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Rauhut, M. M.; Bollyky, L. J.; Maulding, D. R.; Clarke, R. A.; Roberts, B. G.; Semsel, A. M.; Whitman, R. H.; Sandler, S.

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Results from a program designed to optimize the operating characteristics of peroxyoxalate chemiluminescent systems are reported. Efforts to prepare improved chemiluminescent oxalic acid derivatives and improved fluorescers are described. The effects of oxalate structure, fluorescer structure, and reaction variables including solvent, reactant concentrations, additives and temperature are discussed. Results of storage stability tests on component solutions are reported.

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SUMMARY

Results from a program designed to optimize the operating characteristics of peroxyoxalate chemiluminescent systems are reported. Efforts to prepare improved chemiluminescent oxalic acid derivatives and improved fluorescers are described. The effects of oxalate structure, fluorescer structure, and reaction variables including solvent, reactant concentrations, additives and temperature are discussed. Results of storage stability tests on component solutions are reported.

Of a number of new oxalate esters and amides prepared, bis(2,4,6-trichlorophenyl)oxalate (TCPO) gave superior chemiluminescence efficiencies at 0.01 molar concentration in reaction systems containing tetrabutylammonium perchlorate (TBAP). The efficiency was only moderately lower at 0.03 M TCPO concentration with the result that the best previous light capacity was more than doubled to 123 lumen-hours liter^{-1}. Rubrene is poorly stable under these conditions, however, and a more stable fluorescer will be required to take practical advantage of this result. An aliphatic oxalate ester, 1,1,1,3,3,3-hexafluoro-2-propyl oxalate, was found to provide moderately efficient chemiluminescence. Previous efficient oxalates have been aromatic derivatives.

The fluorescer 1,2-bis(phenylethynyl)anthracene was found to provide efficiencies approaching those obtained with rubrene in certain systems. A number of other fluorescers was prepared and examined, but found to be inferior.

Reaction product studies show that yields of oxygen and carbon monoxide are too low to be products of the chemiluminescent process. Carbon dioxide is the major product. A reaction intermediate has been detected by infrared spectroscopy. It absorbs at 1900 cm^{-1} as previously predicted.

Recently initiated storage stability studies indicate that TCPO solutions in benzene and solutions of hydrogen peroxide plus TBAP in dimethyl phthalate have retained initial levels of activity after eight and four weeks storage respectively at room temperature.

INTRODUCTION

In this report we describe the recent results of a program designed to optimize the operating characteristics of peroxyoxalate chemiluminescent systems. Our aims are (1) to expand the scope of the general system in order to select optimum luminants for specific applications, (2) to determine the detailed structural requirements for efficient chemiluminescence (3) to optimize the reaction conditions in terms of light capacities and emission lifetimes, (4) to provide an efficient, stable fluorescer, and (5) to define the underlying characteristics of the system to provide a basis for further improvement.

SECTION I

Oxalic Ester Chemiluminescence

Reactions of certain electronegatively-substituted aryl oxalate esters with hydrogen peroxide in the presence of such fluorescent compounds as 9,10-diphenylanthracene (DPA) or rubrene have been shown to generate light with substantially higher quantum efficiencies than any previously known non-biological chemiluminescent reactions.[11-13] Nine compounds have been demonstrated to have quantum yields in the potentially practical range of 10-16%.

Our current efforts are directed toward optimizing these chemiluminescent systems in terms of light capacity,[11] emission lifetime, and other practical requirements. Such optimization requires the consideration of the following:

(1) The influence of ester structure on chemiluminescent efficiency, solubility, stability, toxicity and cost.

(2) The influence of fluorescer structure on chemiluminescent efficiency, solubility, stability and cost.

(3) The influence of reaction condition variables on chemiluminescent efficiency, emission lifetimes, cost and operating convenience.

In addition to direct optimization studies, a part of our effort is directed toward providing information relating to the chemiluminescent reaction mechanism. In particular, information relating to the identity and properties of the key chemiluminescent intermediate is sought. It is believed that such basic information will be essential to overcome obstacles to further improvements in light capacities.

A. Preparation and Qualitative Evaluation of Oxalic Esters

Newly prepared esters are listed in Table A-1. Oxalyl chloride was reacted with the appropriate phenol or alcohol to prepare the esters according to the general procedure described earlier.[7-13]

The new esters were examined in qualitative chemiluminescence tests as summarized in Tables A-2 and A-3. Of the alkyl esters prepared, only bis(1,1,1,3,3,3-hexafluoro-2-propyl)oxalate (HFPO) was appreciably chemiluminescent. Although quantitative experiments will be required to determine the quantum yield of this ester, it is clear from the qualitative results that HFPO is substantially more efficient in chemiluminescence than previously examined aliphatic oxalate esters. While HFPO appears to be less efficient than the best currently available aromatic oxalates, the feasibility of substantial chemiluminescence from aliphatic oxalates has been established. Since an efficient aliphatic oxalate ester could have the advantages of (1) higher solubility in desirable solvents, (2) improved solution storage stability and (3) resistance to efficiency loss at high concentrations, additional efforts are warranted.

Bis(2,4,5-trichlorophenyl)oxalate (2,4,5-TCPO) was prepared on the basis of high chemiluminescent efficiencies obtained from the 2,4,6-isomer (See Section IB). The qualitative results in Table A-2 indicated 2,4,5-TCPO to have reasonable chemiluminescence efficiency. Quantitative results are reported in part B, where it is shown that inferior efficiencies were in fact found under the conditions examined.

Additional solubility and qualitative chemiluminescence data for TCPO in several solvents are summarized in Table A-4. Reasonable solubilities and chemiluminescence intensities were found in the solvents examined.

TABLE A-1

Oxalic Esters

A. Properties of Oxalate Esters

	Yield (%)	M.P. (°C)	Mol. Wt.	Elemental Analysis: Carbon Calcd	Carbon Found	Hydrogen Calcd	Hydrogen Found	Nitrogen Calcd	Nitrogen Found	Halogen Calcd	Halogen Found	Solid cm^{-1}	Solvent	Cis cm^{-1}	Cis Rel. Int.	Trans cm^{-1}	Trans Rel. Int
Bis(2,4-dimethyl-3-pentyl)oxalate	58.6	25	286.4	67.09*		10.56		-	-	-	-	1765 1768, 1738	CH_2Cl_2	cis, trans undefined 1762	.062	1735	.095
Bis(2,4,5-trichlorophenyl)oxalate	31	171-72.5	448.9	37.45	38.12	0.90	0.91	-	-	47.39	46.51	1775	CH_2Cl_2	.802	.090	1780	.17
Oxalate-Imide of Salicylamilide	75.3	244-45	267.3	67.42*		3.39		5.24		-	-	1765, 1690 1720	CH_2Cl_2	1770,1707,1730 band at 1770 is probably ester			
Bis(2-[Pyridyl-N-oxide]methyl)oxalate	14.5	169-172	304.3	55.26	55.45	3.98	4.07	9.21	9.21	-	-	1750, 1760	CH_2Cl_2	1780	.07	1755	.11
Bis(1,1,1,3,3,3-hexafluoro-2-propyl) oxalate	24	b.p. 26.5° 0.6 mm Hg	390.1	24.63*		0.52		-	-	58.45		1813,1790	CH_2Cl_2	1813	1.0	1790	1.6

* Analysis pending.

B. Approximate Solubilities of Oxalate Esters[a]

	Solvents and Solubilities (Moles l^{-1}): Glyme	DMP	TEP	Benzene
Bis(2,4,5-trichlorophenyl)oxalate	6.2×10^{-2}	2.4×10^{-2}	4.6×10^{-2}	6.0×10^{-2}

a) Solubilities were determined by the periodic addition in 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 solvent were used without further purification with the exception of propylene carbonate and 1,2-dimethoxyethane which were dried and distilled.

TABLE A-2

A. Qualitative Chemiluminescence Tests of Oxalate Esters

	Tests[a]				
	A Anhyd H_2O_2	A' H_2O_2 nBu_4ClO_4	B H_2O_2 + KOH	C H_2O_2 + H_2O	D H_2O_2 + H_3O^+
Bis(2,4-dimethyl-3-pentyl)oxalate	None	None	None	None	None
Bis(2,4,5-trichlorophenyl)oxalate	MS	MS	MS (v. fast)	M	None
Oxalate-Imide of Salicylanilide	None	None	None	None	None
Bis(2-[pyridyl-N-oxide]methyl)oxalate	None	None	VVW	None	None
Bis(1,1,1,3,3,3-hexafluoro-2-propyl)oxalate	MW	W	MS (v. fast)	W	None

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.

A.[1] As test A except approximately 1 mg. tetrabutylammonium perchlorate was also added.

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 H2O2 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. 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.

TABLE A-3

Additional Qualitative Chemiluminescence Tests with Bis(1,1,1,3,3,3-hexafluoro-2-propyl)oxalate

TESTS[a]				
(1) Anhyd H_2O_2	(2) H_2O_2 + nBu_4ClO_4	(3) H_2O_2+Et_3N	(4) H_2O_2 + H_2O	(5) H_2O_2 + H_3O^+
W (long)	W (long)	MW (long)	W (long)	ne

a) The tests were carried out as follows:

1. Approximately 20 mg. of ester is added to a 5 ml. solution of 2 mg. rubrene and 0.25 ml. of a 5.0 M H_2O_2 solution in DMP at 25°.

2. As test (1), except that 20 mg. nBu_4ClO_4 was also added.

3. Approximately 20 mg. of ester is added to a 5 ml. solution of 2 mg. rubrene, 1 drop of 1 x 10^{-2} M Et_3N solution, and 0.25 ml. of 5.0 M H_2O_2 solution in DMP at 25°.

4. As test (1), except that the test solution is saturated with water.

5. Approximately 20 mg. of ester is added to a 5 ml. solution of 2 mg. rubrene, 2 drops of 1 x 10^{-1} M methanesulfonic acid solution, and 0.25 ml. of 5.0 M H_2O_2 solution in DMP at 25°.

The concentrations for the tests were: ester, 1 x 10^{-2} M; H_2O_2, 2 x 10^{-1} M; rubrene, 8 x 10^{-4} M; nBu_4ClO_4, 1 x 10^{-2} M; Et_3N, 5 x 10^{-5} M; methanesulfonic acid, 1 x 10^{-3} M.

TABLE A-4

Solubility of 2,4,6-Trichlorophenyl Oxalate (TCPO) and Qualitative Chemiluminescence in Mixed Solvents

Solvent	Solubility in Pure Solvent at 25°C (mole/l x 10^2)	Chemiluminescence[a] Solvent/DMP Ratio	Result[b]
Chlorobenzene	>3.0	1/2	MS
1,2-Dichlorobenzene	>3.0	1/2	MS
1,1,2,2-Tetrachloroethane	>3.0	1/2	M
Benzene	6-7	1/1	MS
Arochlor 1242[c]	6.85	1/5.8	M

a) The chemiluminescent reaction was between 0.01 M TCPO, 0.02 M H_2O_2, 0.06 M Bu_4NClO_4 and 6.4 x 10^{-4} M rubrene in solvent mixtures with dimethyl phthalate (DMP).

b) Results are visual comparisons with a similar reaction of 2,4-dinitrophenyl oxalate in all-DMP solvent, which is rated S.

c) A commercial mixture of chlorinated polyphenyls manufactured by Monsanto.

EXPERIMENTAL

Oxalic esters prepared by the procedure described for bis(2,4-dinitrophenyl)oxalate[10] are summarized below along with any modifications of the procedure.

