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SUMMARY

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.

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-<u>t</u>-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.

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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⁻¹ 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.

$$I = \frac{\int T = \infty}{\int T = 0 \quad Idt}$$

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

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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 peroxyoxalate 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 sater [5] determine the effects of reaction conditions on light capacities and lifetimes [6] modify the system to accommodate air-activation and [7] to provide efficient, stable fluorescers with high photopic constants.

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SECTION I

OXALIC ESTERS

Preparation and Qualitative Evaluation of Oxalic Esters

In the previous report9, 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 cubstituents 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 illucidate 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.^{7,9} 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 ifficult on the basis of qualitative visual observations, the most promising

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							itary Analysis				Infrare	d: c = 0	Stretching M	requencies (ca	(1-1)	
	PT-IX	ж.Р. С	kal. Vt.	Calrd. Pou		H: d. Pound	E: Calcd. Found	0: Caled. Found	r: Calcd. Pound	Solid In Mujol	Bolvent		ntenaity		Latensity	
1 Bis(2-mitrophenyl)comlate	36	186.4	332 .1 6	50.61 50.	90 2.43	2.61	05°8 E4°8	38.53 36.75		1778	CH2C12	1804	٥.11	1281	0.20	
	¥.	t un	. 81 664	a A	- - 3	69 I	86 of 70 ft			1787	Hore	18cm	8 0	1789		
	ŝ	(dac)	9	-n- co-40		Co-1				1014	5 a-2-a		8		4	
3 Bis($\frac{1}{2}$, 1	%	190.7 190	450.3	42.68 42.	56 2°54	2.23	12.44 12.64			1111	cttec1 ₂	1812	0.03	1788	0 .0 6	
$\begin{array}{c} \begin{array}{c} \begin{array}{c} & & & & \\ \underline{b} \\ \underline{c} \\ \underline{c} \\ \underline{c} \\ \underline{c} \\ \underline{c} \end{array} \end{array} = \begin{array}{c} \begin{array}{c} & & & \\ \underline{c} \\ \underline{c} \\ \underline{c} \\ \underline{c} \end{array} \end{array} = \begin{array}{c} \begin{array}{c} & & \\ \underline{c} \\ \underline{c} \\ \underline{c} \\ \underline{c} \end{array} \end{array} = \begin{array}{c} \begin{array}{c} & & \\ \underline{c} \\ \underline{c} \\ \underline{c} \end{array} \end{array}$	735	186-9	468.24	14 40°14	5 1. 29	1.37	5.98 6.23	46.75	24.35 24.45	1779	CH2C12	1001	0.0	1780	£ 1. 0	
2 Bis (penterlinorophuny1) craites r r r r r r r r r r	24 24 2	170-2	21.234	39-63 39-6	1	ł		15.16	12.44 10.24	1793	"ເວ	1820	60.0	1794	0.27	
$\underline{6} Bis(2, 4-1611 \text{ tro-1-mapirizy1}) \text{ commate}$	X	199- (602) (dec.)		50.58 50.	36 1.95	2.18	æ.01 20.96			1793	⁶ нэ ² он	1789	60°0	1763	01.0	-)-
I Biell's dinitro-2-mapting localete	ě	239-42 (dec.)	¥2.36	50-59 50-0	1.93	2.09	ez.ut 27.ut	। ह.स.		1784	Ю2 ^{сн} 3	17.88	0.08	1766	90 °0	
E Bia(t-buty1)constate (CH ₃) ₃ -c-2 ² L ² -o-c-(CH ₃) ₃	<u>8</u>	70-71	202.25	59.39 55.	ы 8.97	8.81				1762 e bou	lder CC14	1763	0.50	1736	°.62	
2 Bis(2,5,2-trifluoroethy1)calate cf ₃ -ch ₂ -o-E-B-O-cH ₂ -cF ₃	****	8.P. 44-45 at 1.8	1.42	28.36 28.	50 1.5 8	1.53			06.44 39. 44	262.1 202.1	[†] roo .	1802	0.25	7774	0.57	

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 14. 3.p., 69-70.9%.

