>-3</sup>	< 6.8 x 10 <sup>-3</sup>	< 4 x 10 <sup>-3</sup>	< 6.8 x 10 <sup>-3</sup>
2 	< 1.9 x 10 <sup>-3</sup>	< 6.2 x 10 <sup>-3</sup>	< 5.0 x 10 <sup>-3</sup>	< 5 x 10 <sup>-4b</sup>	< 1.9 x 10 <sup>-4</sup>	< 2.3 x 10 <sup>-4</sup>	< 2 x 10 <sup>-4</sup>	< 2 x 10 <sup>-4</sup>	< 2 x 10 <sup>-4</sup>	< 2 x 10 <sup>-4</sup>	< 2 x 10 <sup>-4</sup>
3 	3.5 x 10 <sup>-2</sup>	7.5 x 10 <sup>-2</sup>	2.8 x 10 <sup>-2</sup>	3.6 x 10 <sup>-2b</sup>	1.7 x 10 <sup>-2</sup>	2.1 x 10 <sup>-2</sup>	2.1 x 10 <sup>-2</sup>	2.1 x 10 <sup>-2</sup>	2.1 x 10 <sup>-2</sup>	2.1 x 10 <sup>-2</sup>	2.1 x 10 <sup>-2</sup>
4 	3.1 x 10 <sup>-2</sup>	2.4 x 10 <sup>-1</sup>	4 x 10 <sup>-1</sup>	2.4 x 10 <sup>-2</sup>	4 x 10 <sup>-3</sup>	1.5 x 10 <sup>-3</sup>	2.8 x 10 <sup>-3</sup>	4 x 10 <sup>-3</sup>	2.8 x 10 <sup>-3</sup>	4 x 10 <sup>-3</sup>	2.8 x 10 <sup>-3</sup>
5 	< 1.2 x 10 <sup>-2</sup>	1.7 x 10 <sup>-2</sup>	6 x 10 <sup>-2</sup>	8 x 10 <sup>-2</sup>	1.2 x 10 <sup>-2</sup>	2 x 10 <sup>-2</sup>	2 x 10 <sup>-2</sup>	2 x 10 <sup>-2</sup>	2 x 10 <sup>-2</sup>	2 x 10 <sup>-2</sup>	2 x 10 <sup>-2</sup>
6 	3.8 x 10 <sup>-4</sup>	< 3.8 x 10 <sup>-4</sup>	< 2 x 10 <sup>-3</sup>	< 7.7 x 10 <sup>-4b</sup>	< 2.1 x 10 <sup>-3</sup>	< 2.1 x 10 <sup>-3</sup>	< 2.1 x 10 <sup>-3</sup>	< 4 x 10 <sup>-3</sup>	< 2.1 x 10 <sup>-3</sup>	< 4 x 10 <sup>-3</sup>	< 4 x 10 <sup>-3</sup>
7 	< 1.9 x 10 <sup>-3</sup>	b	< 2 x 10 <sup>-3</sup>	< 7.7 x 10 <sup>-4b</sup>	< 2.1 x 10 <sup>-3</sup>	< 2.1 x 10 <sup>-3</sup>	< 2.1 x 10 <sup>-3</sup>	< 4 x 10 <sup>-3</sup>	< 2.1 x 10 <sup>-3</sup>	< 4 x 10 <sup>-3</sup>	< 4 x 10 <sup>-3</sup>
8 	2.8 x 10 <sup>-2</sup>	3.7 x 10 <sup>-2</sup>	4 x 10 <sup>-1</sup>	4 x 10 <sup>-1</sup>	4 x 10 <sup>-1</sup>	4 x 10 <sup>-1</sup>	4 x 10 <sup>-1</sup>	4 x 10 <sup>-1</sup>	4 x 10 <sup>-1</sup>	4 x 10 <sup>-1</sup>	4 x 10 <sup>-1</sup>

a) Solubilities were determined by the periodic addition of 15 minute intervals of small portions (0.2-0.3 ml.) of solvent to a test tube containing a known amount (~100 mg.) of the compound being stirred by a magnetic stirrer, until all the compound dissolved. Reagent grade solvents were used without further purification with the exception of propylene carbonate and 1,2-dimethoxyethane which were dried and distilled.

b) decomposes or reacts on hydrolysis

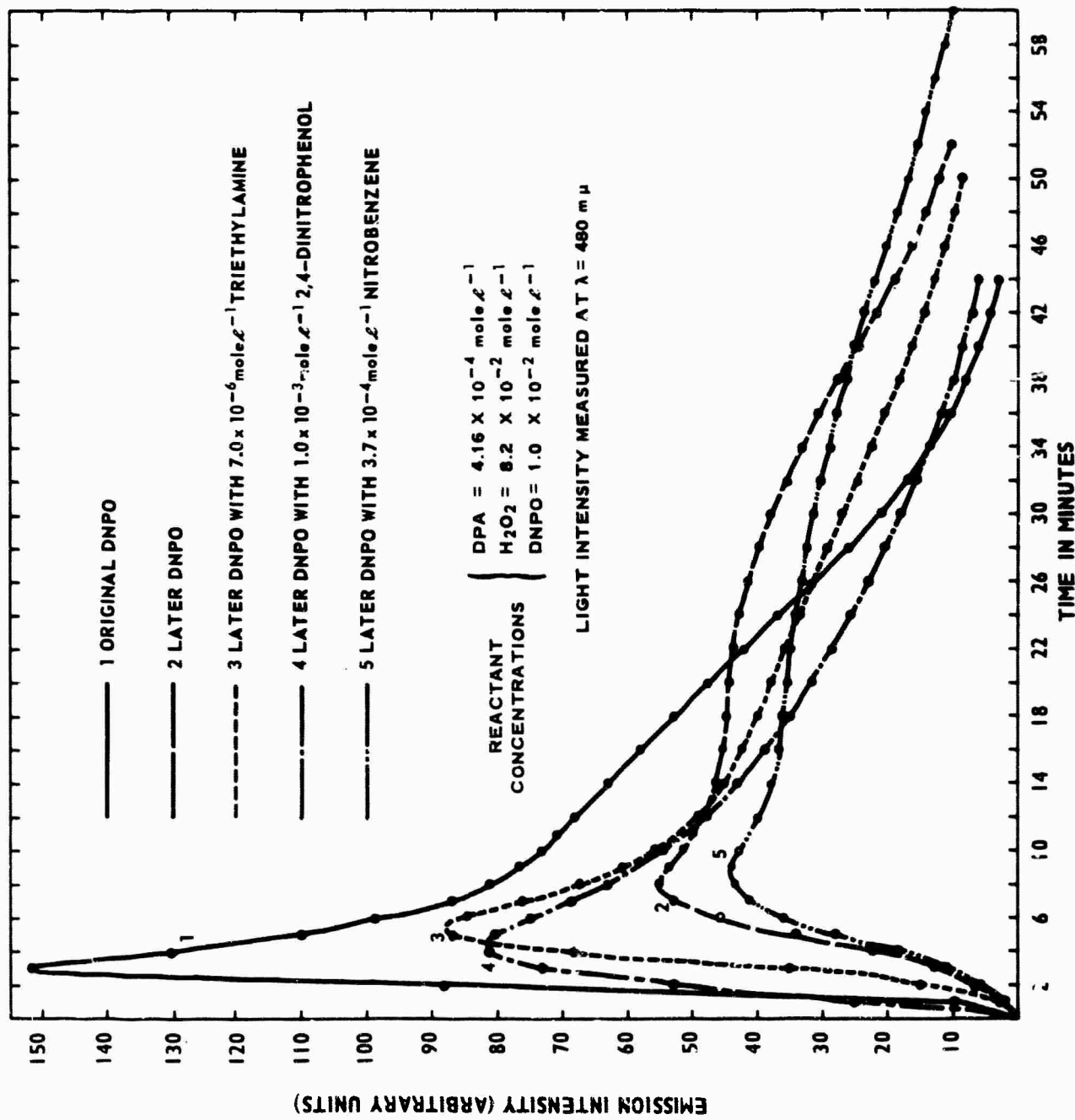
### Quantitative Evaluation of Aryloxalate Chemiluminescence

The chemiluminescent properties of the most promising oxalate esters prepared in our synthesis program are being determined quantitatively to provide mechanistic information and to permit evaluation and comparison of the esters in practical terms. Adequate evaluation requires the measurements of light intensities, lifetimes and quantum yields as a function of [1] reactant concentration, [2] alternative and supplementary reactants, [3] solvent, and [4] temperature. The qualitative measurements to date deal partially with the influence of first two variables on bis[2,4-dinitrophenyl]oxalate chemiluminescence. In addition, less extensive data are provided for two other chemiluminescent oxalate esters.