Bis(1-[1H]-5-nitro-2-pyridonyl)glyoxal - The reaction was carried out in 1,2-dimethoxyethane and the product was crystallized from benzene.

Bis(2,4-dimethyl-3-pentyl)oxalate - The procedure of Karabatsos[14] was employed in the preparation of the product.

Bis(2,4,5-trichlorophenyl)oxalate - The product was crystallized from benzene.

Oxalate-Imide of Salicylanilide - The reaction was carried out in anhydrous ether and the product was crystallized from benzene.

Bis(2-[pyridyl-N-oxide]methyl)oxalate - The reaction was carried out in chloroform and the product crystallized from methylene chloride.

Bis(1,1,1,3,3,3-hexafluoro-2-propyl)oxalate - The product was purified by distillation at 26.5°/0.6 mm Hg.

Solubility of 2,4,6-Trichlorophenyl Oxalate (TCPO) - An amount of solid TCPO was warmed gently and shaken with a volume of test solvent. On cooling, the excess TCPO was collected and weighed. Concentrations of TCPO were calculated from the known weight dissolved and the volume of solvent. Results are recorded in Table A-4.

B. Reaction Condition Studies

1. Bis(2,4,6-trichlorophenyl)oxalate (TCPO)

The results of a preliminary series of quantitative chemiluminescence experiments with the previously prepared TCPO[13] are summarized in Table B-1. Combinations of benzene or Arochlor 1242 (a chlorinated polyphenyl) with dimethyl phthalate (DMP) were used as the solvent in some experiments to permit a higher solubility of TCPO. Addition of 13.3% by volume of benzene to DMP had little effect on the quantum yield but appeared to increase the emission lifetime slightly. Addition of Arochlor 1242 substantially decreased the quantum yield.

In the absence of additives at a TCPO concentration of 0.01 molar, the quantum yield was only 6.47% while the emission lifetime exceeded 6 hours. Addition of tetrabutylammonium perchlorate (TBAP),[13] however, more than tripled the quantum yield to 20.9%, while substantially shortening the emission lifetime. Addition of pyridine in contrast greatly reduced the efficiency. At a TCPO concentration of 0.001 M, the intensity was very low in the absence of additives. Both TBAP and benzyltrimethylammonium hydroxide (BTAH), however, substantially increased reaction rates and intensities, and high quantum yields were obtained. BTAH was effective at remarkably low concentrations showing the powerful effect of basic catalysis on the reaction. In agreement with other oxalate ester chemiluminescent reactions employing TBAP,[13] quantum yields were not lowered by increasing the TCPO concentration from 0.001 M to 0.01 M, although in the absence of TBAP substantial reductions in efficiency are normally observed.[11-13]

At concentrations of TCPO of 0.02 M or 0.03 M consumption of rubrene during the reaction resulted in reduced quantum yields. However, in one experiment with 0.03 M TCPO the rubrene concentration was maintained by successive additions during the reaction, and a quantum yield of 15.1% was obtained. This is by far the highest efficiency yet obtained at higher ester concentrations.

Since increasing the ester concentration 3-fold from 0.01 M to 0.03 M reduced the efficiency only by 28%, the light capacity of the system increased more than 2-fold from 57 to 122 lumen-hours liter^{-1}. The highest light capacity previously obtained was 60 lumen-hours liter^{-1}.[13] It is clear, however, that a more stable fluorescer will be required to take practical advantage of this high light capacity.

Experiments with the fluorescers 9,10-diphenylanthracene (DPA) and 9,10-bis(phenylethynyl)anthracene BPEA indicated that both gave substantially lower quantum yields and longer lifetimes than rubrene under comparable reaction conditions. BPEA was also consumed in the reaction at high TCPO concentrations but the high solubility of BPEA permitted its use at 1.7×10^3 M concentration where its consumption did not appear to affect the quantum yield. Although the quantum yield under these conditions was only 9.0%, as compared to 15.1% with rubrene the light capacity was still 67 lumen-hours liter^{-1}. This is the highest light capacity yet obtained under practical operating conditions and illustrates the advantage of a more stable or more soluble fluorescer.

TABLE B-1

Evaluation of Bis(2,4,6-trichlorophenyl)oxalate (TCPO) Chemiluminescence[a]

TCPO (Moles Liter^{-1})	Fluorescer	Additive[b]	Additive Concentration (Moles Liter^{-1})	Solvent[c]	I_{max}[d] (Ft. Lamberts Cm^{-1})	T1/4[e] (Min.)	T3/4L[f] (Min.)	Quantum Yield[g] (Einsteins Mole^{-1} x 10^2)
0.0010[h]	Rubrene	TBAP	0.067	DMP	0.7	54.6	53.0	17.9
0.0010	Rubrene	BTAH	8×10^{-6}	DMP	0.6	57.1	45.4	17.7
0.0010	Rubrene	BTAH	8×10^{-5}	DMP	32.9	0.7	1.4	12.3
0.010	Rubrene	TBAP	0.067	DMP	15.6	27.0	18.8	19.8
0.010	DPA	TBAP	0.067	DMP	0.2	64.0	56.3	6.2
0.010	BPEA	TBAP	0.067	DMP	2.8	70.7	59.3	10.0
0.010	Rubrene	None	-	13.3% B	2.43	1.0	360	6.47
0.010	Rubrene	TBAP	0.067	13.3% B	11.35	36	30	20.90
0.010	Rubrene	TBAP	0.067	14.6% A	4.4	2.2	1.6	0.37
0.010	Rubrene	Pyridine	0.01	20.0% B	2.78	3.5	17	0.74
0.020[i]	Rubrene	TBAP	0.067	26.6%B	10.9	40	35	10.86
0.020[i]	Rubrene	TBAP	0.30	26.6% B	31.7	14	22	9.30
0.030[j]	Rubrene	TBAP	0.067	39.9% B	15.7	56	39	15.10
0.030[i,k]	BPEA	TBAP	0.067	39.9%B	5.7	124	103	9.00
0.030[j,k]	BPEA	TBAP	0.067	50.0% B	1.4	276	679	9.00

a) Reactions with 0.025 M H_2O_2 and 6.0×10^{-4} M fluorescer except where noted. DPA is 9,10-diphenylanthracene; BPEA is 9,10-bis(phenylethynyl)anthracene.

b) TBAP is tetrabutylammonium perchlorate. BTAH is benzyltrimethylammonium hydroxide.

c) DMP is dimethyl phthalate. "%B" is the volume pracent benzene in combination with DMP. "%A" is the volume percent Arochlor 1242 (a chlorinated polyphenyl) in combination with DMP.

d) Maximum brightness measured in a 1.0 cm. thick cell.

e) Time the intensity remained above one-quarter of its maximum.

f) Time required for three-quarters of total light emission.

g) Based on TCPO.

h) In the absence of TBAP or other additive the intensity was too weak to measure.

i) Fluorescer consumption occurred during the reaction.

j) A few mg. of solid fluorescer was added at several intervals during the reaction.

K) Fluorescer concentration was increased to 1.7×10^{-3} M.

2. Bis(2,4,5-trichlorophenyl)oxalate (2,4,5-TCPO)

The results of a preliminary series of quantitative chemiluminescence experiments with (2,4,5-TCPO) are summarized in Table B-2. Very weak emission was seen in the absence of additives under the conditions studied. In contrast to the results obtained with the symmetrical isomer, the addition of TBAP, had little apparent effect. Triethylamine (Et_3N) and tetrabutylammonium chloride, however, substantially increased the quantum yield, although the efficiency remained well below that obtained with 2,4,6-TCPO.

3. The Effect of Oxalic Acid on Bis(2,4-dinitro-6-methylphenyl)oxalate (DNMPO)

The results summarized in Table B-3 show that the addition of a small concentration of oxalic acid to the DNMPO rubrene system in a dimethyl phthalate (DMP)-benzene solvent mixture substantially increased the quantum yield, while extending the emission lifetime. While oxalic acid also increases the lifetime of the related DNPO system, there it was found to decrease the quantum yield somewhat. Previously in this Section it was noted that tetrabutylammonium perchlorate substantially increases the quantum yield in bis(2,4,6-trichlorophenyl) oxalate experiments but has little effect on related bis(2,4,5-trichlorophenyl)oxalate experiments. It thus appears that the ester structure has a marked influence on the effect of additives on quantum yields.

TABLE B-2

Chemiluminescence from 2,4,5(Trichlorophenyl)oxalate (2,4,5-TCPO)[a]

Stock solution of 2,4,5-Trichlorophenyl oxalate = 6×10^{-2} M in benzene

2,4,5-TCPO (M)	Additive[b]	Additive (M)	Max. I[c] (Ft. Lamberts)	t1/4[d] (Mins.)	t3/4L[e] (Mins.)	Quantum Yield[f] (Einsteins $Mole^{-1} \times 10^2$)
0.0010	Et_3N	1.65×10^{-4}	Too Fast to measure			
0.010	None	None	Too weak to measure			
0.010	Et_3N	1.65×10^{-4}	3.4	49.2	68.8	5.88
0.010	Et_3N	3.3×10^{-4}	17.2	2.5	32.5	7.14
0.010[g]	Et_3N	3.3×10^{-4}	24.1	1.4	10.7	4.16
0.010	TBAP	6.7×10^{-2}	Too weak to measure			
0.010	TBAC	3.3×10^{-4}	14.9	19.1	15.6	7.77
0.010	TBAP TBAC	6.7×10^{-2} 3.3×10^{-4}	21.7	3.3	19.6	8.05

a) Reactions with 0.025 M H_2O_2 and 6.0×10^{-4} M rubrene in 84% dimethyl phthalate - 16% benzene (volume percent) at 25°C.

b) Et_3N is triethylamine. TBAP is tetrabutylammonium perchlorate. TBAC is tetrabutylammonium chloride.

c) Maximum brightness measured in a 1.0 cm thick cell.

d) The time that the light intensity remained above one-quarter its maximum value.

e) The time required for the emission of three-quarters of the total light output.

f) Based on oxalate ester.

g) The H_2O_2 concentration was 0.10 M.

TABLE B-3

The Effect of Oxalic Acid on Bis(2,4-dinitro-6-methylphenyl) (DNMPO) Chemiluminescence[a]

Oxalic Acid (M)	I_{max}[b] (Ft. Lamberts)	T1/4[c] (Mins.)	T3/4L[d] (Mins.)	Quantum Yield[e] (Einsteins $Mole^{-1} \times 10^2$)
None	100.0	1.2	0.8	5.8
6.7×10^{-4}	12.9	16.3	11.6	9.31

a) Reactions of 0.01 M DNMPO, 0.025 M H_2O_2, and 6.0×10^{-4} M rubrene in 50% benzene - 50% dimethyl phthalate (by volume) at 25°C.

b) Maximum chemiluminescent brightness measured in a 1 cm thick cell.

c) The time required for the light intensity to decay to one-quarter its maximum value.

d) The time required for the emission of three-quarters of the total light.

e) Based on oxalate ester.

4. The Interrelationship Between Solvent and Ester Structure on Chemiluminescence Efficiency

Chemiluminescent reactions of bis(2,4-dinitrophenyl) oxalate (DNPO) and bis(3-trifluoromethyl-4-nitrophenyl)oxalate (TFMNPO) with the fluorescer rubrene in the solvents dimethyl phthalate (DMP), triethyl phosphate (TEP), and 1,2-dimethyethane (DME) are compared in Tables B-4 and B-5. DME gave relatively low quantum yeilds with both DNPO and TFMNPO. In the latter reaction, however, rubrene consumption was responsible in part for the low efficiency. With DNPO, DMP provided substantially higher quantum yields than TEP, while with TFMNPO, TEP was substantially superior. Again fluorescer consumption was in part responsible for the low quantum yields in experiments with TFMNPO in DMP. We cannot presently account for the superior performance of TFMNPO relative to DNPO in TEP or for the higher stability of rubrene with DNPO-DMP relative to TFMNPO-DMP. It is clear, however, that the variables solvent, ester structure, fluorescer structure and salt effects are interdependent, and that care must be taken in assigning relative efficiency rankings to esters and fluorescers.