TABLE II

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<u>quaiitative</u> ch	emii uminescento i	Test	s ⁸	
	A [anhvd. H2O2]	B [H=0= + KOH]	C [H=0= + H=0]	D [H=0= + H=0 ⁺]
	M	VS	M	None
	Sp	S -V S	М	None
O ₂ N CH ₃ 2	S	S	MW	W
	sb	vs	W-M	None
	S	VS	М	None
	Ŵ	M	Ŵ	Ŵ
	M-MS	M-MS	Vw-w	None
([CH ₃] ₃ -C-0-Č-) ₂	None	None	None	None
[CF3-CH2-0-C-]2	None	W	None	None

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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 <u>A</u> 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. CH₃SO₃H in 1,2-dimethoxy-sthane containing 5% water and maintained at 25°C. About 0.5 ml. 30% H₂O₂ is added immediately.

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

[b] A brief induction period was observed.

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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.⁹ However, the final evaluation must wait until the planned quantum yield measurements are completed.

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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

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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, hexamethylphosphoremide, 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.

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TABLE III

Test of bis[2,4-dinitrophenyl]oxalate [DHPO] for Chemiluminescence in Various Solventsa

	Solubility of DNPO	Solubility of H202	Te	stab
	[moles 1-1]	[moles 1-1]		B
Acetone	>2 x 10 ⁻²	>1.0	S	8
1,2-Propylene oxide	>2 x 10 ⁻²	>1.0	VS	VS
1,2-Dimethoxyethane	> 2 x 10-2	>1.0	S	S
Dimethylcarbonate	>2 x 10 ⁻²	>1.0	S[long]	8[long]
Propylene Carbonate	>2 x 10 ⁻²	>1.0	S[long]	S[long]
Dimethylphthalate	> 2 x 10 ⁻²	>1.0	8[100g]	S[long]
Tetrahydrofuran	>2 x 10-2	>1.0	MS	MB
Hitromethane	>2 x 10 ⁻²	> 0.1	367	NG
Fther	<2 x 10 ⁻²	>0.1	8	S
Tristhylphosphate	<2 x 10 ⁻²	>0.1	8	
Perfluorokerosene	<2 x 10 ⁻²	>0.1	None	None
Kthyl perfluorooctanoate	<2 x 10 ⁻²	>0.1	None	W
Anisole		Not Soluble		
Benzene	<2 x 10 ⁻²	Not Soluble		
o-Dichlerobensepe	<2 x 10-2	Poorly Soluble	MS[long]	1
Tetralin	<1 x 10-2	~0.03	¥	
Eitrobenzeze ^C	<2 x 10-2	<1.0	101	M
Sulfolane ^C	<2 x 10 ⁻²	>1.0	MB	
Dimethylformamide ^d	> 2 x 10-2	> 1.0	S[very sh	ort] S[very
Dimethylsulfoxide	>2 x 10 ⁻²	>1.0	None	•
Hexansthylphosphoramide	>2 x 10 ⁻²	>1.0	None	
Tetramethylurea	>2 x 10 ⁻²	>1.0	None	
Chloroform	<2 x 10 ⁻²	>1.0	V,	M[long]
Methylene Chloride	<2 x 10 ⁻²	<1.0	¥	M[long]
Carbontetrachloride		Not Soluble		
Acetonitrile	<2 x 10 ⁻²	≥1.0	N	ж
t-Butyl alcohol	<2 x 10 ⁻²	> 1.0	W	W[long]
Glycerine	<2 x 10 ⁻² [deep yellow color pr	>1.9 esent]	None	None
F*'ylacetate	<2.1 10 ⁻²	> 0.1	S[short] S[short]
Diethyloxalate	≪ x 10 ⁻²	> 1.0	MB[long]
Cyclohexane	<2 x 10 ⁻²	<1.0	VV	W[long]
Chlorobenzene	<2 x 10-2	<1.0	S	VS
Pyridine	reacts with DWPO	>1.0	None	None
Acetic Acid	<'. x 10-2	>1.0	н	S[long]

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NOTES TO TABLE III

[a] The bis[2,4-dinitrophenyl]oxalate [DNPO]-hydrogen peroxide-9,10diphenylanthracene 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.

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[b] A 50 mg. DNPC was added to 5 ml. magnetically stirred solvent in a test tube. After 15 minutes the solubility of DTPO was observed. Approximately 1 mg. 9,10-diphenyls thracene was added and then sufficient 90% hydrogen peroxide was added to give either 1 mole 1- or 0.1 mole 1-1 concentration as noted. Chemiluminescence was observed in the dark, and then the solubility of hydrogen peroxide was noted.