#### Bis[2,4-dinitrophenyl]oxalate [DNPO]

It was evident from the considerable number of quantum yield and intensity decay rate measurements reported in the previous report<sup>9</sup> that while quantum yields could be determined with satisfactory reproducibility, decay rates varied substantially under apparently constant conditions. The problem of reproducing intensities and decay rates is emphasized by the new results summarized in Figure I, where decay curves are presented for identical chemiluminescent reactions of two separately prepared, but analytically and spectroscopically pure samples of DNPO. While the quantum yields, represented by the areas under the curves, varied little between samples [1] and [2], it is seen that sample [2] was substantially less bright initially but longer lived than sample [1]. Specifically, the discrepancy appears in the length of the induction period in the value of maximum light intensity and in the rate of chemiluminescent decay. Provided the solvent was carefully distilled, individual repetition of experiments [1] and [2] showed that the separate

FIGURE 1  
THE EFFECT OF TRACE ADDITIVES ON DNPO CHEMILUMINESCENT LIGHT INTENSITY  
AND LIFETIME IN DIMETHYLPHTHALATE



results could be reproduced satisfactorily, indicating that the discrepancy resulted from an impurity present in DNPO. The effect of small concentrations of possible impurities were then examined. As indicated in Figure I, low concentrations of triethylamine [curve 3] or 2,4-dinitrophenol [curve 4] substantially accelerated the reaction, while a low concentration of nitrobenzene [curve 5] which is used to recrystallize DNPO appeared to retard the rate. Thus any of these materials may be the cause of irreproducible rates. It is clear from the low concentration required for catalytic activity that very high purity DNPO will be required for reproducible rate measurements. Since 2,4-dinitrophenol is a product of the chemiluminescent reaction, its strong accelerating effect shows that the reaction is subject to autocatalysis; this effect, if general for phenols, may cause difficulty in providing long lifetimes at high phenolic ester concentrations, unless inherently slower reactions are found. The apparent effect of nitrobenzene in retarding the reaction will thus be given extensive study. The effect of acids and bases on the reaction rate, however, also offer the prospect of rate control, which may make possible the flexible adjustment of emission lifetimes.

The effects of several additives on quantum yields are summarized in Table VI. Under the conditions studied, triethylamine and nitrobenzene had little effect on quantum yield, while 2,4-dinitrophenol decreased the quantum yield only moderately. In contrast, the free radical inhibitor 2,6-di-*t*-butyl-4-methylphenol strongly depressed the quantum yield. The smaller  $1/4$  lifetime listed for the inhibitor experiment in Table V, implies that

TABLE VI  
The Effect of Impurities on DNPO Chemiluminescence<sup>a</sup>

<u>Additives</u> <u>[mole l<sup>-1</sup>]</u>	<u>t<sub>I max.</sub><sup>b</sup></u> <u>[min.]</u>	<u>t<sub>1/4 I max.</sub><sup>c</sup></u> <u>[min.]</u>	<u>Quantum Yield<sup>d</sup></u> <u>[einstein mole<sup>-1</sup> x 10<sup>2</sup>]</u>
None <sup>e</sup>	6.2	26.9	7.66
None	8.0	40.7	7.79
7 x 10 <sup>-6</sup> triethylamine	5.0	29.6	7.42
3.7 x 10 <sup>-4</sup> nitrobenzene	9.0	49.5	7.45
1 x 10 <sup>-3</sup> 2,4-dinitrophenol	4.4	23.5	6.35
2.87 x 10 <sup>-2</sup> 2,6-di-t-butyl- 4-methylphenol	9.2	18.0	0.37

a DNPO sample [2] was used except where noted. The concentrations were DNPO, 1 x 10<sup>-2</sup> mole l<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub>, 0.82 x 10<sup>-1</sup> mole l<sup>-1</sup>; DPA, 4.16 x 10<sup>-4</sup> mole l<sup>-1</sup> in dimethylphthalate at 25°C.

b Time required for the chemiluminescent light to reach maximum intensity.

c Time required for the light intensity to decrease to one quarter of its maximum value.

d Quantum yield is based on DNPO.

e DNPO sample [1] was used.

the inhibitor strongly accelerates the decay rate; but the acceleration is actually only moderate as demonstrated by the decay curves in Figure II. One-quarter intensities are evidently misleading indications of rate effects. The absence of a pronounced induction period from the inhibited reaction in Figure II and the relative minor effect on reaction rate indicates that the rate controlling step in the chemiluminescent reaction is not a free radical chain process. The reduction in quantum yield, however, suggests that following the rate-determining step a rapid reaction leading to chemiluminescence is subject to inhibition.

The effect of hydrogen peroxide concentration on the reaction rate and quantum yield is summarized in Table VII and Figure III. As indicated in Table VII the hydrogen peroxide concentration did not effect the quantum yield substantially below about  $0.1 \text{ mole l}^{-1}$ . At high concentrations, however, hydrogen peroxide decreased the quantum yield significantly. Thus mole ratios of from 1 to 8 moles of hydrogen peroxide:DNPO caused no large change in quantum yield, and even when somewhat less than 1 mole hydrogen peroxide per DNPO was present, the quantum yield decreased only moderately. These observations indicate that the chemiluminescent reaction requires a 1:1 hydrogen peroxide:DNPO stoichiometry.

The hydrogen peroxide concentration, as illustrated by Figure III did not substantially effect the rate of the chemiluminescent reaction in the range of  $1 \times 10^{-2}$  to  $8 \times 10^{-2} \text{ mole l}^{-1}$  hydrogen peroxide. The reaction is slightly slower and slightly more efficient when  $0.04 \text{ mole l}^{-1}$  hydrogen peroxide is used than at lower or somewhat higher hydrogen peroxide concentration. At very high concentrations of hydrogen peroxide, however, the decay curve is changed profoundly and the rate of the chemiluminescent reaction is

FIGURE II  
THE EFFECT OF A FREE RADICAL INHIBITOR ON THE DNPO CHEMILUMINESCENT LIGHT INTENSITY AND LIFETIME IN DIMETHYLPHTHALATE

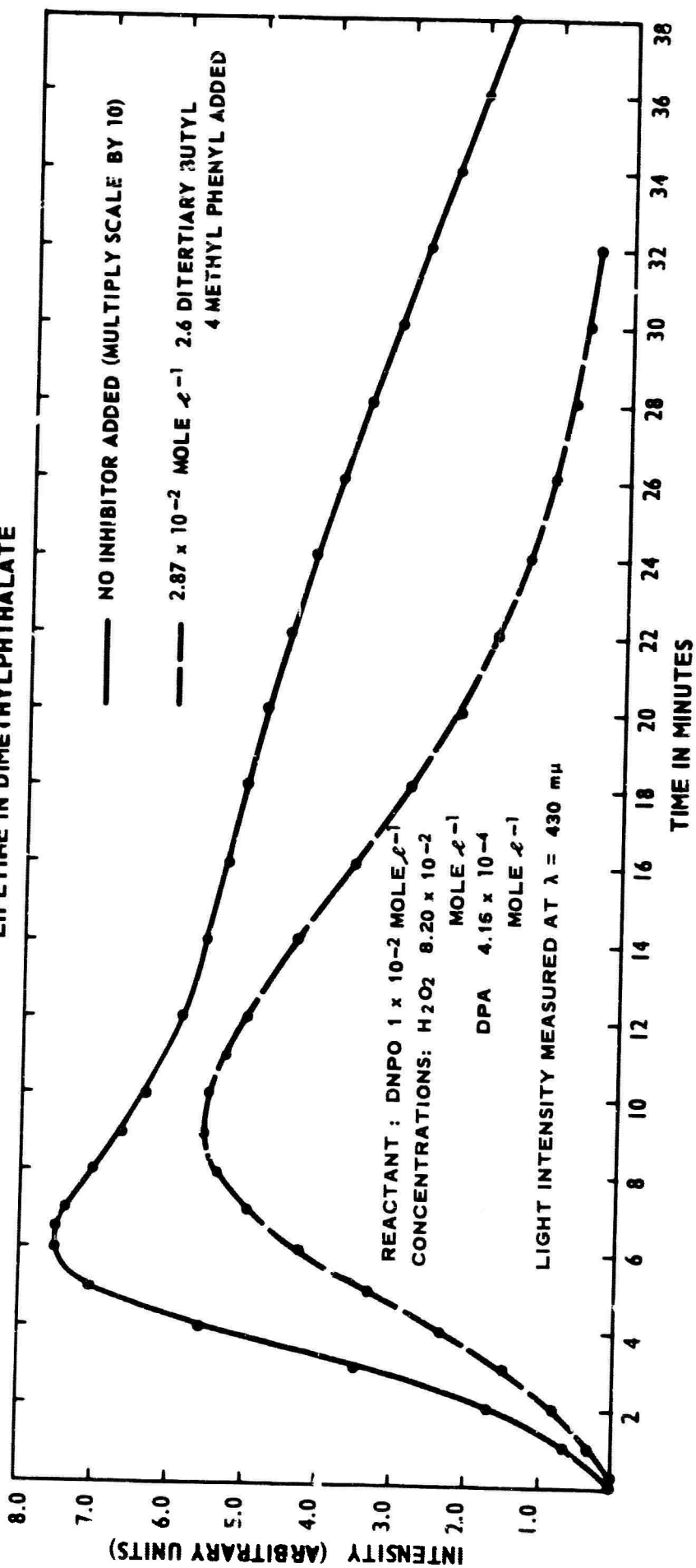


FIGURE III  
THE EFFECT OF HYDROGEN PEROXIDE CONCENTRATION ON THE DNPO CHEMILUMINESCENT  
LIGHT INTENSITY AND LIFETIME IN DIMETHYLPHTHALATE