In other experiments replacement of dissolved air by carbon dioxide appeared to have little effect.

5. The Effect of Polyvinylpyrrolidone (PVP) and Tetrabutylammonium Perchlorate (TBAP) on Bis(2,4-dinitrophenyl)oxalate (DNPO) Chemiluminescence with Rubrene

The effects of PVP and TBAP on DNPO chemiluminescence in dimethyl phthalate (DMP) with rubrene are summarized in Table B-6. PVP was found to decrease the lifetime substantially while having little effect on the quantum yield. TBAP increased both emission rates and

quantum yields. It appears that the ability of TBAP to increase the quantum yield is not related to its effect on lifetime. PVP will probably be a satisfactory thickener for slower systems.

6. The Effect of Temperature on Bis(2,4-dinitrophenyl) oxalate (DNPO) Chemiluminescence

Results showing the effect of temperature on the quantum yield and lifetime of the reaction of DNPO, hydrogen peroxide, and rubrene in dimethyl phthalate (DMP) are summarized in Table B-7 and in Figure 1. It is evident from Table B-7 that the quantum yield is not significantly different at 7.5°C than at 24.5°C, but decreases moderately at 50.5°C. The results thus indicate that satisfactory efficiencies can be obtained at practical operating temperatures. It is evident from Figure 1, however, that the maximum intensity and lifetime are substantially altered by temperature changes. The magnitude of both effects will undoubtedly depend on the ester structure and reaction condition, and lifetime dependence on temperature may well be smaller in other systems.

7. Bis(1,1,1,3,3,3-hexafluoro-2-propyl)oxalate (HFPO)

Quantitative chemiluminescence experiments with the aliphatic ester HFPO were obtained as this report was in press and are summarized in Table B-8. The fluorescer rubrene was seriously consumed in the system and the quantum yield was low. Consumption of the fluorescer 9,10-bis (phenylethynyl)anthracene (PEA) at higher concentration was less pronounced and a quantum yield of 1.8% was observed. It is clear that substantially more active aliphatic oxalate will be required to provide the efficiencies obtained with the best aryl oxalates now available.

TABLE B-4

The Effect of Solvent and CO_2 on the Chemiluminescent Reaction: Bis(2,4-dinitrophenyl)oxalate,(DNPO) H_2O_2 and Rubrene at 25°C[a]

Solvent	Additive	Max. Intensity[b] (Ft Lamberts)	t 1/4[c] (Mins.)	t 3/4L[d] (Mins.)	Quantum Yield x 10^2[e] (Einsteins $Mole^{-1}$)
DMP[f]	None	222.9	1.3	3.3	18.6
DMP	CO_2 (Sat.)	274.0	1.0	3.5	18.6
TEP	None	5.7	23.1	21.8	5.9
TEP	CO_2 (Sat.)	3.9	24.7	21.7	4.3
DME	None	8.0	5.9	37.3	4.1

a) Reactions were carried out with 0.01 M DNPO, 0.025 M H_2O_2, 6 x 10^{-4} M rubrene.

b) Maximum brightness measured in a 1.0 cm thick cell.

c) Time the intensity remained above one quarter of its maximum value.

d) Time required for three quarters of the total light emission.

e) Based on DNPO concentration

f) DMP is dimethyl phthalate
TEP is triethyl phthalate
DME is 1,2-dimethoxy ethane

TABLE B-5

The Effect of Solvent and CO_2 on the Chemiluminescent Reactions of Bis(3-trifluoromethyl-4-nitrophenyl)oxalate (TFMNPO), H_2O_2 and Rubrene at 25°C[a]

Solvent	Additive	Max. Intensity[b] (Ft Lamberts)	t 1/4[c] (Mins.)	t3/4L[d] (Mins.)	Quantum Yield[e] (Einsteins $Mole^{-1} \times 10^2$)
DMP*	None	0.6	197.0	188.7	2.7
TEP	None	59.0	7.2	5.8	18.1
TEP	CO_2(Sat)	114.0	3.4	4.1	17.8
DME*	None	10.9	16.1	23.6	6.7

*Fluorescer consumption was observed

a) Reactions were carried out with 0.01 M TFMNPO, 0.025 M H_2O_2, 6×10^{-4} M rubrene.

b) Maximum brightness measured in a 1.0 cm. thick cell.

c) The time required for the light intensity to decay to one-quarter of its maximum value.

d) The time required for the emission of three-quarters of the total light.

e) Based on oxalate ester.

TABLE B-6

The Effect of Polyvinylpyrrolidine (PVP) and Tetrabutylammonium Perchlorate (TBAP) on Bis(2,4-dinitrophenyl)oxalate (DNPO), Rubrene, H_2O_2 Chemiluminescence in Dimethyl Phthalate (DMP) at 25°C[a]

PVP (Wt. %)	TBAP (Moles Liter^{-1})	Max. Intensity[b] (Ft. Lamberts)	t 1/4[c] (Mins.)	t 3/4L[d] (Mins.)	Quantum Yield x 10^2[e] (Einsteins Mole^{-1})
None	None	330.0	0.7	2.3	15.0
0.33	None	632.0	0.5	0.7	14.9
None	1.7×10^{-2}	1842.0	0.2	0.3	18.4

a) Reactions with 0.01 M DNPO, 0.025 M H_2O_2 and 6×10^{-4} M rubrene.

b) Maximum brightness measured in a 1.0 cm thick cell.

c) Time the intensity remained above one quarter of its maximum value.

d) Time required for three quarters of total light emission.

e) Based on DNPO concentration.

TABLE B-7

The Effect of Temperature on Chemiluminescence from DNPO, Rubrene, and H_2O_2 in DMP[a]

Temp. (°C)	Max Intensity[b] (Ft. Lamberts cm^{-1})	t 1/4[c] (Min.)	t 3/4L[d] (Min.)	Quantum Yield[e] (Einsteins $Mole^{-1} \times 10^2$)
7.5	21.7	14.0	19.8	13.90
24.5	163.7	1.3	3.2	14.40
50.5	426.6	0.3	0.8	7.90

a) Reactions of 0.010 M bis(2,4-dinitrophenyl)oxalate (DNPO), 0.025 M H_2O_2, and 6.0×10^{-4} M rubrene in dimethyl phthalate (DMP).

b) Maximum brightness measured in a 1.0 cm thick cell.

c) Time the intensity remained above one quarter of its maximum value.

d) Time required for three quarters of total light emission.

e) Based on DNPO

TABLE B-8

Chemiluminescence from Bis(1,1,1,3,3,3-hexafluoro-2-propyl)oxalate in DMP[a]

Fluorescer	Concentration (M)	Max. Intensity (Ft. Lamberts)[b]	T1/4[c] (Mins.)	T3/4 L[d] (Mins.)	Quantum Yield[e] (Einstein mole^{-1} x 10^2)
Rubrene[f]	6.0×10^{-4}	0.38	35.0	29.7	0.56
PEA[g]	3.6×10^{-3}	0.17	219.9	170.0	1.80

a) Experiments carried out with 0.01 M ester, .025 M H_2O_2, and 1.33×10^{-4} M triethyl amine in dimethyl phthalate (DMP) at 25°C.

b) One cm. deep cell.

c) Time requiref for the intensity to decrease to 1/4 of its maximum.

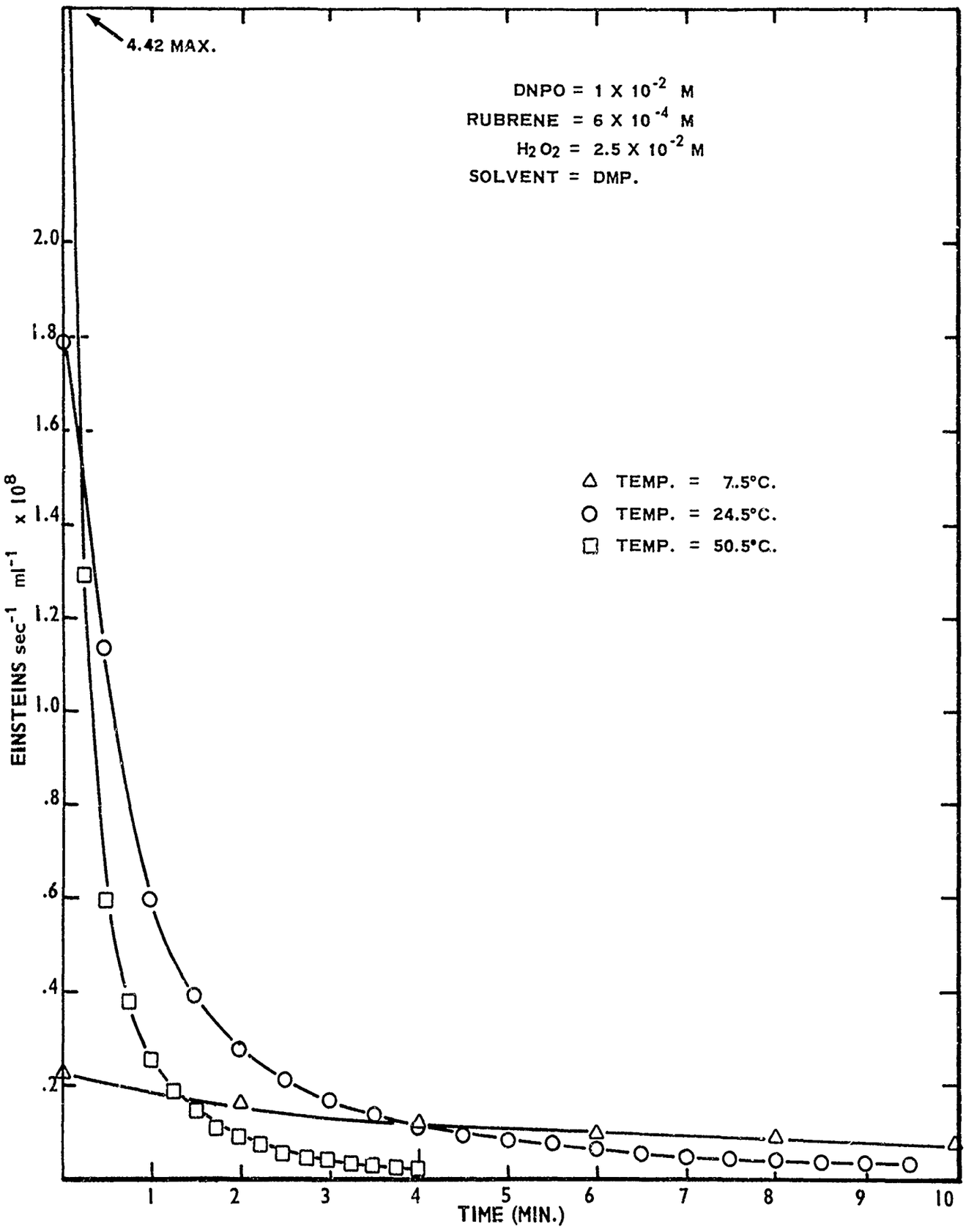
d) Time required for 3/4 of the total emission.

f) Rubrene consumption reduced the quantum yield and lifetime.

g) 9,10-Bis(phenylethynyl)anthracene.