<u>B</u> As test <u>A</u> 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.

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

	Testa
100% water	None
95% water - 5% 1,2-dimethoxyethane	VW
75% water - 25% 1,2-dimethoxyethane	W
50% water - 25% 1,2-dimethane	W
25% water - 75% 1,2-dimethoxyethane	W
0% water - 100% 1,-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⁻¹ 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 oxulate 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 featibility of using a very high concentration of liquid moderately efficient oxalic ester for chemiluminescence.

Approximate Solubilities of Oxalic Reters" (mole 1-1) V TIBAT

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	ļ	Acetone					-13-	
	rahydrofuran Dimethyl Carbonate 1,2-Fropylene Oxide							
	Disthyl Chalate Benkens Tetralin Tet	<8×10 ⁻³ <6.8×10 ⁻³ <4×10 ⁻³ ^b	««» » » » » » » » «» » «» «» «» «» «» «»	1.7 × 10 ⁻² ניו × 10 ⁻² ליו0 × 10 ⁻²	1.5 × 10° ¹ (2.8 × 10° ⁻¹ ≪ غند	1.2 × 10 ⁻² 2 × 10 ⁻² 1 × 10 ⁻²		⁵⁻ 01 × 4 > ⁵⁻ 01 × 1.5 > ⁵⁻ 01 × 1.5 >
	Dioctylphthelate	≪ 1.4 ± 10 ⁻²	⁴⁻ 01 x 9.1≫	<1.0 × 10 ⁻²	k z 10−5	<7 × 10 ⁻³		<2,2 × 10 ⁻³
ol ve nte	Dimethyladipate	2-01 x 1.1>	qnµ_ot × s≫	3,6 x 10 ^{-2 b}	2.4 x 10-2	8 x 10 ⁻²		8 ⁴⁻ 01 x 7.73
đ	1,2-Dimethoryethane	2,8 x 10 ⁻²	<5.0 x 0.3	2.8 x 10 ⁻²	4 x 10 ⁻¹	6 x 10"2		€ × 10 ⁻³
	Propylene Carbonate	1.5 × 10 ⁻²⁰	< 6.2 x 10 ⁻³	7.5 × 10 ⁻²	2.4 x 10 ⁻¹	1.7 × 10 ⁻²	⁴⁻ 01 × 8.5 <	م
	Dimethyl phthelate	€=ot = t.€>	<1.9 × 1 ⁶⁻³	3.5 x 10 ⁻²	3.1 × 10 ⁻²	<1.5 × 10 ⁻²	3.8 x .^-4	< 1.9 × 10 ⁻³
			2 (02 - 0-2) 2	² (2 ² M (2 ^{H3}) 2 ² (2 ^{H3}) 2 ²	<u><u></u></u>	2 (r) 2) 2		I and a second s

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a) Solubilities were determined by the periodic addition it 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 propyleme carbonate and 1,2-dimethoxyethume which were dried and distilled.

*

4.6 × 10-2

4.3 × 10-2

2.2 × 10-2

5 x 10⁻³ <1.0 x 10⁻² 4.7 x 10⁻²

4 × 10-2

3.7 × 10-2

2.8 x 10⁻²

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b) decomposes or reacts or hydrolyses

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Quantitative Evaluation of Aryloxalate Chemiluminescence

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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] reactart concentration, [2] alternative and suplementary reactants, [3] solve..., and [4] temperature. The qualitative measurements to date deal partially with the influence of first two variables on bis[2,4-dinitropheny1] 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 report⁹ 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 cruves 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 mample [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 repitition of experiments [1] and [2] showe_ that the semarate

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FIGURE 1



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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

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The Effect of I	mpurities on D	NPO Chemiluminesce	ncea
Additives [mole 1-1]	t _{Imax} . ^b [min.]	t _{1/4 I max.} c [min.]	Quantum Yield ^d [einstein mole-1 x 10 ²]
None ^e	6.2	26.9	7.66
None	8.0	40.7	7.19
7 x 10 ⁻⁶ triethylamine	5.0	29.6	7.42
3.7 x 10 ⁻⁴ nitrobenzene	9.0	49.5	7-45
1 x 10 ⁻³ 2,4-dinitrophenol	4.4	23.5	6.35
2.87 x 10 ⁻² 2,6-di-t-butyl- 4-methylphenol	9.2	18.0	0.37