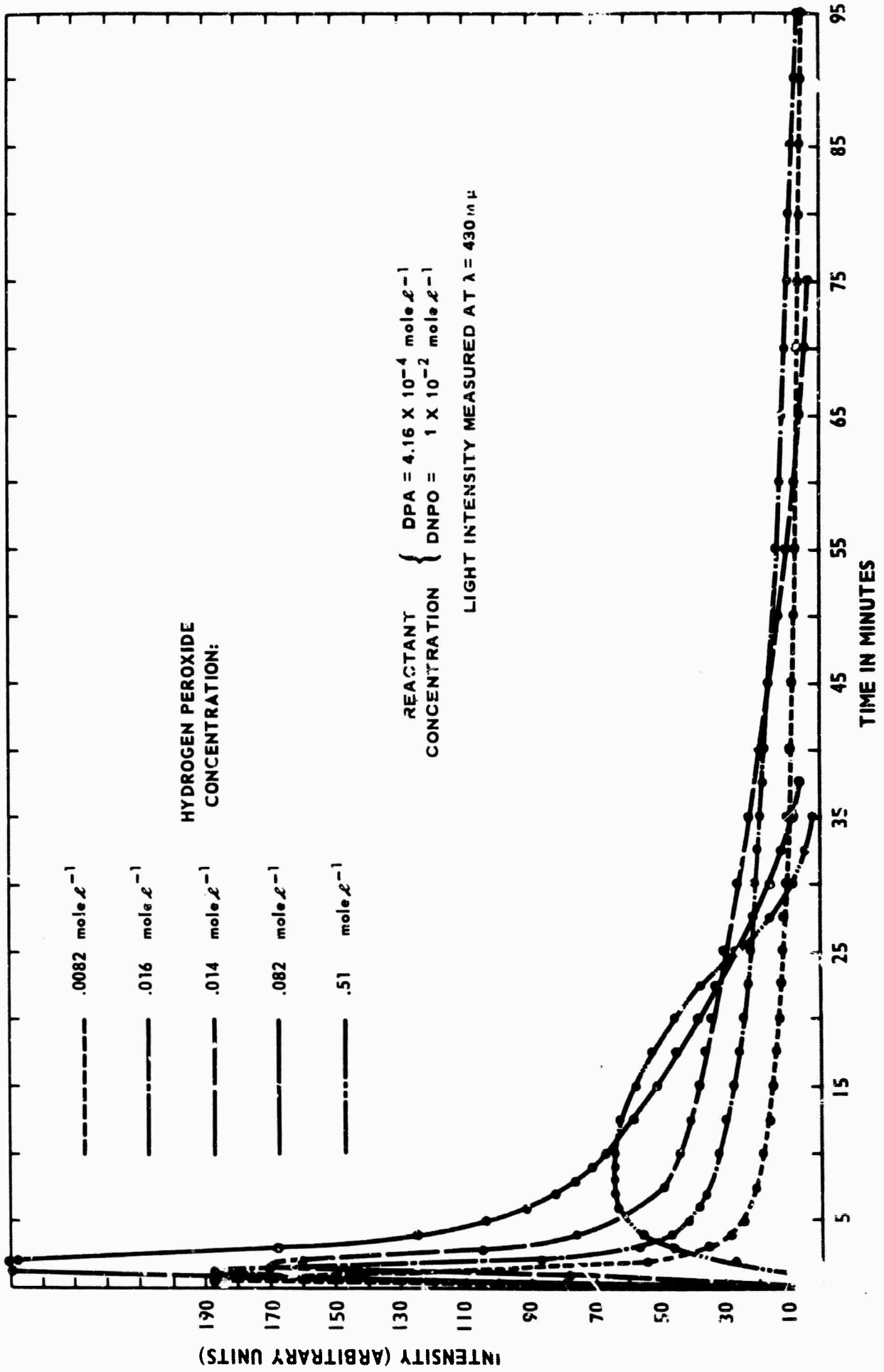




TABLE VII

The Effect of Hydrogen Peroxide Concentration on DNPO  
Chemiluminescence<sup>a</sup>

<u>[H<sub>2</sub>O<sub>2</sub>]</u> <u>[mole l<sup>-1</sup>]</u>	<u>[H<sub>2</sub>O<sub>2</sub>]</u> <u>[DNPO]</u>	<u>t<sub>max.</sub><sup>b</sup></u> <u>[min.]</u>	<u>t<sub>1/4 I max.</sub><sup>c</sup></u> <u>[min.]</u>	<u>Quantum Yield<sup>d</sup></u> <u>[einstein mole<sup>-1</sup> x 10<sup>2</sup>]</u>
0.0082	0.82	0.75	1.5	7.2
0.0164	1.64	0.9	3.0	8.2
0.041	4.1	1.3	9.0	8.7
0.082	8.2	1.6	8.0	8.1
0.514	51.4	7.5	20.0	5.5

a Concentration of Reactants:

DNPO:  $1 \times 10^{-2}$  mole l<sup>-1</sup>; DPA =  $4.16 \times 10^{-4}$  mole l<sup>-1</sup> in dimethylphthalate solution containing  $9 \times 10^{-3}$  mole l<sup>-1</sup> water at 25°C.

b Time required to reach maximum chemiluminescent light intensity.

c Time required for the light intensity to decrease to one quarter of its maximum value.

d Based on DNPO.

decreased substantially. Results showing the effect of water are summarized in Table VIII and Figure IV. Water had little effect on the quantum yield but was found to accelerate the reaction moderately.

Results indicating the effect of several fluorescers on the DNPO-hydrogen peroxide system at relatively high hydrogen peroxide concentrations are summarized in Table IX. The fluorescers examined were chosen because of their fluorescent light emission which is close to the yellow region of the spectrum where the human eye is most sensitive to light. DPA is provided for comparison.

The stability of several of the fluorescers under the reaction conditions was determined by ultraviolet spectral analysis. Substantial fluorescer consumption was observed for the yellow Calcofluor<sup>®</sup> dyes at high hydrogen peroxide concentrations. Substantial fluorescer consumption would be expected to cause lower quantum yields and faster light decay rates. Indeed the higher quantum yield and slower decay rate observed for Calcofluor yellow 7G<sup>®</sup> at low hydrogen peroxide concentration suggests that fluorescer consumption decreases with decreasing hydrogen peroxide concentrations. This conclusion is supported by the data of Table X as discussed below. The effect of hydrogen peroxide concentration and other reaction conditions on fluorescer stability will be studied in detail.

Highest quantum yields were obtained with DPA and rubrene. The lower quantum yield observed for Calcofluor 7G<sup>®</sup> is in line with its lower fluorescence quantum yield. The faster light decay rate observed for 7G is a possible consequence of rate catalysis by the amino group in its structure.