FIGURE 1

THE EFFECTOF TEMPERATURE ON THE DNPO, RUBRENE, H_2O_2 CHEMILUMINESCENT REACTION IN DMP



EXPERIMENTAL

Materials

Triethyl Phosphate was dried over anhydrous sodium carbonate and molecular sieves, and then distilled under reduced pressure through a packed column to give material of BP 47°/0.2 mm Hg.

1,2-Dimethoxyethane was stirred with lithium aluminum hydride under nitrogen until no further gas was evolved. A small additional amount of hydride was then added and the solvent distilled in an argon atmosphere through a packed column to give material, b.p. 85°/1 atm.

Dimethyl phthalate was distilled under reduced pressure through a packed column to provide material, b.p. 96°/0.3 mm Hg.

Tetrabutylammonium perchlorate (Southwestern Analytical Chemicals) was polarographic grade material which was dried 2 hours at 70°C prior to use.

Arochlor 1232 and Arochlor 1242 were provided by the Monsanto Company. Arochlor 1232 was distilled under reduced pressure prior to use to obtain a center cut boiling at 110°-130°/0.8 mm Hg. Arochlor 1242 was used without further purification.

All other materials were of highest purity commercial stock and were used as received.

Chemiluminescent Measurements were carried out as previously described.[9]

C. Fluorescer Studies

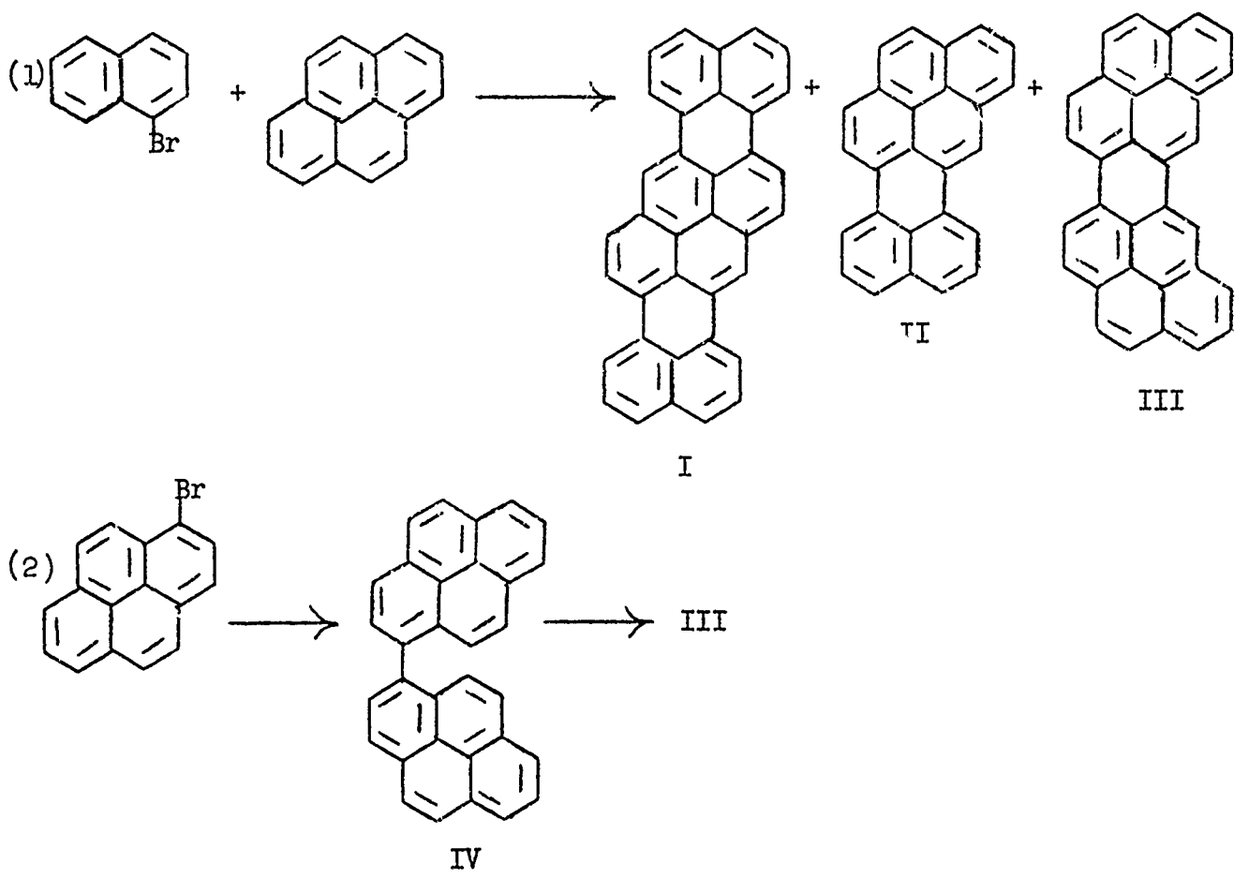
To maximize the light capacity of the oxalate ester chemiluminescence system a fluorescer is needed which has: (1) a high fluorescence efficiency ($\bar{\emptyset}$ F), (2) a spectral distribution providing most of the emission between 510 mu and 610 mu in the visible spectrum, (3) a solubility exceeding 5.0×10^{-3} molar in suitable solvents, (4) satisfactory stability under the chemiluminescent reaction conditions and (5) moderate cost.[13] No presently available fluorescer meets all of these requirements. In particular, light capacities are presently limited to about 60 lumin-hours $liter^{-1}$ by fluorescer consumption at ester concentrations above about 0.01 M (See Section IB-1). It has now been demonstrated that a more stable fluorescer would permit light capacities of at least 120 lumin-hours $liter^{-1}$ [Section IB-1]. Such high light capacities would greatly extend chemiluminescence utility.

Since a screening program using available fluorescers has failed thus far to provide a superior fluorescer, we have begun a program of fluorescer design and synthesis. Certain polycyclic aromatic hydrocarbons have been selected initally to facilitate prediction of fluorescence efficiencies and spectral distributions. In general, high fluorescence efficiencies requires a $\pi - \pi^*$ first excited state with a large extinction coefficient and this requirement is met by many aromatic hydrocarbons. Moreover the "mirror image rule"[15] permits the estimation of fluorescer spectra if absorption data is available or can be estimated.

A substantial body of information bearing on the synthesis and properties of polycyclic aromatic hydrocarbons is available and has been reviewed by Clar.[16] In his books Clar discusses preparation, ultraviolet and visible spectra (including the positions of α, β and p- bands), isolation, reactions and in some cases the fluorescence emission of more than 200 aromatic hydrocarbons.

1. Terrylene Derivatives and Related Compounds

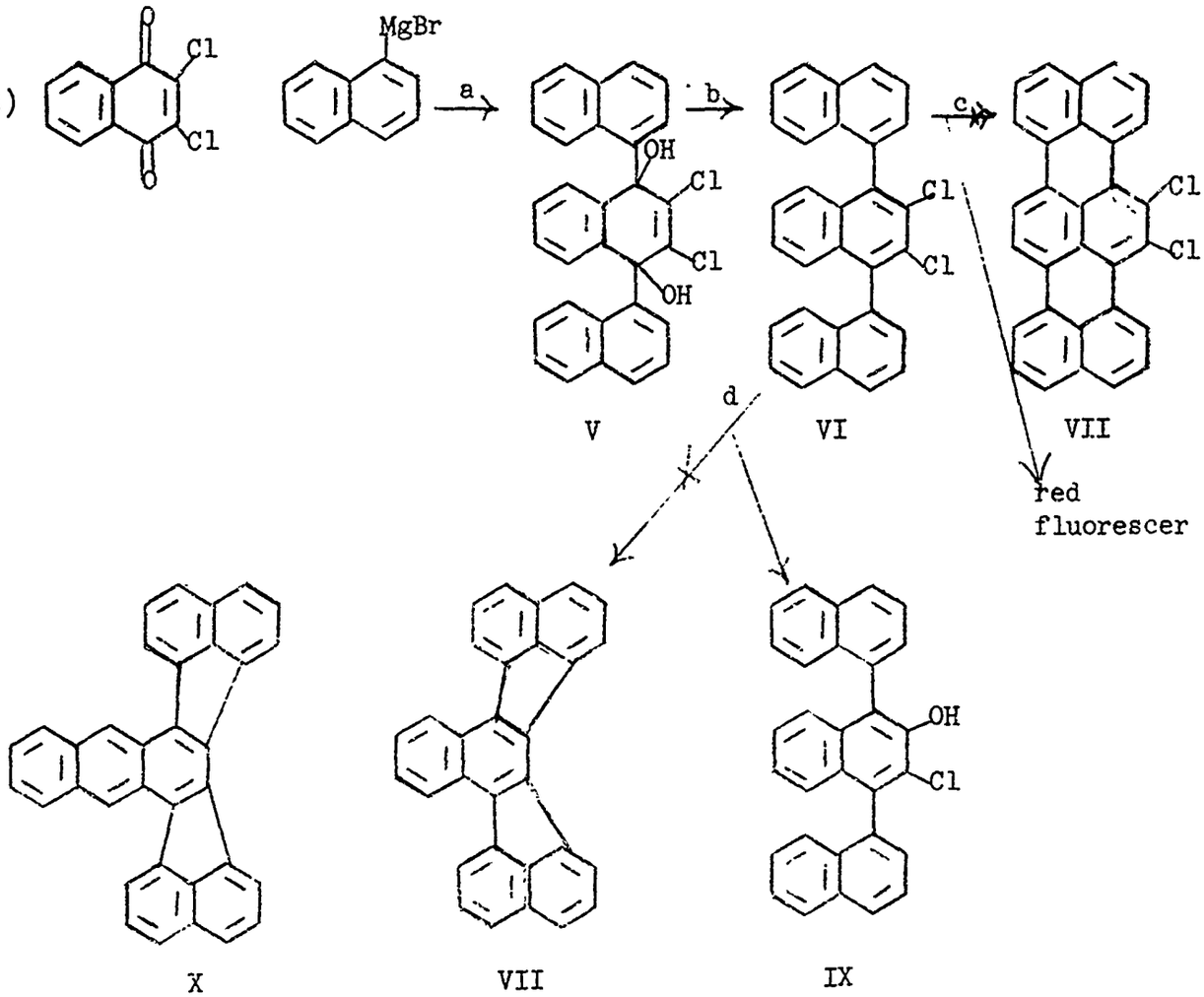
Depending on the reaction conditions, three fluorescent hydrocarbons (I, II and III) can be obtained from the first reaction of 1-bromonaphthalene and pyrene in an aluminum chloride-sodium chloride melt [17] (Reaction (1)). Hydrocarbon III is also formed from the copper-coupling of IV, which is prepared from 1-bromopyrene [17] (Reaction 2). The fluorescence emission of I is orange, while that for II and III is yellow-green.[17]



In repeating the procedure described for Reaction (1),[17] pure 1,10:5,6-diperinaphthylenepyrene (I) was obtained, along with mixtures of hydrocarbons II and III with other highly fluorescent hydrocarbons which could not be separated. Qualitative tests (see Table I) showed that in the oxalate-peroxide system fluorescer I gave weak emission for a short period, but that a mixture containing II and III produced strong emission with a long lifetime. Other product fractions obtained from reaction (1) were also tested. All were bright fluorescers with colors ranging from blue to orange and with long lifetimes.