TABLE VI

-17-

a DNPO sample [2] was used except where noted. The concentrations were DNPO, 1 x 10-2 mole 1-1; H₂O₂, 0.82 x 10-1 mole 1-1; DPA, 4.16 x 10⁻⁴ mole 1-1 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 is 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 form 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 mole 1^{-1} . At high concentrations, however, hydrogen peroxide decreased the quantum yield significantly. Thus mole ratios of from 1 to 8 moles of hydrogen peroxide:DNFO caused no large change in quantum yield, and even when somewhat less than 1 mole hydrogen peroxide per DNFO was present, the quantum yield decreased only moderately. These observations indicate that the chemiluminescent reaction requires a 1:1 hydrogen peroxide:DNFO stoichicmetry.

The hydrogen peroxide concentration, as illustrated by Figure III did not substantially effect the rate of the chemiluminescent reaction in the range of 1×10^{-2} to 8×10^{-2} mole 1^{-1} hydrogen peroxide. The reaction is slightly slower and slightly more efficient when 0.04 mole 1^{-1} hydrogen peroxide is used then 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

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The	Effect	of	Hydrogen	Peroxide	Concentration	on	DNPO
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TABLE VII

[H ₂ O ₂] [mole 1 ⁻¹]	[H2D2] [DNP0]	t _{Imax.} b [min.]	^t 1/4 I max. ^c [min.]	Quantum Yield ^d [einstein mole ⁻¹ x 10 ²]
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: 1×10^{-2} mole 1^{-1} ; DPA = 4.16 x 10^{-4} mole 1^{-1} in dimethylphthalate solution containing 9×10^{-3} mole 1^{-1} water at 25°C.

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b Time required to reach maximum chemiluminescent light intensity.

<u>c</u> 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.

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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 ⁽¹⁾ 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 ⁽²⁾ 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[®] 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

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TABLE VIII

The Effect of Water on DNPO Chemiluminescence^a

H ₂ 0 [mole 1 ⁻¹]	t _{I max.b} [min.]	t _{1/4 I max.} c [min.]	Quantum Yield ^d [einstein mole ⁻¹ x 10 ²]
0.5 x 10 ⁻²	4.8	27.5	8.2
0.9 x 10 ⁻²	3.0	17.0	8.2
2.83 x 10-2	3.0	17.0	8.1
10.6 x 10 ⁻²	1.7	7.5	7.8
12.8 x 10 ⁻²	2.3	12.0	7.7
12.3 x 10 ⁻² D ₂ 0	2.0	14.0	7.8
21.6 x 10-2	1.4	6.0	8.0

a Concentrations: DNPO, 1×10^{-2} mole 1^{-1} ; H_2O_2 , 0.82 x 10^{-1} mole⁻¹; DPA, 4.16 x 10^{-4} mole 1^{-1} 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 Chemiluminescence⁸

Fluorescer	Initial Concentration [moles liter-1 x 10 ⁴]	Concentration Following Reaction [moles liter-1 x 10 ⁴]	Emission Maximum [mu]	tI max. ^b [min.]	t _l /4 I max. ^c [min.] [e	Quantum Yield instein mole ⁻¹ x 1	સિ
DPA	کل ، ب ا	ę.,	h30	0.1	0.6	7.9	
DPA ^e	4.16	ę.	1 , 30	1.3	7.2	7.9	
Rubrene	۵۱. 4	ډې	560	<0.2	1.3	10.0	
Rubrene ^e	۵1.1	6 -1	560	0.2	1.5	10.4	
Calcofluor (C) Yellow HEB	ð ī .4	17.0	515	0.1	5•5	- <i>27</i> 2•5	-25
Calcofluor ® Yellow 6G	ک ل.4	2.05	510	0.1	4.5	3.0	_
Calcofluor Carlow 7G	ð ī. ,4	0°.94	510	0.1	3.0	3.8	
Calcofluor (1) Yellow 70 g	کل ۰4	6 4	510	0.5	5.0	5.6	

Footnote on next page.