FIGURE IV  
THE EFFECT OF WATER ON THE DNPO CHEMILUMINESCENT LIGHT INTENSITY  
AND LIFETIME IN DIMETHYLPHTHALATE

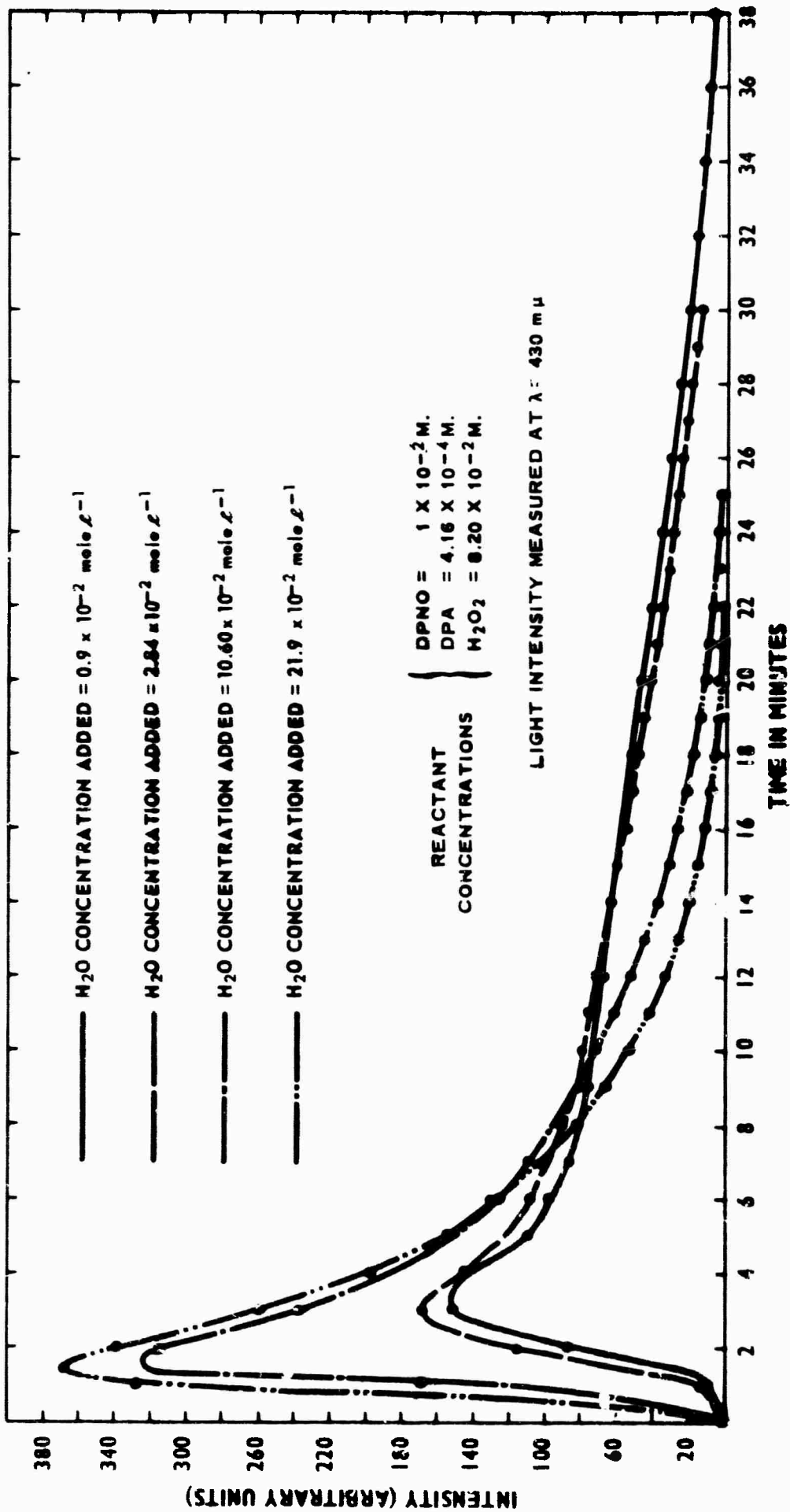


TABLE VIII

The Effect of Water on DNPO Chemiluminescence<sup>a</sup>

<u>H<sub>2</sub>O</u> <u>[mole l<sup>-1</sup>]</u>	<u>t<sub>I</sub> max.<sup>b</sup></u> <u>[min.]</u>	<u>t<sub>1/4 I</sub> max.<sup>c</sup></u> <u>[min.]</u>	<u>Quantum Yield<sup>d</sup></u> <u>[einstein mole<sup>-1</sup> x 10<sup>2</sup>]</u>
0.5 x 10 <sup>-2</sup>	4.8	27.5	8.2
0.9 x 10 <sup>-2</sup>	3.0	17.0	8.2
2.83 x 10 <sup>-2</sup>	3.0	17.0	8.1
10.6 x 10 <sup>-2</sup>	1.7	7.5	7.8
12.8 x 10 <sup>-2</sup>	2.3	12.0	7.7
12.3 x 10 <sup>-2</sup> D <sub>2</sub> O	2.0	14.0	7.8
21.6 x 10 <sup>-2</sup>	1.4	6.0	8.0

a Concentrations: DNPO, 1 x 10<sup>-2</sup> mole l<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub>, 0.82 x 10<sup>-1</sup> mole<sup>-1</sup>; DPA, 4.16 x 10<sup>-4</sup> mole l<sup>-1</sup> in dimethylphthalate at 25°C.

b Time required to reach maximum chemiluminescent light intensity.

c Time required for the light intensity to decrease one quarter of its maximum value.

d Based on DNPO.

TABLE IX

The Effect of Several Fluorescers on DNPO Chemiluminescence<sup>a</sup>

Fluorescer	Initial Concentration [moles liter <sup>-1</sup> x 10 <sup>4</sup> ]	Concentration Following Reaction [moles liter <sup>-1</sup> x 10 <sup>4</sup> ]	Emission Maximum [mμ]	<sup>t</sup> I max. <sup>b</sup> [min.]	<sup>t</sup> <sub>1/4</sub> I max. <sup>c</sup> [min.]	Quantum Yield <sup>d</sup> [einstein mole <sup>-1</sup> x 10 <sup>2</sup> ]
DPA	4.16	f	430	0.1	9.0	7.9
DPA <sup>e</sup>	4.16	f	430	1.3	7.2	7.9
Rubrene	4.16	f	560	<0.2	1.3	10.0
Rubrene <sup>e</sup>	4.16	f	560	0.2	1.5	10.4
Calcofluor <sup>®</sup> Yellow HEB	4.16	0.71	515	0.1	5.5	3.2
Calcofluor <sup>®</sup> Yellow 6G	4.16	2.05	510	0.1	4.5	3.0
Calcofluor <sup>®</sup> Yellow 7G	4.16	0.94	510	0.1	3.0	3.8
Calcofluor <sup>®</sup> Yellow 7G 8	4.16	f	510	0.5	5.0	5.6

Footnote on next page.

FOOTNOTES FOR TABLE IX

- a Concentration of reactants: DNPO =  $1 \times 10^{-2}$  mole  $l^{-1}$ ;  $H_2O_2$  = 0.1 mole  $l^{-1}$  in dimethylphthalate solvent at 25°C.
- b Time required to reach maximum chemiluminescent light intensity.
- c Time required for the light intensity to decrease to one quarter of its maximum value.
- d Based on DNPO
- e The  $H_2O_2$  concentration was  $2.05 \times 10^{-2}$  mole liter $^{-1}$ .
- f Not determined.
- g The  $H_2O_2$  concentration was  $1.0 \times 10^{-2}$  moles liter $^{-1}$ .

Results showing the effect of DPA concentration on light intensity and lifetime are summarized in Table X and Figure V. The data indicate that at DPA concentrations below  $4 \times 10^{-4}$  mole liter<sup>-1</sup> the quantum yield decreases substantially. However, in the higher concentration range no significant variation of the quantum yield was observed. As indicated in Figure V a higher decay rate was observed below  $4 \times 10^{-4}$  mole l<sup>-1</sup> DPA than in the higher concentration range. The higher decay rate observed at low DPA concentration suggests that under those conditions fluorescer consumption decreases the quantum yield as the reaction proceeds.

Results indicating the effect of Calcofluor 7G<sup>®</sup> concentration on the chemiluminescence at low hydrogen peroxide concentration are summarized in Table XI. The quantum yield is significantly lower at concentrations below  $4 \times 10^{-4}$  mole l<sup>-1</sup> than in the range of  $4 \times 10^{-4}$  -  $10 \times 10^{-4}$  mole l<sup>-1</sup>, where it is essentially constant. The constant quantum yield above  $4 \times 10^{-4}$  molar fluorescer indicates that fluorescer consumption is relatively small at low hydrogen peroxide concentrations.

#### Bis[4-cyanophenyl]oxalate [CPO]

The CPO-hydrogen peroxide-DPA chemiluminescent system has been examined briefly to provide the results summarized in Table XII and Figure 1. These data indicate that CPO chemiluminescence can be efficient and very long lived. Thus a quantum yield of 9% was obtained in the absence of water and triethylamine. Furthermore, the light emission was fairly evenly distributed during the 3 hours chemiluminescent life time as indicated by the decay curve in Figure VI. The long lifetime of course results in low light intensities. Initial attempts to increase the rate of the chemiluminescent reaction by the addition of water or triethylamine have lead to a decrease of both lifetime and quantum yield.

TABLE X

The Effect of DPA Concentration on the DNPO Chemiluminescence<sup>a</sup>

<u>DPA Concentration</u> [moles liter <sup>-1</sup> ]	<u>t<sub>Imax.</sub></u> <sup>b</sup> [min.]	<u>t<sub>1/4 Imax.</sub></u> <sup>c</sup> [min.]	<u>Quantum Yield</u> <sup>d</sup> [einstein mole <sup>-1</sup> x 10 <sup>2</sup> ]
1 x 10 <sup>-4</sup>	3.0	8.5	3.2 <sup>e</sup>
4.16 x 10 <sup>-4</sup>	2.75	18.0	8.6
7.5 x 10 <sup>-4</sup>	2.5	15.5	9.1
10 x 10 <sup>-4</sup>	3.0	17.0	8.6

a Concentration of reactants: DNPO = 1 x 10<sup>-2</sup> mole l<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub> = 0.836 x 10<sup>-1</sup> mole l<sup>-1</sup> in dimethylphthalate containing 0.9 x 10<sup>-2</sup> mole l<sup>-1</sup> water at 25°C.

b Time required to reach maximum chemiluminescent light intensity.

c Time required for the light intensity to decrease to one quarter of its maximum value.

d Based on DNPO

e All DPA was consumed by the end of the reaction.



TABLE XI

The Effect of Calcofluor Yellow 7G<sup>®</sup> Concentration on the  
DNPO Chemiluminescence<sup>a</sup>

<u>Calcofluor Yellow 7G<sup>®</sup> Concentration [mole l<sup>-1</sup>]</u>	<u>t<sub>I</sub> max.<sup>b</sup> [mi..]</u>	<u>t<sub>1/4 I</sub> max.<sup>c</sup> [min.]</u>	<u>Quantum Yield<sup>d</sup> [einstein mole<sup>-1</sup> x 10<sup>2</sup>]</u>
1.0 x 10 <sup>-4</sup>	0.7	3.75	2.2
4.16 x 10 <sup>-4</sup>	0.6	6.5	5.7
7.5 x 10 <sup>-4</sup>	0.4	4.0	5.7
10 x 10 <sup>-4</sup>	0.5	5.0	5.6

a Concentration of Reactants: DNPO = 1 x 10<sup>-2</sup> mole l<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub> = 1.68 x 10<sup>-2</sup> mole l<sup>-1</sup> in dimethylphthalate containing 9 x 10<sup>-3</sup> mole l<sup>-1</sup> water at 25°C.

b Time required to reach maximum chemiluminescent light intensity.

c Time required for the light intensity to decrease to one quarter of its maximum value.

d Based on DNPO.