"Strong yellow fluorescence from solutions of 7,8-dichloroterrylene (VII)" has been reported.[18] Preparation of this compound (Equation 3) begins with the Grignard reaction of 1-naphthylmagnesium bromide and 2,3-dichloro-1,4-naphthoquinone to yield diol V. Hydriodic acid reduction of V provides VI, which is reported[18] to cyclize in an aluminum chloride-sodium chloride melt to give VII. When this sequence was repeated, compounds V and VI were obtained in steps (3a and 3b), but dichloroterrylene VII was not obtained in step (3c). The results of reaction (3c) differed from those of Clar and coworkers,[18] in that we isolated two blue fluorescers (one of which was perylene) and a brillant red fluorescer. Clar apparently obtained the same two blue fluorescers, and some of VII, but none of the red fluorescing material. A comparison of fluorescence intensity and lifetime of the red fluorescer with rubrene is given in Table C-1. The qualitative tests indicated possible utility of the unknown red fluorescer in oxalate chemiluminescence.

(3)



The mass spectrum of the red-fluorescing material indicates a mixture of three compounds having molecular weights 410, 376 and 326. While the last is unidentified, none of its possible structures would seem to be capable of red fluorescence. Candidates having m/e = 376 are terrylene and VIII, but terrylene is an orange fluorescer,[18] and since X is expected to be a red or orange fluorescer,[19] VIII can probably be eliminated. Thus the red fluorescence is probably caused by the compound having a molecular weight of 410. Monochloroterrylene is a possible structure.

TABLE C-1

Qualitative Fluorescer Tests

Compounds(s)	Color of Emission	Intensity	Lifetime
1,10:5,6-Diperinaphthylenepyrene (I)	O	W	B
Mixture containing II and III	YG	VS	VL
Red fluorescer from Reaction (3C)	R	VS	VL
3,4,9,10-Perylenetetracarboxylic-3,4:9,10-dianhydride	R	W	M
3,4,9,10-Perylenetetracarboxylic-3,4:9,10-diimide	RP	W	M
3,4,9,10-Perylenetetracarboxylic-3,4:9,10-diimide, N,N'-p-methoxyphenyl	R	W	M
3,4,9,10-Perylenetetracarboxylic-3,4:9,10-diimide, N,N'-p-ethoxyphenyl	R	W	M
1,2-Diphenylaceperylene	No Emission	-	-
9,10-Dihydroxy-9,10-diphenylethynyl-9,10-dihydroanthracene	GB	VW	M

Tests were carried out in dimethyl phthalate solutions 2×10^{-2} M in DNPO, 1×10^{-2} M in hydrogen peroxide and 1×10^{-3} M in fluorescer. The resultant light was compared against a rubrene standard.

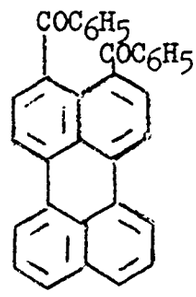
Symbols

Color	Intensity	Lifetime
O = Orange	W = Weak	B = Brief, 2-5 minutes
Y = Yellow	VS = Very Strong	VL = Very Long $>$ 3 hours
G = Green	VW = Very Weak	M = Medium, 5 - 15 minutes
R = Red		
P = Purple		
B = Blue		

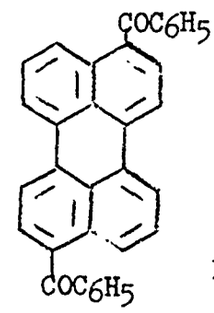
The preparation of VIII was attempted by the dehydrohalogenation of VI in potassium hydroxide an quinoline (Reaction 3d), but the only product isolated was IX.

2. Perylene Derivatives

After considering the ease of synthesis, and region of fluorescence emission, the 3,4- and 3,9-dibenzoylperylene (compounds XI and XII) were selected and prepared by reported procedures.[20, 21] The quantitative emission data listed in Table II, show that while diketone XI has a longer lifetime than rubrene, neither XI nor XII gives a chemiluminescence quantum yield comparable to that of rubrene.



XI



XII

3. Phenylethylanthracene

The strong fluorescence of 9,10-bis(phenylethynyl) anthracene (BPEA) (XIII) has recently been brought to our attention.[22] Quantitative measurements of XIII as the fluorescer in the oxalate-peroxide system show (Table C-2) that the light capacity is greater than that from all other fluorescers tested, except rubrene. It was shown that the emission in the chemiluminescent reaction is derived from the excited singlet state of XIII by the superimposition of the chemiluminescence and fluorescence emission spectra.

TABLE C-2

TABLE C-2

Fluorescence[a] and Chemiluminescence[b] Data for Various Fluorescers

Fluorescer	Fluorescence: Maximum Emission Wavelength (mμ)	Fluorescence: Fluorescence Efficiency (Φ)	Fluorescence: P[c]	Chemiluminescence: I_{max} (Ft. Lamberts)[d]	Chemiluminescence: Lifetimes T1/4[e]	Chemiluminescence: (Mins.) T3/4L	Chemiluminescence: Quantum Yield[g] (Einsteins Mole^{-1} x 10^2) (ΦCl)	Chemiluminescence: Radiation Capacity (Einsteins Liter^{-1}x10^4)	Chemiluminescence: Light Capacity (Lumen Hrs. Liter^{-1})
9,10-Diphenylanthracene	430	0.84	0.04	0.21	64.0	56.3	6.15	6.15	1.0
Rubrene	565	0.75	0.67	15.58	27.0	18.8	19.80	19.80	54.0
9,10-Bis(phenylethynyl)athracene(XIII)	510	0.96	0.61	2.76	70.7	59.3	9.97	9.97	24.8
3,9-Dibenzoylperylene (XIII)[h]	515	0.47	0.72	45.70	1.9	6.4	5.46	5.46	16.0
3,4-Dibenzoylperylene (XI)	530	0.18	0.79	1.14	54.6	49.1	2.14	2.14	6.9
3,9-Bisphenylacetylperylene[h]	535	0.52	0.76	1.65	39.1	33.0	3.49	3.49	10.8
2-(2-Oxo-2H-1-benzopyran-3-yl)naphth[1,2-d]oxazole	495	0.67	0.55	0.10	94.9	108.6	0.54	0.54	1.5
12-Phthaloperinone	560	0.010	0.66	----------	No emission detected	----------			
2,5-Diphenylfuran	388, 367	-	-	----------	Very weak emission at 390 mu	----------			
Violanthrone	495, 630	.047	0.29	Fluorescer destroyed;-emission max (very weak) changed from 695 to 630 during reaction					
Diindenoperylene	560	Too weak and insoluble in DMP and Benzene - no calculations were made							
Ovalene	505	"		"	"	"			
Rubicene	555	0.15	0.71	32.3	7.7	10.8	2.52[i]	2.52	7.5

a) Fluorescer concentration = 6 x 10^{-4} M in dimethyl phthalate except for note h.

b) Chemiluminescent data was obtained from reactions with 0.01 M bis(2,4,6-trichlorophenyl)oxalate, 0.025 M H_2O_2, 6.7 x 10^{-2} M tetrabutylammonium perchlorate and 6 x 10^{-4} M fluorescer except notes h and i.

c) Photoptic luminosity factor.

d) Maximum brightness measured in a 1.0 cm. thick cell.

e) Time during which the intensity remains above one-quarter of maximum value.

f) Time required for the emission of three-quarters of the total light

g) Based on the oxalate ester

h) Low solubility of the fluorescer limited its concentration to about 4 x 10^{-4} M.

i) 2,4-Dinitrophenyl oxalate was used to obtain the chemiluminescence data.

4. Fluorescer-Oxalate Interactions

The interrelationship of three fluorescers and three chemiluminescent oxalate derivatives is summarized in terms of chemiluminescence quantum yields in Table C-3. It is clear that the interrelationship is complex. While rubrene provides almost twice the efficiency of BPEA in the TCPO system it is only 23% more efficient in the DNPO system and about equal to BPEA in the NPG system under the conditions studied. Evidently quenching processes involving the oxalate or its bi-products are a major factor in determining the efficiency of fluorescers in oxalate. It is also apparent that the choice of fluorescer is a major factor in determining the relative efficiencies of chemiluminescent oxalates.

TABLE C-3

Comparison of Efficient Fluorescers in Several Chemiluminescent Reactions

Fluorescer[a]	Fluorescence[b] Quantum Yield	Emission max (mμ)	Chemiluminescence Quantum Yield (Einsteins Mole^{-1}) TCPO[c]	DNPO[d]	NPG[e]
Rubrene	0.75	560	19.8	18.6	9.9
BPEA	0.96	510	10.0	15.1	10.3
DPA	0.84	430	6.2	8.0	-

a) BPEA is 9,10-bis(phenylethynyl)anthracene; DPA is 9,10-diphenylanthracene.

b) Fluorescence quantum yield in dimethyl phthalate. The rubrene value is an estimate.

c) Chemiluminescent reaction of 0.01 M bis(2,4,6-trichlorophenyl)oxalate (TCPO), 0.025 M H_2O_2, 6.0×10^{-4} M fluorescer, and 0.067 M tetrabutylammonium perchlorate in dimethyl phthalate (DMP) at 25°.

d) Chemiluminescent reaction of 0.01 M bis(2,4-dinitrophenyl)oxalate (DNPO), 0.025 M H_2O_2, and 6.0×10^{-4} in fluorescer in DMP at 25°.

e) Chemiluminescent reaction of 0.01 M bis(1-[1H]-5-nitro-2-pyridonyl) glyoxal (NPG), 0.025 M H_2O_2, and 6.0×10^{-4} M fluorescer in DMP at 25°.

EXPERIMENTAL

The following compounds were prepared according to known procedures: 2,3:7,8-diperinaphthylenepyrene (I);[17] 1-bromopyrene;[23] 2,3-dichloro-1,4-dihydroxy-1,4-di(α-naphthyl)-1,4-dihydronaphthalene (V);[18] 2,3-dichloro-1,4-di(α-naphthyl)naphthalene (VI);[18] 3,4-dibenzoylperylene (XI);[20] 3,9-dibenzoylperylene (XII);[21] 9,10-bis(phenylethynyl) anthracene (XIII);[24] 1,4-dimethoxy-9,10-anthraquinone (XXXI);[25] 3,10-perylenequinone (XXXV);[26] and 1,2-diphenylaceperylene.[20]

The samples of XI and XII that were used for fluorescence measurements had purities of at least 99%, as determined by V.P.C. The conditions for the chromatography on a F and M810 (flame ionization) were temperature of column at 300°, detector at 300° and injector at 400°, with a 2 ft. 1% SE 30 column (silicon rubber on 60-80 mesh Gaschrome P).

Reaction of 1-Bromonaphthalene and Pyrene - A mixture of 60 g. (0.3 mole) of pyrene and 62 g. (0.3 mole) of bromonaphthalene was added to a hot melt (120°) of 415 g. aluminum chloride and 83 g. of sodium chloride. The pot temperature rose to 160° and was maintained at 140-160° for seven minutes. After cooling the black solid was treated with ice cold dilute hydrochloric acid. The resultant suspension was heated then filtered. The solid which was collected was washed successively with dilute hydrochloric acid, 6N ammonium hydroxide, water and ether. The material was then extracted with four 800 ml. portions of boiling xylene. The xylene was removed with a rotatory evaporator leaving a hard, black resin-like material. This was distilled *in vacuo* at temperatures up to 400°.

Column chromatography (neutral alumina with benzene) of the distillates yielded mixtures of hydrocarbons. The solids (8.4 g.) from these fractions had melting points from 260° to $>$330°. The fluorescence ranged from blue and blue-green to yellow-green.