FOOTNOTES FOR TABLE IX

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- <u>a</u> Concentration of reactants: DNP2 = 1 x 10^{-2} mole 1^{-1} ; H₂O₂ = 0.1 mole 1^{-1} in dimethylphthalate solvent at 25°C.
- b Time required to reach maximum chemiluminescent light intensity.
- <u>c</u> Time required for the light intensity to decrease to one quarter of its maximum value.
- d Based on DNPO

r.

- The H₂O₂ concentration was 2.05 x 10^{-2} mole liter⁻¹.
- f Not determined.
- <u>g</u> The H₂O₂ concentration was 1.0 x 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 4×10^{-4} mole liter-1 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 4×10^{-4} mole 1⁻¹ 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 $^{(3)}$ concentration on the chemiluminescence at low hydrogen peroxide concentration are summarized in Table XI. The quantum yield is significantly lower at concentrations below 4 x 10⁻⁴ mole 1⁻¹ than in the range of 4 x 10⁻⁴ - 10 x 10⁻⁴ mole 1⁻¹, where it is essentially constant. The constant quantum yield above 4 x 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 Figu I. 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 "T. 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.

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TABLE	Х

DPA Concentration [moles_liter ⁻¹]	t _{Imax} .b [min.]	^t 1/4 Imax. ^c [min.]	Quantum Yield [<u>einstein mole⁻¹ x 10²]</u>
$1 \times 10^{-l_{+}}$	3.0	8.5	3.2 ^e
4.16 x 10 ⁻⁴	2.75	18.0	8.6
7.5 x 10 ⁻⁴	2.5	15.5	9.1
10×10^{-4}	3.0	17.0	8.6

The	Effect	of	DPA	Concentration	On	the	DNPO	Chemiluminescence ⁸
			~ ~ ~ ~		· · · · ·	0110		

- **a** Concentration of reactants: DNPO = 1×10^{-2} mole 1^{-1} ; H₂O₂ = 0.836 x 10^{-1} mole 1^{-1} in dimethylphthalate containing 0.9 x 10^{-2} mole 1^{-1} 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.

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TABLE XI

The	Effect	of	Calcofluor	Yellow	7G 🕲	Concentration	on	the
			DNPO Chem	ilumines	cence	a		

Yellow 7G Concentration [mole 1 ⁻¹]	^t I max. ^b [mi]	^t 1/4 I max. ^c [min.]	Quantum Yield ^d [einstein mole ⁻¹ x 10 ²]
1.0 x 10 ⁴	0.7	3.75	2.2
4.16 x 10 ⁻⁴	0.6	6.5	5.7
7.5 x 10 ⁻⁴	0.4	4.0	5.7
10 x 10 ⁻⁴	0.5	5.0	5.6

 $\frac{\bar{\theta}_{1}}{2\pi}$

a Concentration of Reactants: DNPO = 1×10^{-2} mole 1^{-1} ; H₂O₂ = 1.68 x 10⁻² mole 1^{-1} in dimethylphthalate containing 9×10^{-3} mole 1^{-1} 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] a

Water _[mole 1 ⁻¹]	Triethylamine [mole 1-1]	tI max.b [min.]	^t 1/4 I max. ^c [min.]	Quantum Yield ^d [einstein mole ⁻¹ x 10 ²]
None	None	5.5-260 ^e	100	9.3
0.4	None	5.0	165	2.9
None	1 x 10-3	0.2	1.5	2.8

- a Concentration of Reactants: CPO = 3.3×10^{-1} mole 1^{-1} ; H₂O₂ = 0.1 mole⁻¹; DPA = 5×10^{-4} mole 1^{-1} 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

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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 1^{-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.

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TABLE XIII

Chemiluminescence of bis[4-nitrophenyl]oxalate [NPO]^a

Hydrogen Peroxide [mole 1 ⁻¹]	Water [mole 1 ⁻¹]	t _{I MAX.} b [min.]	^t 1/4 I MAX. ^c [min.]	Quantum Yield [einstein mole ⁻¹ x 10 ²]
0.4	None	14	1+14	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

<u>a</u> Concentration of Reactants: NPO = 6.67×10^{-4} mole 1⁻¹; DPA = 3.3×10^{-4} mole 1⁻¹ in dimethylphthalate solvent at 25°C.

b Time required to reach maximum light intensity.

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

d Based on NPO.