TABLE XII

Chemiluminescence of bis[4-cyanophenyl]oxalate [CPO] <sup>a</sup>

<u>Water</u> <u>[mole l<sup>-1</sup>]</u>	<u>Triethylamine</u> <u>[mole l<sup>-1</sup>]</u>	<u>t<sub>I</sub> max.<sup>b</sup></u> <u>[min.]</u>	<u>t<sub>1/4 I</sub> max.<sup>c</sup></u> <u>[min.]</u>	<u>Quantum Yield<sup>d</sup></u> <u>[einstein mole<sup>-1</sup> x 10<sup>2</sup>]</u>
None	None	5.5-260 <sup>e</sup>	100	9.3
0.4	None	5.0	165	2.9
None	1 x 10 <sup>-3</sup>	0.2	1.5	2.8

a Concentration of Reactants: CPO =  $3.3 \times 10^{-4}$  mole l<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub> = 0.1 mole<sup>-1</sup>; DPA =  $5 \times 10^{-4}$  mole l<sup>-1</sup> in dimethylphthalate at 25°C.

b Time required to reach maximum chemiluminescent light intensity.

c Time required for the light intensity to decrease to one quarter of its maximum value.

d Based on CPO.

e There are two maxima.

FIGURE V  
THE EFFECT OF DPA CONCENTRATION ON THE DNPO CHEMILUMINESCENT LIGHT INTENSITY AND LIFETIME IN DIMETHYLPHTHALATE

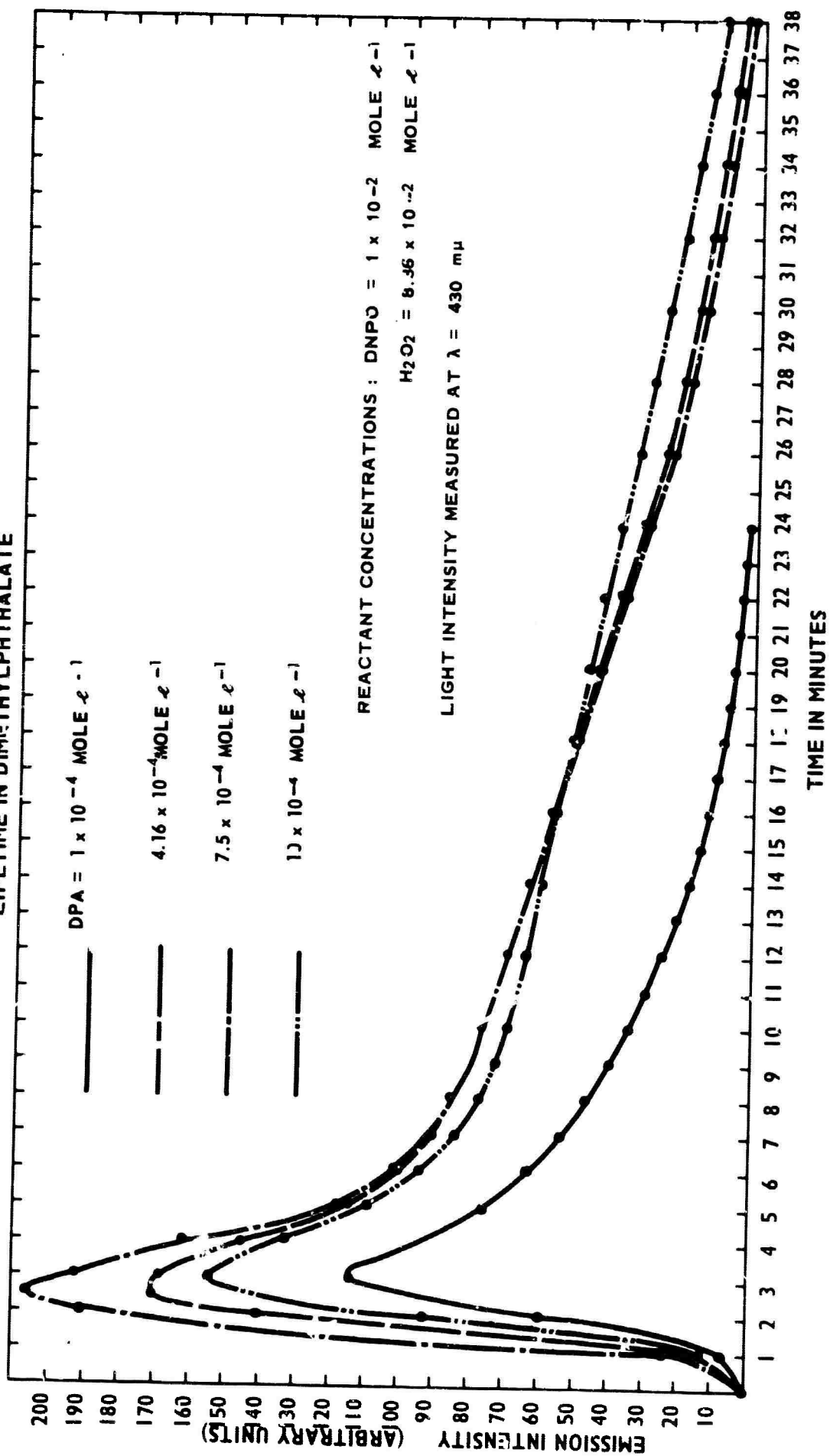
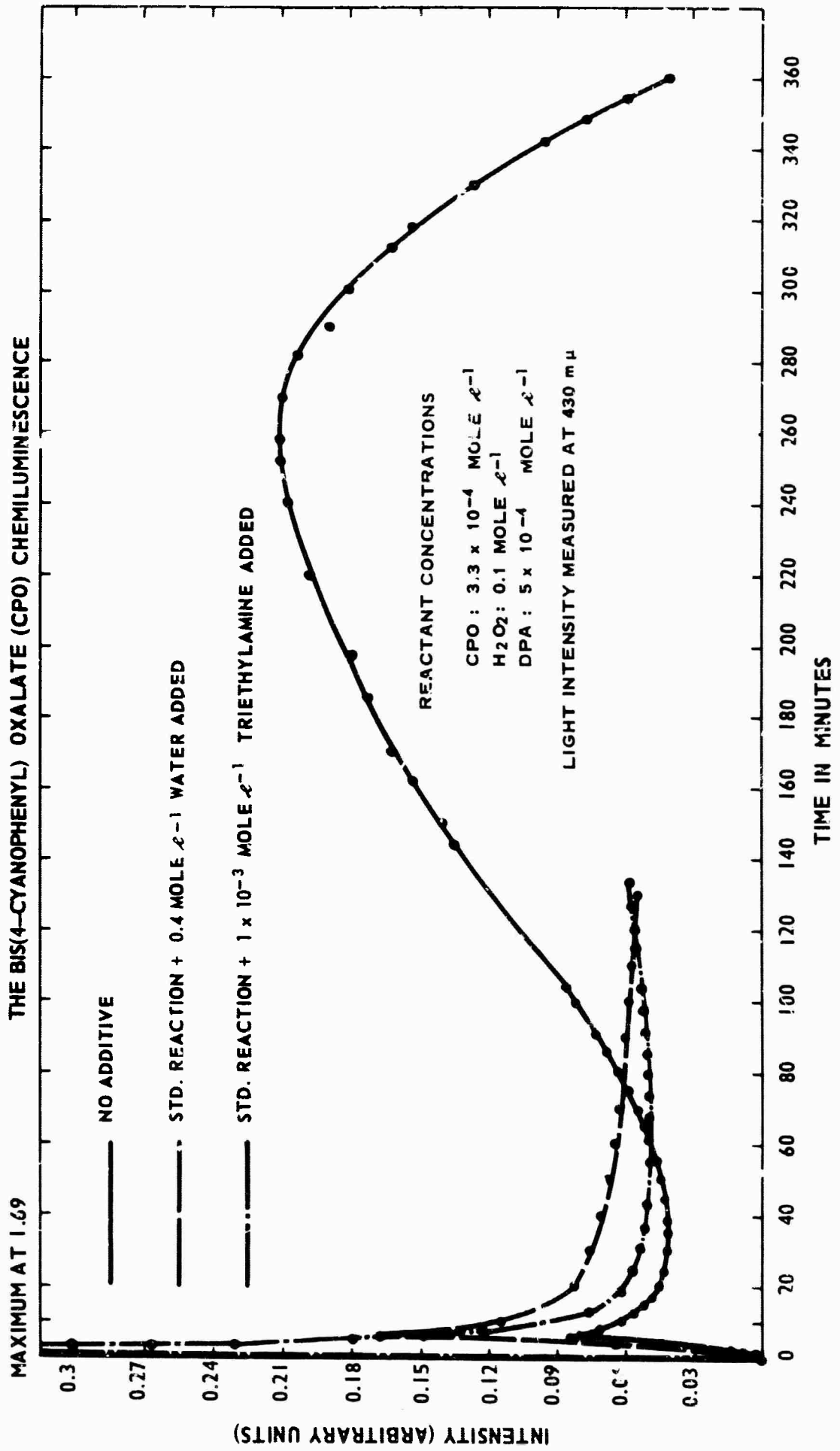


FIGURE VI  
THE BIS(4-CYANOPHENYL) OXALATE (CPO) CHEMILUMINESCENCE



Bis[4-nitrophenyl]oxalate [NPO]

The chemiluminescence of NPO-hydrogen peroxide-DPA system was examined, and the results are shown in Table XIII. In the absence of water the quantum yield was slightly less than 1%, however, it was almost doubled by the addition of 0.4 mole  $l^{-1}$  water. The lifetime of the chemiluminescent reaction, and the general shape of the decay curve appeared to be similar to that of DNPO discussed above. But the available chemiluminescent light intensity is 5-10 times lower than from the DNPO system. A further drawback of this system lies in the very poor solubility of NPO in organic solvents.