The pot residue from the distillation was extracted with chloroform and four attempts were made to separate products chromatographically. Alumina, silica gel and florosil were used as packings with several solvents and solvent mixtures. A variety of fluorescent solids was obtained, none of them pure as evidenced by thin layer chromatography tests. A mass spectrum of the fraction which gave yellow-green fluorescence in benzene solutions showed that the major component has a molecular weight of 326 (corresponding to II). Small peaks at m/e 400 (corresponding to III), 376, 366, 364, 352 and 350 appeared to be molecular ions.

Attempted Preparation of 1,1'-Dipyrenyl (IV) - A high-pressure reaction vessel was charged with 20 g. (0.052 mole) of bromopyrene, 25 g. (0.32 g.-atm) of powdered copper and 25 g. of Devarda's alloy. The clave was heated to 290° and maintained there for one hour. The solid reaction product was extracted with boiling xylene. The xylene was removed at reduced pressure in a rotatory evaporator leaving a dark colored solid. Sublimation of this solid afforded a mixture of deep red and yellow crystals. The red crystals, 450 mg. m.p. 365-375° were separated manually, dissolved in benzene and chromatographed on Woelm neutral alumina. The major fraction obtained was a yellow-green fluorescer in benzene. Its mass spectrum had m/e 400.

Attempted Preparation of 7,8-Dichloroterrylene (VII) - To a melt of 15 g. of aluminum chloride and 3 g. of sodium chloride at 110° was added all at once 1.5 g. of 2,3-dichloro-1,4-di(α-naphthyl) naphthalene (VI). The mixture was stirred at 115° for 5 minutes, then decomposed by cooling and adding ice and dil. hydrochloric acid. The crude product was heated in water at 70-80°, then dried. The dried product was treated with 25 ml. of boiling benzene and the resulting solution was chromatographed on Woelm neutral alumina. There were three distinct bands on the column; the first was yellow, the second was orange-yellow and the third was violet. Elution with benzene gave 110 mg. of perylene. Further elution with 50% ethyl ether-benzene gave 40 mg. of a yellow solid (a bright blue fluorescer in benzene). The third fraction, 45 mg. of a violet solid, m.p. 204-209°, with brillant red fluorescence in benzene was obtained by elution with 25% acetone-ethyl ether.

The mass spectrum of fraction three contained peaks m/e 410, 376 and 326.

Attempted Cyclization of 2,3-Dichloro-1,4-di(α-naphthyl) naphthalene (VI) - The conditions used in this reaction were the same as those used for the preparation of rubicene from 1,5-dichloro-9,10-diphenylanthracene.[27]

A solution of 160 mg. of VI, 280 mg. of potassium hydroxide and 5 ml. of quinoline was heated at 200° for 3 hours. During the heating period the color of the solution changed from yellow to colorless to red-brown. The cooled solution was poured into dil. sulfuric

acid. The solid that precipitated was dissolved in benzene and the solution was chromatographed on Woelm neutral alumina. Elution with 1% methanol-ethyl ether gave 120 mg. of buff-color solid, which had a weak blue-green fluorescence in benzene. Recrystallization from benzene-hexane gave colorless crystals of 2-chloro-3-hydroxy-1,4-di (α-naphthyl)naphthalene (IX), m.p. 302-304°; infrared, 2.85 mu; mass spec. m/e 430.

Perylene - A mixture of 120 g. of perylene-3,4,9,10-tetracarboxylic acid,[28] 312 g. of potassium hydroxide and 1400 ml. of water was heated at 250°C in a 2.5 liter Inconel autoclave for 16 hours. The mixture was cooled, filtered and washed with water to obtain 70 g. (100%). Gold crystals, m.p. 278-280° were obtained when the product was recrystallized from 1,2,4-trichlorobenzene.

3,9-Bis(phenylacetyl)perylene (XXXIII) - To an ice-cooled mixture of 2.5 g. (0.01 mole) of perylene, 3.3 g. (0.025 mole) of aluminum chloride and 100 ml. of carbon disulfide was added during a 15 minute period 3.1 g. (0.02 mole) of phenylacetyl chloride. The mixture was stirred at 5° for 2 hours, then at room temperature for 22 hours. The solvent was evaporated at room temperature and the mixture was treated with 500 ml. of benzene and dil. sulfuric acid. The organic solution was washed with 10% sodium carbonate and water. Some solid (2.85 g.) was insoluble in both phases. It was treated with 40 ml. of hot 1,2,4-trichlorobenzene. The insoluble material, 1.05 g. melted above 360° and its infrared spectrum had no -CH aromatic peaks in the

13.5-15.0 u region. Addition of hexane to the trichlorobenzene solution gave a solid that was combined with the solid isolated from the benzene solution. Recrystallization from benzene gave a red solid, m.p. 220-235°, which was purified by recrystallization from 50% benzene-chloroform. The yield of XXXIII, m.p. 238-241°, infrared, 5.99 u was 3.14 g. or 64%. In benzene it gave a yellow-green fluorescence.

Anal. Calcd. for $C_{36}H_{24}O_2$: C, 88.48; H, 4.95. Found: C, 88.18; H, 5.01.

D. Infrared Analyses of Bis(2,4,6-trichlorophenyl)oxalate (TCPO) System

In a continuing effort to detect and identify the intermediates responsible for chemiluminescence in the highly efficient oxalate ester-hydrogen peroxide-fluorescer system, TCPO reactions with hydrogen peroxide were examined by infrared spectroscopy. It was believed that the greater solubility of TCPO in solvents with little or no 2000-1600 cm^{-1} absorption would offer a greater possibility for observing the appearance of new carbonyl bands during the course of the reaction. Preliminary examination of chlorobenzene-triethyl phosphate (TEP), and benzene-TEP solvent mixtures indicated interfering overtone absorption in the 2000-1600 cm^{-1} region. However, the chlorinated polyphenyl mixture Arochlor 1232 in a mixture containing 2 parts by volume Arochlor and one part TEP gave sufficient energy transmission between 2000 cm^{-1} and 1600 cm^{-1} to permit experimentation.

The initial experiments were carried out with only TCPO and H_2O_2 as the reactants. Results are summarized in Table D-1. A rather slow reaction rate is evident from the data. The fluorescer DPA appears to have an accelerating effect on the rate of carbonyl disappearance. No new carbonyl bands were noted. It was felt that it would be desirable to study a faster system so similar experiments were done in the presence of 0.5 mole percent (based on TCPO) benzyltrimethylammonium hydroxide (BTAH). The results are recorded in Tables D-2 and D-3.

In Tables D-2 and D-3 it is noted that the rate of carbonyl disappearance is substantially faster in the presence of BTAH and that DPA has little effect on the reaction rate under these conditions. In both cases a new carbonyl band at 1895 cm^{-1} is formed and the absorbance of this new band changes as the reaction progresses. The carbonyl absorbance of , a possible intermediate in the chemiluminescent reaction, has been postulated to be at approximately 1900 cm^{-1}. The presence of the fluorescer DPA has no effect on the rate of carbonyl disappearance in this system. However, Table D-2 shows a slow build-up of the 1895 cm^{-1} absorption to a maximum at 15 minutes followed by a slow decay. Table D-3 shows that in the presence of DPA the 1895 cm^{-1} absorption reaches a maximum no later than 2 minutes after the start of the reaction, and that this absorption decreases slowly. Changes in the carbonyl absorption below 1780 cm^{-1} occur, but are obscure, in both reactions. The experiments were carried out as previously described.[12]

TABLE D-1

Reaction of TCPO with H_2O_2 in Arochlor/TEP[a]

Time (Min.)	Absorbance at 1780 cm^{-1}	% Carbonyl Remaining
0	1.16[b]	100
2.6	1.14[b]	98.2
8.3	1.14[b]	98.2
45	1.08[b]	93.2
104	1.03[b]	88.8
157	0.90[b]	77.6
1350	0.39[b]	33.7
2.3	1.12[c]	96.6
7.5	1.12[c]	96.6
120	0.95[c]	81.9
223	0.86[c]	74.2
392	0.65[c]	56.1

a) Solvent mixture was 9 volumes Arochlor/volume TEP.

b) Reaction of 3.46×10^{-2} M TCPO, with 5.0×10^{-2} M H_2O_2 at 25°C.

c) Reaction of 3.46×10^{-2} M TCPO, 5.0×10^{-2} M H_2O_2, and 1.0×10^{-3} M DPA at 25°C.

TABLE D-2

Infrared Study of the Reaction of 0.04 M TCPO, 0.05 M H_2O_2 and 0.0002 M Triton B in Arochlor/TEP[a]

Time (Min.)	Absorbance 1780 cm^{-1}	Remaining Carbonyl (%)	Absorbance 1895 cm^{-1}
0	1.34	100	0
1.7	0.70	52.2	0.001
5.9	0.43	32.1	0.005
10.5	0.39	29.1	0.07
15.5	0.39	29.1	0.12
19.5	0.34	25.4	0.06
40.8	0.24	17.9	0.03
97.6	0.14	10.4	0.025

a) The solvent mixture was 9 volumes Arochlor/volume TEP.

TABLE D-3

Infrared Study of the Reaction of 0.04 M TCPO, 0.05 M H_2O_2, 0.0002 M Triton B and 0.001 M DPA in Arochlor/TEP[a]

Time (Min.)	Absorbance (1780 cm^{-1})	Remaining Carbonyl (%)	Absorbance (1895 cm^{-1})
0	1.34	100	0
2.3	0.61	45.5	0.12
6.2	0.46	34.3	0.05
10.3	0.43	32.1	0.03
15.2	0.36	26.8	0.06
23.8	0.32	23.9	0.03
79.7	0.15	11.2	0.025

a) Solvent mixture was 9 volumes Arochlor/volume TEP.

E. Reaction Product Studies

The gaseous products from a reaction of 0.01 M DNPO with 0.050 M H_2O_2 and 5.6×10^{-4} M DPA were collected under reduced pressure in a system of known volume and analyzed by mass spectroscopy. Carbon dioxide (0.0138 moles, 69% of oxalate carbon), and carbon monoxide (0.00094 moles, 4.7% of oxalate carbon) were found. About 26% of oxalate carbon was thus not accounted for. Less than 0.0002 moles of oxygen was found. Since the quantum yield, 8.1×10^{-2} einsteins $mole^{-1}$, was more than 4 times the oxygen yield, it appears that singlet oxygen is not a major contributor to light emission.

In a separate experiment, infrared spectroscopic analysis of the liquid phase reaction mixture in triethyl phosphate indicated an essentially quantitative yield of 2,4-dinitrophenol. Coulometric titration of the bis(pentafluorophenyl)oxalate reaction mixture in dimethyl phthalate also showed a quantitative yield of pentafluorophenol. Oxalic acid was not detected.

EXPERIMENTAL

Gaseous Products from the Reaction of Bis(2,4-dinitrophenyl)oxalate (DNPO), Hydrogen Peroxide and 9,10-Diphenylanthracene (DPA) - The reactions were carried out in a magnetically stirred three neck flask equipped with a gas sample bulb, a pressure equalized dropping funnel, a differential manometer, and a connection to a vacuum pump. The total volume of the system was 180 ml. The hydrogen peroxide and DPA solutions were placed into the flask and the DNPO solution into the funnel. The concentrations were designed to produce after mixing a solution 1×10^{-2} M in DNPO, 5×10^{-2} M in H_2O_2, and 5.6×10^{-4} M in DPA. The system was evacuated and isolated from the pump by a vacuum stopcock, and the solutions were stirred. This degassing procedure was repeated several times until no pressure change was observed on 30 minutes standing. The solutions were mixed under vacuum (less than 0.1 mm. Hg) and the reaction was continued until the pressure became constant. A sample of the gaseous products was analyzed with Consolidated Engineering Co. 21-103A and 21-110 mass spectrometers. The latter instrument can readily distinguish nitrogen from carbon monoxide. The gas sample contained CO_2, CO and traces of oxygen and water, but no atmospheric contamination.