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SECTION I

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Experimental

<u>Bis[2,4-dimitrophenyl]oxalate [DNPO].</u> - The procedure described eurlier7,9 was modified for larger scale preparation. 2,4-Dimitrophenol [368.2 g., 2 moles] was dissolved in 4 liters of reagent grade benzene in a 5 liter-three mecked 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 triethylomine was added, followed by the addition during 30 minutes of 139.6 g. [1.7] moles] of oxalyl chloride. The temperature was maintained between 'J-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^a

distilled 44-45°C/1.8mm. Hg

his[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[pertafluorophenyl]oxalate methylene chloride nitrobenzene-hexane [1:2] bis[2,4-dinitro-l-naphthyl]oxalate bis[1,6-dinitro-2-naphthyl]oxalate not recrystallized but washed with hot chlorobenzene then with methylene chloride

bis[2,2,2-trifluoroethyl]oxalate

a All solvents used were reagent grade.

SECTION II

OXALIC AMIDES

The substantial chemiluminescence observed from electronegatively-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,¹¹it seemed possible that active amides,¹² in particular amides electronegatively substituted on nitrogen, would show sufficient hydrolytic activity to accommodate the general peroxyoxalate chemiluminescence mechanism. Oxamic acids, moreover, might offer a direct route to monoperoxyoxalic acid by reaction with hydrogen peroxide and thus provide increased efficiency.

 $\begin{array}{ccc} & & & & & & & & \\ R_2 NCCOH & & & & & & & \\ \hline & & & & & & & \\ HOOCCOH + R_2 NH \end{array}$

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.

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TABLE I

Compound	Structure	Tests	Chemiluminescence
I	[C6H5]2NCOCO2H	A and B	None
II	[(C ₆ H _{5 2} NCO] ₂	A and B	None
III	[02N-NHCO]2	С	None
IV		С	Weak - 30 sec.
V	[C6H5SO2NCO]2 C6H5	A B	Weak - 2 hrs. None
VI		D	Weak - 45 sec.
VII	(N-CO) ₂	D	Weak - 15 sec.
VIII	[C6H5]2•NCOCO2C2H5	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 percxide.
- 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 bissulfonamide 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.

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TABLE II

Experiment Number	Test ^a	Solvent Che	miluminescence
1	A	Tetrahydrofuran	None
2	Α	Dimethylsulfoxide	None
3	A	Ethanol	None
4	A	Acetonitrile	Weak - 4 minutes ^b
5	Α	1,2-Dimethoxyethane	lione
6	В	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 ^C
9	D	1,2-Dimethoxyethane and water [4:1]	None ^C
10	D	1,2-Dimethoxyethane and Dimethylphthalate [1:9]	None
11	B	1,2-Dimethoxyethane and Dimethylphthalate [1:9]	Weak ^D
12	C	1,2-Dimethoxyethane and Dimethylphthalate [1:9]	None ^d
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 ^C
17	D	Dimethylformamide and water [4:1]	None ^e

- a The tests were curried out as follows:
 - A. Approximately 3-5 mg. of V was added to 1 mg. of "luorescein, 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.

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EXPERIMENTAL

<u>Diphenyloxamic acid []</u>. Oxalyl chloride [5.19 g., 40 mmoles] was added portionwise to 3.38 g. [20 mmoles] 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.¹³,m.p. 146°].

Tetraphenyloxamide [II] and Ethyl diphenyloxamate [VIII]. -Oxalyl chloride [5.1 g., 40 mmoles] was added portionwise to 1.69 g. [10 mmole] 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.¹³, m.p. 169°] was 140 mg. Evaporation of the mother liquors afforded 1.68 g. of ethyl diphenyloxamate, 1.p. 85-86.5° [lit.¹⁴, m.p. 86-87°].

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

<u>2,2'-[oxalyldimino]bis[5-nitrobenzenesulfonic] acid [III]</u>. -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 u [VS]. Anal.: Calcd for $C_{14}H_8N_6O_{10}$: C, 40.00; H, 1.92; N, 20.00. Found: C, 39.70; H, 2.40; N, 19.94. Bis[4-nitrophthaly]]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.

<u>di-l-Imidazolylglyoxal [VII].</u> - 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 amixture 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.⁹

HOCCH \div 02 \longrightarrow HOCCOOH $\xrightarrow{\text{fluorescer}}$

$$H_20 + 2CO_2 + fluorescer*$$

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. 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.