TABLE XIII

Chemiluminescence of bis[4-nitrophenyl]oxalate [NPO]<sup>a</sup>

<u>Hydrogen Peroxide</u> <u>[mole l<sup>-1</sup>]</u>	<u>Water</u> <u>[mole l<sup>-1</sup>]</u>	<u>t<sub>I</sub> MAX.<sup>b</sup></u> <u>[min.]</u>	<u>t<sub>1/4</sub> I MAX.<sup>c</sup></u> <u>[min.]</u>	<u>Quantum Yield<sup>d</sup></u> <u>[einstein mole<sup>-1</sup> x 10<sup>2</sup>]</u>
0.4	None	14	44	0.91
0.4	None	12	35	0.93
0.4	0.4	10	27	1.56
0.1	0.4	8	60	1.68

a Concentration of Reactants: NPO =  $6.67 \times 10^{-4}$  mole l<sup>-1</sup>; DPA =  $3.3 \times 10^{-4}$  mole l<sup>-1</sup> in dimethylphthalate solvent at 25°C.

b Time required to reach maximum light intensity.

c Time required for the light intensity to decrease to one quarter of its maximum value.

d Based on NPO.

SECTION I

Experimental

Bis[2,4-dinitrophenyl]oxalate [DNPO]. - The procedure described earlier<sup>7,9</sup> was modified for larger scale preparation. 2,4-Dinitrophenol [368.2 g., 2 moles] was dissolved in 4 liters of reagent grade benzene in a 5 liter-three necked flask equipped with a stirrer. The solution was dried by azeotropic distillation of 1 liter of solvent. [A smaller amount [3 liter] of benzene is sufficient when a Dean-Stark apparatus is used for the azeotropic distillation.]

The dried solution was cooled to 10°C under a nitrogen atmosphere. With good stirring, 202.4 g., [2 moles] of freshly distilled triethylamine was added, followed by the addition during 30 minutes of 139.6 g. [1.2 moles] of oxalyl chloride. The temperature was maintained between 10-25°C by cooling during the addition.

The thick yellow slurry was stirred for an additional 3 hours at 25°C and was evaporated to dryness under reduced pressure. The dry residue was stirred well with 1 liter of reagent grade chloroform. The insoluble ester was filtered on a sintered glass funnel, washed twice with 500 ml. portions of chloroform and dried under vacuum. The product was dissolved in 600 ml. nitrobenzene at 100° and crystallized at 5°C. After washing five times with 150 ml. portions of chloroform to remove nitrobenzene, the product was dried under vacuum to obtain 151.3 g. [35.8%] of pale yellow crystals, m.p. 189-92°C.

Oxalic esters prepared by the procedure described for DNPO above are summarized below.

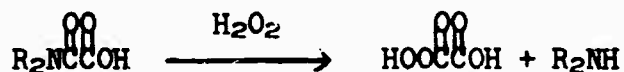
Solvents Used for the Recrystallization of Crude Oxalic Esters<sup>a</sup>

bis[2-nitrophenyl]oxalate	methylene chloride
bis[2,5-dinitrophenyl]oxalate	nitrobenzene
bis[2-methyl-4,6-dinitrophenyl]oxalate	benzene-petroleum ether [1:1]
bis[3-trifluoromethyl-4-nitrophenyl]-oxalate	methylene chloride
bis[pentafluorophenyl]oxalate	methylene chloride
bis[2,4-dinitro-1-naphthyl]oxalate	nitrobenzene-hexane [1:2]
bis[1,6-dinitro-2-naphthyl]oxalate	not recrystallized but washed with hot chlorobenzene then with methylene chloride
bis[2,2,2-trifluoroethyl]oxalate	distilled 44-45°C/1.8mm. Hg

<sup>a</sup> All solvents used were reagent grade.

SECTION IIOXALIC AMIDES

The substantial chemiluminescence observed from electro-negatively-substituted oxalic esters in reactions with hydrogen peroxide and fluorescent compounds has encouraged us to examine selected oxamides and oxamic acids for chemiluminescence. Although in general, amides are less hydrolytically active than esters,<sup>11</sup> it seemed possible that active amides,<sup>12</sup> in particular amides electronegatively substituted on nitrogen, would show sufficient hydrolytic activity to accommodate the general peroxy-oxalate chemiluminescence mechanism. Oxamic acids, moreover, might offer a direct route to monoperoxyoxalic acid by reaction with hydrogen peroxide and thus provide increased efficiency.

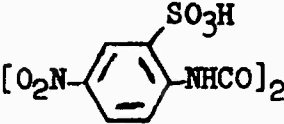
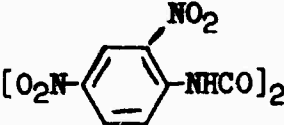
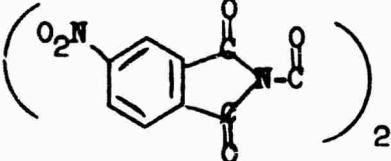
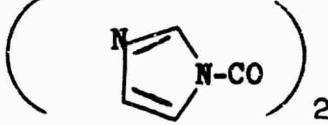


Oxamic acids might also be suitable for use in an aqueous chemiluminescence system.

Preliminary experiments have been carried out with the compounds in Table I. As indicated in the table, chemiluminescence was observed from compounds IV through VII. The results with compounds III, VI, and VII, however, are only tentative since these materials have not yet been entirely characterized. It appears from these preliminary results that chemiluminescence can be obtained from oxamides derived from relatively acidic amine and imides, but not from oxamides prepared from less acidic amines such as diphenylamine. Base catalysis is evidently required; chemiluminescence was not observed under neutral or acidic conditions.



TABLE I

<u>Compound</u>	<u>Structure</u>	<u>Tests</u>	<u>Chemiluminescence</u>
I	$[\text{C}_6\text{H}_5]_2\text{NCOCO}_2\text{H}$	A and B	None
II	$[(\text{C}_6\text{H}_5)_2\text{NCO}]_2$	A and B	None
III		C	None
IV		C	Weak - 30 sec.
V	$[\text{C}_6\text{H}_5\text{SO}_2\text{NCO}]_2$ $\text{C}_6\text{H}_5$	A B	Weak - 2 hrs. None
VI		D	Weak - 45 sec.
VII		D	Weak - 15 sec.
VIII	$[\text{C}_6\text{H}_5]_2\text{NCOCO}_2\text{C}_2\text{H}_5$	A and B	None

a The tests were carried out as follows:

- A. Approximately 3-5 mg. of the amide was added to 5 ml. of anhydrous dimethylphthalate containing 1 mg. of 9,10-diphenylanthracene [DPA], 0.2 ml. of 50% potassium hydroxide and 0.2 ml. of 90% hydrogen peroxide.
- B. Approximately 3-5 mg. of the amide was added to a solution of 1 mg. DPA, 0.2 ml. of 90% hydrogen peroxide and 0.2 ml. of trifluoroacetic acid in 5 ml. of anhydrous 1,2-dimethoxyethane.
- C. Approximately 3-5 mg. of the amide was added to a solution of 1 mg. of DPA, 0.2 ml. of 90% hydrogen peroxide and 0.2 ml. of 50% potassium hydroxide in 5 ml. of anhydrous 1,2-dimethoxyethane.
- D. Same as Test 3, except no base is used.

By far the most efficient amide investigated was the oxalyl bisulfonamide V. Chemiluminescence intensities and lifetimes derived from V were investigated under a variety of conditions. The results are summarized in Table II.

As indicated in Table II, the best results in terms of intensity and lifetime were obtained with sodium carbonate in polar solvents. In future quantitative light measurements, the quantum yield of V will be determined under several sets of conditions.