F. Storage Stability Studies

Component solutions for practical chemical lighting systems must be capable of extended storage without serious loss of light capacity. The oxalate ester system involves two chemical reactants, the ester and hydrogen peroxide, and thus requires storage of two separate component solutions which produce light on mixing. A fluorescer is also required for chemiluminescence and must be present in one of the two component solutions. Moreover, at least one of the component solutions must also contain any additional ingredients required for lifetime control, light capacity improvement, or physical property adjustment.

Satisfactory storage stability of a system component solution clearly requires that the active ingredients in that component be unreactive with each other, and with the solvent, and the container, and that reactive impurities be absent. This places obvious limitations on the formulation of components. High chemiluminescence efficiency in oxalate esters requires that the ester be highly reactive toward nucleophiles. Thus the ester-containing component must be stored in a non-nucleophilic solvent, which is free of nucleophilic additives or impurities. The purity requirement is substantial, since useful ester storage concentrations are as low as 0.02 molar; as little as 0.01% water, alkali or other nucleophilic impurity would be sufficient to decrease light capacities by as much as 25% in a 0.02 M ester solution.

Similarly, the hydrogen peroxide component solution must be free of trace metals or other impurities which decompose hydrogen peroxide. Since hydrogen peroxide will oxidize certain organic fluorescers, it is clear that such fluorescers must be stored in the ester component. Non-oxidizable fluorescers and certain additives, however, might, in principle, be combined with the hydrogen peroxide component.

The results of preliminary storage stability studies[13] reflected the rigid requirements outlined above, and indicated the need for a detailed investigation of storage stability parameters. Initial results from a study of three esters, four solvents, and three container materials are described below. In summary the results to date indicate (1) that a solution of bis(2,4,6-trichlorophenyl)oxalate (TCPO) in benzene is entirely stable for at least 8 weeks at room temperature (2) that a solution of bis(2,4-dinitrophenyl)oxalate (DNPO) in the ether solvent 1,2-dimethoxyethane (DME) appears to be stable for at least 4 weeks when stored at room temperature in Pyrex but unstable when stored in polypropylene; (3) that solutions of DNPO or bis(3-trifluoro-4-methylphenyl)oxalate (TFMNPO) in the ester solvents dimethyl phthalate (DMP) and triethyl phosphate (TEP) are poorly stable. However, since storage of such solutions under carbon dioxide greatly improves storage stability, weak acids in general may prove to be useful stabilizers; and (4) that a component solution of hydrogen peroxide and tetrabutylammonium perchlorate (TBAP) in DMP is stable for at least eight weeks at room temperature.

Thus, relatively stable conditions for room temperature storage of hydrogen peroxide and at least one oxalate have been established and presumably others will also be found. However, no information is yet available on long term storage at room temperature or high temperature storage. Also, the solution stability of oxalate-fluorescer and hydrogen peroxide-fluorescer combinations remain to be investigated and the examination of stabilizing additives appear to be fruitful. For some purposes, storage of mixed solids would be useful, with activation occurring on addition of solvent. No data is yet available on such systems.

Storage stability testing has been complicated by observation of container effects, which may be due in the case of plastic containers, to solvent leaching of soluble components from the plastics or to moisture permiability. Pyrex containers, may also exert an effect on storage, while Teflon containers appear to be inert. The effects of metal containers are as yet unknown.

1. Experiments with TCPO

Solutions of TCPO in benzene are being stored in Teflon or Pyrex bottles at room temperature. The TCPO concentration is being monitored by infrared analysis and by chemiluminescence assay under standard conditions. The results to date are summarized in Table F-1. No significant changes have been observed in quantum yield or lifetime within the experimental error of the assay experiments. Infrared analysis also indicates that the TCPO concentrations have not decreased.

TCPO chemiluminescence presently requires a quaternary salt additive such as TBAP for high efficiency. A solution of hydrogen peroxide and TBAP in DMP, as a potential system component, has been stored at room temperature for 8 weeks. As indicated in Table F-1, the light capacity and lifetime obtained from this aged reagent and aged TCPO solution has not changed significantly. The storage stability of a TCPO and rubrene combination as a potential system component remains to be determined. We expect, however, to replace rubrene with a more suitable fluorescer in further work in any event (See Section IC).

2. Experiments with DNPO

Solutions of 0.02 M DNPO in DMP, TEP or DME were stored in Pyrex, polypropylene, or Teflon containers at 25°C, and the chemiluminescence quantum yields and lifetimes were determined as a function of storage time under standard reaction conditions. The results summarized in Table F-2 indicate that unsatisfactory storage stability was found for solutions in the ester solvents DMP andTEP but that solutions in the ether solvent DME appeared relatively stable when stored in Pyrex, although the light yield was low. It is evident that DNPO solutions in both DMP and DME are more stable than solutions in TEP, and that DNPO solutions in DMP are more stable when stored in polypropylene or Teflon than when stored in Pyrex. Solutions in DME, however, were more stable in Pyrex than in polypropylene. It is also evident that solutions in DMP saturated and stored with carbon dioxide are substantially more stable than degassed solutions stored under argon. It was found that oxalic acid reacts rapidly with DNPO and that storage of a component solution containing both is not feasible.

TABLE F-1

Storage Stability Experiments with Bis(2,4,6-trichlorophenyl) oxalate (TCPO)[a]

Container	TCPO Concentration (M)		0	4	8
Teflon	0.075	Q	21.8	20.8	20.5
		T3/4L	41	20	33
Pyrex	0.060	Q	21.8	20.8[b]	21.7[b]
		T3/4L	40	42[b]	26[b]

a) Benzene solutions stored at 25 °C. Chemiluminescence assay reactions were carried out with 0.01 M TCPO, 0.025 M H_2O_2, 6×10^{-4} M rubrene and 0.067 M tetrabutylammonium perchlorate (TBAP) in 13.5% (by volume) benzene in dimethyl phthalate (DMP) in the Teflon experiments or 16.7% benzene in DMP in the Pyrex experiments by diluting an aliquot of stored TCPO benzene solution with appropriate aliquots of the other reagents in DMP. The quantum yield (Q) in units of einstein $mole^{-1} \times 10^2$ and lifetime (T3/4L, the time in minutes required for three quarters of total light emission) are tabulated as a function of storage time.

b) An aliquot from a solution of 0.25 M H_2O_2 and 0.667 M TBAP in DMP which was stored concurrently with the TCPO-benzene solution, was used as a reagent in the chemiluminescence assay reaction.

TABLE F-2

Storage Stability Experiments with Bis(2,4-dinitrophenyl)oxalate (DNPO)[a]

Solvent[b]	Container	Stored Additive (Concentration, M)		Storage Time in Weeks 0	1	2	3	4	8
DMP	Pyrex	None	Q	18.6	12.7	9.9	8.3	5.3	0.2
			T3/4L	3.3	2.8	3.3	3.9	3.8	3.7
DMP	Pyrex	CO_2 (Sat.)	Q	18.6	13.6	11.7	10.5	10.0	8.8
			T3/4L	3.5	3.1	2.6	2.4	2.7	3.1
DMP	Pyrex	Oxalic Acid (0.00268)	Q	13.9[c]	8.8	7.5	4.8	3.7	-
			T3/4L	3.0[c]	3.0	2.7	3.4	2.9	-
DMP	Polypropylene	None	Q	18.6	15.3	14.2	14.4	12.8	8.4
			T3/4L	3.3	2.8	3.4	3.4	3.5	4.2
DMP	Teflon	None	Q	15.6[d]	-	-	12.5	11.2	-
			T3/4L	4.3[d]	-	-	11.7	6.5	-
TEP	Pyrex	None	Q	5.9	2.3	0.8	0	-	-
			T3/4L	21.8	31.0	22.6	0	-	-
TEP	Polypropylene	None	Q	5.9	0.2	0	-	-	-
			T3/4L	21.8	39.1	0	-	-	-
TEP	Polypropylene	Oxalic Acid (0.00268)	Q	4.4[c]	0	-	-	-	-
			T3/4L	21.3[c]	0	-	-	-	-
TEP	Polypropylene	CO_2 (Sat.)	Q	4.3	0	-	-	-	-
			T3/4L	21.7	0	-	-	-	-
DME	Polypropylene	None	Q	4.1	0	-	-	-	-
			T3/5L	37.3	0	-	-	-	-
DME	Pyrex	Oxalic Acid (0.00268)	Q	5.0	4.5	4.2	3.4	3.3	-
			T3/4L	31.3	16.5	23.0	14.6	21.1	-
DME	Pyrex	None	Q	4.1	5.2	4.7	4.3	3.9	-
			T3/4L	37.3	21.1	46.9	44.6	50.8	-

Q = Quantum Yield x 10^2 based on oxalate concentration.
T3/4L = Time in minutes required for three-quarters of the total light to have been emitted.

a) Solutions of 0.02 M DNPO in the indicated solvent stored at 25°C. Containers were washed well and shaken 48 hours with the reaction solvent prior to use. Chemiluminescence assay reaction was carried out with 0.01 M DNPO, 0.025 M H_2O_2 and 6 x 10^{-4} M rubrene in the indicated solvent by diluting an aliquot of the stored DNPO solution with freshly prepared reagent solutions. The quantum yield is given in units of einsteins $mole^{-1}$ x 10^2, and the lifetime, T3/4L, is in minutes.

b) DMP is dimethyl phthalate
TEP is triethyl phosphate
DME is 1,2-dimethoxyethane

c) Measured 30 minutes after preparation of the DNPO-oxalic acid solution.

d) This sample of DNPO, while purified in the usual way, gave initial quantum yields substantially below the norm, and the instability observed may be caused by impurities.

3. Experiments with TFMNPO

Solutions of 0.02 M TFMNPO in DMP, TEP, or DME were stored in Pyrex, polypropylene, or Teflon containers and chemiluminescence quantum yields and lifetimes were determined under standard reaction conditions, as a function of storage time. The results are summarized in Table F-3. Experiments in DMP and DME gave unusable storage stability results because rubrene consumption during the chemiluminescence assay reactions caused unreproducible quantum yield and lifetime measurements. However, it was found surprisingly that rubrene consumption substantially decreased after one week storage of a TFMNPO-tetrabutylammonium perchlorate (TBAP) solution in DMP so that meaningful results could be obtained. The result suggests that an impurity which is destroyed on standing with TBAP contributes to rubrene destruction. Nevertheless, the quantum yield obtained from the TFMNPO-TBAP solution in DMP decreased on further storage indicating that this is an impractical combination. Storage stability of TFMNPO solutions in TEP was also poor although much better stability was obtained in Teflon than in Pyrex or polypropylene containers. It is evident that carbon dioxide substantially increases the stability of TFMNPO in TEP-polypropylene in agreement with the increase in stability that carbon dioxide produces in the DNPO-DMP-Pyrex system. The effect of carbon dioxide on TFMNPO-TEP and on DNPO-DMP in Teflon remains to be determined. Other acids, particularly weak acids are also expected to have stabilizing activity but remain to be studied.