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 $RCH + O_2 \longrightarrow RCOOH$ $R COOCCX + H_2O \longrightarrow R COOCCOH$ 0 00 fluorescer 0 RCOH + 2CO₂ + fluorescer*

Since chemiluminescence is obtained under appropriate conditions from reactions of percoxyacids 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 auotoxidation is known to produce hydroperexides. The weak light intensities, however, indicate that substantially better conditions must be found.

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Reactant	[Moles/1 x 10 ²]	Solvent	Additive	Result
носсн	1.84	DMSC ³	KOBu ^t [6.0 x 10-2M]	Ор
носсн	2.0	HMPAC	KOBu ^t [6.0 x 10 ⁻² M]	od
ро носсн	2.0	EtOAce	Co ⁺⁺ [8.0 x 10 ⁴ M]	0 a
носси	8.0	H2O	co ⁺⁺ [8.0 x 10 ⁴ #]	Op
носсн	20	HOAC	co ⁺⁺ [4 x 10-3m]	0 8
ро носсн	8.0	tBuOH		0 a
[СН30]2СНСОСН3	70	EtQAc	Co ⁺⁺ [5.0 x 10 ^{-h} M]	0 e
[CH30]2CHCOCH3	24	HDADA	$\frac{\text{KOBu}^{\text{t}}}{[7.2 \times 10^{-1} \text{M}]}$	0
[CH30]2CHCOH	8.0	HMPA	KOBut	op
CH30]SCHCOH	20	HQAC	co ^{+→} [4 x 10 ⁻³ M]	Oar

a DMSO is disethylsulfoxide <u>5.0 x 10⁻⁴ M</u> rubrene was present as fluorescer. <u>c HMPA is heptanethylphosphoramide</u> <u>d</u> 5.0 x 10⁻⁴ M disodium fluorescein was present as fluorescer <u>e EtOAc is ethyl acetate</u>.

TABLE I

Tests for Chemiluminescence from Glyoxylic Acid and Dimethoxy Acetic Acid

TABLE II

Compound	[moles/l x 10 ²]	Solvent	Base	Catalyst	Rate [moles 1 ⁻¹ sec ⁻¹]
Luminol ^a	0**0	H ₂ 0	Kacoa	KeS208	9.8c x 10 ⁻⁴
[сн _з о] _г снсон	2t	HMPA	KOBut		2.53 x 10-7
ноевн	Ø	DMSO	KOBut		13.06 × 10 ⁻⁷
ноеен	8	H ₂ 0		t+02	1.41 × 10 ⁻⁷

a Rate of K2S208 oxidation of luminol provided for comparison.²

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TABLE III

DNPG	$J = 5 \times 10^{-5} M$		$DPA = 10^{-5} M$	
Aldehyde	Conc. [mole/1]	Solvent_	Catalyst ^a	Result
øch	10 - 2	EtOAc	Co ⁺⁺	Weak
øCH	10-2	øн	Co++	Weak
C1 O-CH	10 ⁻²	EtOAc ØH	Co++ Co++	None None
снзо О-Сн	10 ⁻²	EtOAc ØH	Co++ Co++	None None
[CH3]2N- O-CH	10-2 10-2	EtQAc ØH	Co ⁺⁺ Co ⁺⁺	None None
но-О-Сн	10-2 10-2	EtOAc ØH	Co++ Co++	None None
O-BH	10-2 10-2	EtOAc ØH	Co++ Co++	None None
H N-NH	10 ⁻² 5 x 10-3 5 x 10-3 5 x 10-3	рн рн рн рн	 	None ^a Weak Weak ^D Weak ^C
H H ¢C=N-Ň-Ø	10-2 10-2	рн рн		Weak None ^a
Hac-O-SO2H	10-2	EtOAc		None

None

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 $\begin{array}{c} \underline{a} & \text{No DNPO present} \\ \underline{b} & 0.5 \text{ g. naphthaldehyde present} \\ \underline{c} & 0.5 \text{ g. anisaldehyde present} \end{array}$

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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_2 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. $> 250^{\circ}$ C.

Calculated for C4H704Na: 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_2O and showed -CH at 4.60 σ and -OCH₃ at 3.33 σ . The proton ratio CH/CH₃ was 1/6, in agreement with the assigned structure.

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

Autooxidation rates were determined by the Warburg technique.¹⁶ 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.

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