TABLE II

Experiment Number	Test <sup>a</sup>	Solvent	Chemiluminescence
1	A	Tetrahydrofuran	None
2	A	Dimethylsulfoxide	None
3	A	Ethanol	None
4	A	Acetonitrile	Weak - 4 minutes <sup>b</sup>
5	A	1,2-Dimethoxyethane	None
6	B	1,2-Dimethoxyethane	Medium - 9 minutes
7	C	1,2-Dimethoxyethane	Medium - 95 minutes, then weak for 5 1/2 hrs.
8	D	1,2-Dimethoxyethane	None within 45 minutes <sup>c</sup>
9	D	1,2-Dimethoxyethane and water [4:1]	None <sup>c</sup>
10	D	1,2-Dimethoxyethane and Dimethylphthalate [1:9]	None
11	B	1,2-Dimethoxyethane and Dimethylphthalate [1:9]	Weak <sup>b</sup>
12	C	1,2-Dimethoxyethane and Dimethylphthalate [1:9]	None <sup>d</sup>
13	A	Dimethylformamide	None
14	B	Dimethylformamide	Weak - 3 minutes
15	C	Dimethylformamide	Medium - 25 minutes, then weak for 5 1/2 hrs.
16	D	Dimethylformamide	None <sup>c</sup>
17	D	Dimethylformamide and water [4:1]	None <sup>e</sup>

a The tests were carried out as follows:

- A. Approximately 3-5 mg. of V was added to 1 mg. of fluorescein, 0.2 ml. of 90% hydrogen peroxide and 0.2 ml. of 50% potassium hydroxide in 5 ml. of solvent.
- B. The same as A, except 0.2 ml. of 5% potassium hydroxide was used.
- C. The same as A, except 0.2 ml. of 10% sodium carbonate was used.
- D. The same as A, except no base was used.

b The reaction occurred in a heterogeneous medium.

c Light of medium intensity was observed for 15-30 minutes when 0.2 ml. of 10% sodium carbonate was added. Lifetime of light of weaker intensity was 2-4 hours.

d Dilution with 10 ml. of 1,2-dimethoxyethane gave a weak light.

e Addition of 0.2 ml. of 10% sodium carbonate produced light of medium intensity for 2 minutes.

EXPERIMENTAL

Diphenyloxamic acid [I]. - Oxalyl chloride [5.19 g., 40  $\mu$ moles] was added portionwise to 3.35 g. [20  $\mu$ moles] of diphenylamine at 5°C, and an exothermic reaction took place. The slurry was stirred at room temperature for one hour, then poured into 100 ml. of water. The solid formed was dissolved in 50% ethyl ether-benzene and the solution was washed with water. Evaporation of the aqueous phase and recrystallization of the resulting solid from benzene gave 3.54 g. [79%] of colorless prisms, m.p. 145-147.5° [lit.<sup>13</sup>, m.p. 146°].

Tetraphenyloxamide [II] and Ethyl diphenyloxamate [VIII]. - Oxalyl chloride [5.1 g., 40  $\mu$ moles] was added portionwise to 1.69 g. [10  $\mu$ mole] of diphenylamine and an exothermic reaction took place. Within 5-10 minutes the temperature of the mixture had dropped to 30° and the mixture was then refluxed for 15 minutes. The solution was cooled and poured over 100 g. of ice. An oil formed and was triturated with ethanol to provide a solid, which was recrystallized from absolute ethanol. The yield of tetraphenyloxamide, m.p. 167-170° [lit.<sup>13</sup>, m.p. 169°] was 140 mg. Evaporation of the mother liquors afforded 1.68 g. of ethyl diphenyloxamate, m.p. 85-86.5° [lit.<sup>14</sup>, m.p. 86-87°].

bis-N,N'-Benzenesulfonyloxanalide [V]. - The oxanalide was prepared from benzenesulfonanilide and oxalyl chloride according to the procedure described by Mustafa and Ali.<sup>15</sup>

2,2'-[oxalyl(dimino)]bis[5-nitrobenzenesulfonic] acid [III]. - To a mixture of 18.6 g. [0.1 mole] of 4-nitroaniline-2-sulfonic acid, 75 ml. of pyridine and 75 ml. of benzene was slowly added 12.6 g. [0.1 mole] of oxalyl chloride. A solid product was obtained having an infrared spectrum different from the starting aniline. The product decomposed when an attempt was made to recrystallize it from pyridine.

2,2',4,4'-Tetranitrooxanilide [IV]. - Oxalyl chloride [20 ml., 0.23 mole] was added dropwise to 100 ml. of dimethyl formamide [DMF] at 25° to form a ten slurry. A solution of 18.3 g. [0.1 mole] of 2,4-dinitroaniline in 50 ml. of DMF was added over 30 minutes to the slurry at room temperature. After stirring for three hours the reaction mixture was poured into 400 ml. of ice-water mixture. The solution was filtered to obtain 18.7 g. of yellow crystals. After recrystallization from ether the product, m.p. dec. at 135° and 168° melting 171-174°; infrared, 2.90 [W], 3.0 [S] and 5.86  $\mu$  [VS]. Anal.: Calcd for C<sub>14</sub>H<sub>8</sub>N<sub>6</sub>O<sub>10</sub>: C, 40.00; H, 1.92; N, 20.00. Found: C, 39.70; H, 2.40; N, 19.94.

Bis[4-nitrophthalyl]oxamide [VI]. - To a mixture of 15 ml. [0.11 mole] of triethylamine, 19.2 g. [0.1 mole] of 4-nitrophthalimide and 100 ml. of benzene was added dropwise over 10 minutes 6.35 g. [0.05 mole] of oxalyl chloride. The reaction mixture was filtered and the collected solids were washed several times with water. A small portion of the solid was recrystallized from ethyl acetate benzene. A product was obtained having an infrared spectrum in agreement with that expected for the desired amide. The material gave a positive chemiluminescent test when 5 mg. was added to a mixture of 5 ml. of 1,2-dimethoxyethane, 0.2 ml. of 90% hydrogen peroxide and 3-5 mg. DPA. An attempt to recrystallize a large amount of the product from pyridine gave only a negligible amount of triethylamine hydrochloride.

di-1-Imidazolylglyoxal [VII]. - To a suspension of 13.6 g. [0.2 mole] of imidazole in 100 ml. of benzene was added 6.35 g. [0.05 mole] of oxalyl chloride. The liquid portion of the reaction mixture was decanted, leaving a large amount of gummy yellow solid. This gum was extracted with 1,2-dimethoxyethane. The solvent was removed on the rotary evaporator, leaving a heterogeneous yellow salt-like solid, which became colorless on standing. The infrared spectrum of the colorless material was different from that of the yellow solid. Due to the instability of the yellow solid characterization could not be completed, although the infrared spectrum appears to be in agreement with that expected for the desired product. The product produces a bright brief flash of light when added to a mixture of 5 ml. of 1,2-dimethoxyethane, 0.2 ml. of hydrogen peroxide and 3-5 mg. of DPA.

SECTION III

Chemiluminescent Autooxidation

Two approaches toward the development of efficient chemiluminescent autooxidation reactions are being examined. The first requires a rapid reaction of oxygen with glyoxalic acid or a dialkoxyacetic acid to give monoperoxyoxalic acid.<sup>9</sup>

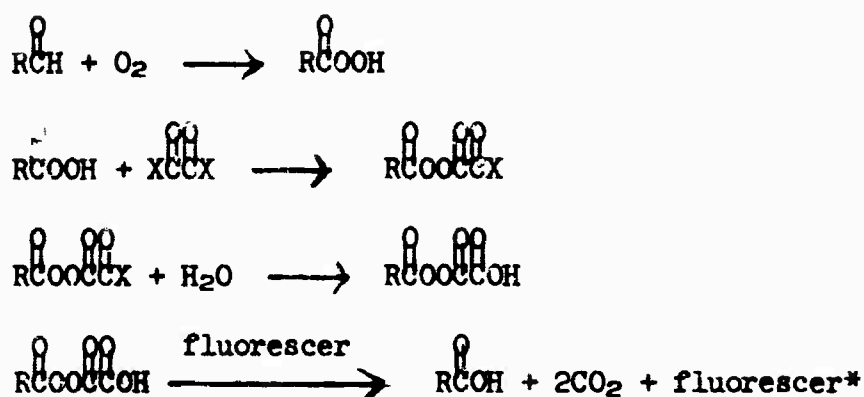


The second approach requires the rapid formation of a hydroperoxide in the presence of a chemiluminescent oxalate and a fluorescer.

Attempts to provide chemiluminescence by autooxidizing glyoxalic acid or dimethoxyacetic acid have given poor results. The results of a series of qualitative tests for chemiluminescence are summarized in Table I. Chemiluminescence was not observed under conditions which have been shown to be active for related autooxidations.

The rate at which glyoxylic acid and its dimethyl acetal are autooxidized under such conditions were determined by measuring the rate of oxygen uptake in a Wiberg apparatus.<sup>16</sup> The results summarized in Table II show that autooxidation is too slow for reasonable light intensities to be possible.

The second approach is illustrated by the equations below.







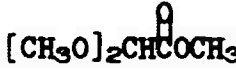
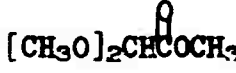
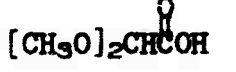
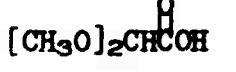


Since chemiluminescence is obtained under appropriate conditions from reactions of peroxyacids and other hydroperoxides with chemiluminescent oxalate derivatives, the formation of peroxides in such systems might be expected to provide chemiluminescence.

This approach has been investigated in a preliminary way by autooxidizing several aldehydes, phenylhydrazones and a sulfinic acid in the presence of DNPO and a fluorescer, and observing the systems for chemiluminescence. The qualitative results, summarized in Table III, indicate that weak chemiluminescence can be obtained from benzaldehyde, and two hydrazones under conditions where autooxidation is known to produce hydroperoxides. The weak light intensities, however, indicate that substantially better conditions must be found.

TABLE I

Tests for Chemiluminescence from Glyoxylic Acid and Dimethoxy  
Acetic Acid

<u>Reactant</u>	<u>[Moles/l x 10<sup>2</sup>]</u>	<u>Solvent</u>	<u>Additive</u>	<u>Result</u>
	1.84	DMSO <sup>a</sup>	KOBu <sup>t</sup> [6.0 x 10 <sup>-2</sup> M]	0 <sup>b</sup>
	2.0	HMPA <sup>c</sup>	KOBu <sup>t</sup> [6.0 x 10 <sup>-2</sup> M]	0 <sup>d</sup>
	2.0	EtOAc <sup>e</sup>	Co <sup>++</sup> [8.0 x 10 <sup>-4</sup> M]	0 <sup>a</sup>
	8.0	H <sub>2</sub> O	Co <sup>++</sup> [8.0 x 10 <sup>-4</sup> M]	0 <sup>b</sup>
	20	HOAc	Co <sup>++</sup> [4 x 10 <sup>-3</sup> M]	0 <sup>a</sup>
	8.0	tBuOH		0 <sup>a</sup>
	70	EtOAc	Co <sup>++</sup> [5.0 x 10 <sup>-4</sup> M]	0 <sup>a</sup>
	24	HMPA	KOBu <sup>t</sup> [7.2 x 10 <sup>-1</sup> M]	0
	8.0	HMPA	KOBu <sup>t</sup>	0 <sup>b</sup>
	20	HOAc	Co <sup>++</sup> [4 x 10 <sup>-3</sup> M]	0 <sup>a</sup>

a DMSO is dimethylsulfoxide

b 5.0 x 10<sup>-4</sup> M rubrene was present as fluorescer.

c HMPA is heptanethylphosphoramide

d 5.0 x 10<sup>-4</sup> M disodium fluorescein was present as fluorescer

e EtOAc is ethyl acetate.



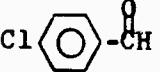
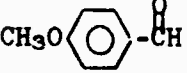
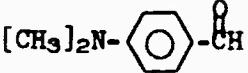
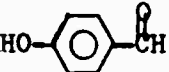
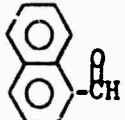
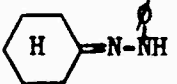
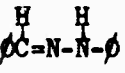
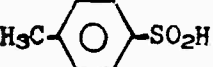


TABLE II

<u>Compound</u>	<u>[moles/l x 10<sup>2</sup>]</u>	<u>Solvent</u>	<u>Base</u>	<u>Catalyst</u>	<u>Rate</u> <u>[moles l<sup>-1</sup> sec<sup>-1</sup>]</u>
Luminol <sup>a</sup>	0.40	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	9.80 x 10 <sup>-4</sup>
[CH <sub>3</sub> O] <sub>2</sub> CHCOH	24	HMPA	KOBut		2.53 x 10 <sup>-7</sup>
HOCC <sub>4</sub> H <sub>9</sub>	8	DMSO	KOBut		13.06 x 10 <sup>-7</sup>
HOCC <sub>4</sub> H <sub>9</sub>	8	H <sub>2</sub> O		Co <sup>++</sup>	1.41 x 10 <sup>-7</sup>

a Rate of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> oxidation of luminol provided for comparison.<sup>2</sup>

TABLE III

Aldehyde	DNPO = $5 \times 10^{-3}$ M		DPA = $10^{-3}$ M	
	Conc. [mole/l]	Solvent	Catalyst <sup>a</sup>	Result
	$10^{-2}$	EtOAc	Co <sup>++</sup>	Weak
	$10^{-2}$	ØH	Co <sup>++</sup>	Weak
	$10^{-2}$	EtOAc	Co <sup>++</sup>	None
	$10^{-2}$	ØH	Co <sup>++</sup>	None
	$10^{-2}$	EtOAc	Co <sup>++</sup>	None
	$10^{-2}$	ØH	Co <sup>++</sup>	None
	$10^{-2}$	EtOAc	Co <sup>++</sup>	None
	$10^{-2}$	ØH	Co <sup>++</sup>	None
	$10^{-2}$	EtOAc	Co <sup>++</sup>	None
	$10^{-2}$	ØH	Co <sup>++</sup>	None
	$10^{-2}$	EtOAc	Co <sup>++</sup>	None
	$10^{-2}$	ØH	Co <sup>++</sup>	None
	$10^{-2}$	ØH	--	None <sup>a</sup>
	$5 \times 10^{-3}$	ØH	--	Weak <sup>b</sup>
	$5 \times 10^{-3}$	ØH	--	Weak <sup>b</sup>
	$5 \times 10^{-3}$	ØH	--	Weak <sup>c</sup>
	$10^{-2}$	ØH	--	Weak
	$10^{-2}$	ØH	--	None <sup>a</sup>
	$10^{-2}$	EtOAc	--	None

<sup>a</sup> No DNPO present

<sup>b</sup> 0.5 g. naphthaldehyde present

<sup>c</sup> 0.5 g. anisaldehyde present

SECTION III

Experimental

Sodium Salt of Glyoxylic Acid Dimethyl Acetal [Sodium Dimethoxy Acetate]. - Dichloro acetic acid [130.0 g., 1.01 mole] was added to 3.0 moles of sodium methoxide [freshly prepared from 69 g. [3.0 g.-atoms] of sodium metal and 620 ml. of anhydrous methanol] at a rate which maintained gentle reflux [50 min.] The reaction mixture was refluxed for 20 hours, cooled to 0-5°C, and neutralized with CO<sub>2</sub> gas. Evaporation of the clear filtrate obtained by removal of the solids left a sticky mass which was boiled with 300 ml. of 1:1 hexane-trichloroethylene for 1 hour to give 116 g. [82%] of a white solid which had an IR spectrum in agreement with the assigned structure.

A 3.0 g. sample was crystallized from a mixture of 35 ml. of tertiary butanol and 15 ml. of methanol to obtain an analytical sample m.p. > 250°C.

Calculated for C<sub>4</sub>H<sub>7</sub>O<sub>4</sub>Na: C, 33.81; H, 4.97; Na 16.18.  
Found: C, 31.71; H, 4.99; Na, 16.31.

An NMR spectrum of the compound was taken in D<sub>2</sub>O and showed -CH at 4.60  $\sigma$  and -OCH<sub>3</sub> at 3.33  $\sigma$ . The proton ratio CH/CH<sub>3</sub> was 1/6, in agreement with the assigned structure.

Cyclohexanone phenyl hydrazone and benzaldehyde phenyl hydrazone were prepared by literature procedures.<sup>17</sup> The sodium salt of glyoxylic acid dimethyl acetal is reported above. All other materials were from commercial sources and were purified by crystallization or distillation prior to use.

Autooxidation rates were determined by the Warburg technique.<sup>16</sup> The rate of oxygen uptake in a constant volume apparatus at 29.2°C was followed by the change in pressure with time. Chemiluminescence experiments were conducted in an oxygen filled 500 ml. glass stoppered erlenmeyer flask in the dark, the flask being shaken vigorously for 3-5 minutes to insure maximum oxygen absorption.

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. American Cyanamid Company "Chemiluminescent Materials" Technical Report No. 8, Contract Nonr 4200[00].
9. American Cyanamid Company "Chemiluminescent Materials" Technical Report No. 9, Contract Nonr 4200[00].
10. G. J. Karabatsos, J. M. Corbett and K. L. Krumel, J. Org. Chem., 30, 689 [1965].
11. E. E. Reid, Am. Chem. J., 21, 284 [1899]; 24, 397 [1902]. I. Meloche, K. J. Laideer, J. Am. Chem. Soc., 73, 1712 [1951]. A Bruylants and F. Kezdy, Rec. Chem. Prog., 21, 213 [1960].
12. H. A. Staab, Chem. Ber., 89, 1927, 288 [1956]; 90, 1320, 1326 [1957].
13. R. Stolle, Ber., 46, 3915 [1913].
14. P. A. Petyunin and V. S. Shklyayev, Zhur. Obshchei Khim., 27, 731 [1957]: C.A. 51:155523C.
15. A. Mustafa and M. I. Ali, J. Am. Chem. Soc., 79, 1945 [1957].
16. W. W. Umbreit, R. H. Burris, and J. F. Stauffer, "Manometric Techniques" 4th Edition, Burgess, Minneapolis, Minnesota, 1964.
17. A. I. Vogel, "Practical Organic Chemistry," Longmans, London, 1959, p. 343, 720.