The concentration of TFMNPO in stored TEP solutions was also monitored by infrared spectral analysis. The results summarized in Table F-4 show that the decrease in quantum yield approximately parallels the destruction of TFMNPO. Thus the loss in quantum yield results from loss of active ester rather than from the appearance of quenchers.

TABLE F-3

Storage Stability Experiments with Bis(3-trifluoromethyl-4-nitrophenyl)oxalate (TFMNPO)[a]

Solvent[b]	Container	Additive Concentration(M)		Storage Time in Weeks 0	1	2	3	4	8
DMP	Pyrex	None	Q.Y.	2.7[c]	3.2[c]	-	-	-	-
			T3/4	188.7[c]	120.4[c]	-	-	-	-
DMP	Pyrex	$Bu_4N^+ClO_4^-$ (0.02)	Q.Y.	7.5[c]	14.4	12.7	10.6	-	6.7
			T3/4L	85.7[c]	22.8	97.7	100.1	-	83.4
DMP	Polypropylene	None	Q.Y.	2.7[c]	5.8[c]	2.9[c]	-	-	-
			T3/4L	188.7[c]	414.5[c]	169.0[c]	-	-	-
TEP	Pyrex	None	Q.Y.	18.1	13.1	7.8	5.6	-	-
			T3/4L	5.8	3.3	2.3	3.7	-	-
TEP	Polypropylene	None	Q.Y.	18.1	10.2	4.7	-	-	0.03
			T3/4L	5.8	3.0	1.3	-	-	7.4
TEP	Polypropylene	$Bu_4N^+ClO_4^-$ (0.02)	Q.Y.	16.1	7.3	4.7	-	-	-
			T3/4L	3.1	2.0	3.2	-	-	-
TEP	Polypropylene	CO_2 (Sat)	Q.Y.	17.8	16.5	15.8	14.0	13.5	-
			T3/4L	4.1	6.7	12.9	12.6	25.1	-
TEP	Teflon	None	Q.Y.	18.7	16.6	16.0	15.1	14.2	11.4
			T3/4L	16.1	95.2	36.7	87.1	64.6	70.3
DME	Pyrex	None	Q.Y.	6.7[c]	4.0[c]	-	-	-	-
			T3/4L	23.6[c]	12.0[c]	-	-	-	-
DME	Polypropylene	None	Q.Y.	6.7[c]	7.3[c]	-	-	-	-
			T3/4L	23.6[c]	115.8[c]	-	-	-	-

a) Solutions of 0.02 M TFMNPO in the indicated solvent stored at 25°C. Containers were washed well and shaken 48 hours with the reaction solvent prior to use. Chemiluminescence reactions were carried out with 0.01 M TFMNPO, 0.025 M H_2O_2 and 6×10^{-4} M rubrene in the indicated solvent by diluting an aliquot of the stored TFMNPO with freshly prepared reagent solutions. Q.Y. = quantum yield in units of einstein $mole^{-1} \times 10^2$ and T3/4L, the lifetime, is in minutes.

b) DMP is dimethyl phthalate
TEP is triethyl phosphate
DME is 1,2-dimethoxyethane

c) Fluorescer consumption was noted.

TABLE F-

Infrared Spectroscopic Analyses of Stored TFMNPO Solutions in TEP

Absorbance at 1803 cm^{-1} in a 0.5 mm Cell	[TFMNPO][a] (Moles $Liter^{-1}$)	Quantum Yield x 10^2[b] (Einsteins $Mole^{-1}$)
0.36[c]	2×10^{-2}[c]	18.1
0.22	1.2×10^{-2}	14.2
0.07	0.39×10^{-2}	4.9
0.00	0	0

a) Concentration based on IR absorbance and Beer's Law.

b) Chemiluminescence quantum yield measured with 0.01 M TFMNPO, 0.025 M H_2O_2 and 6×10^{-4} M rubrene in TEP at 25°C. Representative experiments from Table F-3, stored under various conditions.

c) Stock solution of TFMNPO made up to be 2×10^{-2} M in triethyl phosphate (TEP).

SECTION II

Pyridonylglyoxal Chemiluminescence

The reaction of bis(1-[1H]-2-pyridonyl)glyoxal (PG), hydrogen peroxide and fluorescent compounds has been shown to generate bright chemiluminescent light in a strongly acidic medium.[11,13] Evidence was presented which indicates than an acid catalyzed rearrangement of PG to bis(2-pyridyl)oxalate (PO) precedes the chemiluminescent reaction and PO is the species reactive with hydrogen peroxide.[13] Acid catalysis is a unique feature of PG chemiluminescence; chemiluminescent reactions of oxalic esters and amides are retarded or quenched by strong acids.[10-13]

Additional quantum yield and lifetime data have now been obtained for chemiluminescent reactions of PG with hydrogen peroxide and fluorescers, and such data has also been obtained for chemiluminescent reactions with the newly prepared bis(1-[1H]-5-nitro-2-pyridonyl) glyoxal (NPG). In contrast to PG, chemiluminescent reactions with NPG were found to be base catalyzed as well as acid catalyzed, although the efficiency was lower under basic conditions. Maximum quantum yields of 15.6% and 10.3% respectively were obtained for acid catalyzed reactions of PG and NPG. In contrast to chemiluminescent reactions of oxalate esters, concentration-derived efficiency losses were not observed at concentrations up to 1.3×10^{-2} M with PG. Product analyses show that CO_2 is the major product from the PG-H_2O_2 reaction; yields of O_2 and CO were so low that they can be excluded as chemiluminescent reaction products.

A. Preparation and Properties of NPG

NPG was prepared in 25% yield by reaction of 2-hydroxy-4-nitropyridine with oxalyl chloride and triethylamine in 1,2-dimethoxyethane at 25°C. Solubilities of NPG and PG in several solvents are summarized in Table A-1.

TABLE A-1

Solubilities of Bis(1-[1H]-2-pyridonyl)glyoxal (PG) and Bis(1[1H]-5-nitro-2-pyridonyl)glyoxal (NPG)

Solvent	Solubilities (Moles Liter^{-1} x 10^2) PG	NPG
Triethylphosphate	4.4	2.7
Benzene	3.6	-
1,2-Dimethoxyethane	3.3	2.3
Arochlor 1242	$\lesssim$ 1.5	-
Dimethyl phthalate	3	3.6
Propylene carbonate	3.8	-

a) Determined by periodic addition of 0.5 ml. solvent in 15 minute intervals to a test tube containing a known amount (~ 10 mg) PG being stirred by magnetic stirrer, until all dissolved at 25°C.

B. Qualitative Chemiluminescence Experiments with Bis(1-[1H]-2-pyridonyl)glyoxal (PG) and Bis(1-[1H]-5-nitro-2-pyridonyl)glyoxal (NPG)

The standard qualitative chemiluminescent test results for PG and NPG are shown in Table B-1. Both compounds produce medium intensity chemiluminescent light in dimethoxyethane solvent at neutral condition. A strong acid, methane sulfonic acid, increases the brightness of both reactions substantially while base retards it.

The effect of acid strength on the PG reaction was tested in dimethyl phthalate solvent. Results are summarized in Table B-2. The PG reaction produces light emission only where a strong acid is present. The addition of 3,4,5-trimethoxybenzoic or 4-nitrobenzoic acids failed to induce light emission. Very strong light emission was obtained in the presence of trichloroacetic acid and a somewhat weaker emission with oxalic acid. Picric acid produced medium bright light. Thus a strong acid pKa $\lesssim$ 1.5 is required for efficient PG chemiluminescence in dimethyl phthalate. However, the relative strength of organic acids may not parallel their pKa measured in water as the example of picric acid shows. The general solvent dependence of acidic strength is known and has been discussed.[29]

TABLE B-1

Qualitative Chemiluminescence with PG and NPG

Compound	Tests[a]			
	A	B	C	D
PG	M	W	M	S
NPG	M	MW	M	MS

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. DPA and 0.2 ml. CH_3SO_3H in 1,2-dimethoxyethane containing 5% water and maintained 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.

TABLE B-2

The Effect of Various Organic Acids on the Chemiluminescent Reaction of Bis(1-[1H]-2-pyridonyl)glyoxal (PG)[a]

Acid	pKa[b]	Chemiluminescent Light[c]
None	-	None
3,4,5-Trimethoxybenzoic	-	None
4-Nitrobenzoic	3.41	None
Oxalic	1.23	MS
Trichloroacetic	0.70	VS
Picric	0.38	M

a) Approximately 2 mg. PG was added to a 5ml. solution of 1 mg. 9,10-diphenylanthracene and 0.2 ml. 5×10^{-2} M H_2O_2 and about 2 mg. acid in dimethyl phthalate at 25°C.

b) Dissociation constant in aqueous solution.

c) The qualitative light intensities are based on the oxalyl chloride reaction taken as strong (s).

Other designations are M = medium, VS = very strong, MS = medium strong, VW = very weak, barely visible.

C. Quantitative Chemiluminescence Experiments with Bis(1-[1H]-2-pyridonyl)glyoxal (PG)

The results of a series of experiments with PG, three acidic catalysts and two fluorescers are summarized in Table C-1. The fluorescer rubrene gave substantially higher quantum yields than the fluorescer DPA (Experiments 4 vs. 7 and 9 vs. 12) as has been observed for oxalate esters.[13] However, emission lifetimes with the two fluorescers were not markedly different. In contrast to oxalate ester reactions,[11-13] loss in efficiency was not observed when the PG concentration was increased from 0.010 M to 0.013 M (Experiments 7 and 8). Increasing hydrogen peroxide concentrations in the range studied appears to have little effect on efficiency and only a moderate effect in decreasing lifetimes (Experiments 2, 4, and 6). Increasing acid concentration substantially decreases the lifetime but decreases the quantum yield only at high acid concentrations (Experiments 3, 4, and 5). Similar quantum yields were obtained with trichloroacetic acid, trifluoroacetic acid and oxalic acid, but lower concentrations of the stronger trifluoroacetic acid (pK 0.23)[30] were required for reasonable lifetimes, (Experiments 3, 9, and 13). Longer lifetimes were obtained with oxalic acid (pK, 1.23) than with trichloroacetic acid (pK 0.70) under comparable conditions, (Experiments 4 and 9). Gradual addition of acid increased the overall lifetime as expected, and had a moderate, variable effect on efficiency (Experiments 9 vs. 10 and 13 vs. 14). Addition of tetrabutylammonium perchlorate (TBAP) decreased the lifetime and efficiency moderately in experiments with the fluorescer DPA (Experiments 9 and 11), in contrast to earlier experiments with rubrene where TBAP increased the quantum yield somewhat.[13]

TABLE C-1

Quantum Yields and Lifetimes of Chemiluminescence from the Reaction of Bis(1-[1H]-2-pyridonyl)glyoxal (PG), Hydrogen Peroxide and Fluorescers in Acidic Media[a]

A. In the Presence of Trichloroacetic Acid

No.	PG (Mole l^{-1} x 10^2)	H_2O_2 (Mole l^{-1} x 10^2)	Fluorescer (Mole l^{-1} x 10^{-4})	Acid (Mole l^{-1} x 10^2)	I_{max}[b] (Ft.-Lambert)	Lifetimes (min)[c] T1/4	T3/4L	Quantum Yield[d] (Einstein Mole^{-1} x 10^2)
1	0.1	1.0	5.0 DPA	1.0	0.07	27.2	26.6	9.6
2	1.0	1.0	5.0 "	3.3	0.58	11.7	10.8	3.8
3	1.0	5.0	5.0 "	1.0	0.21	23.1	30.6	3.3
4	1.0	5.0	5.0 "	3.3	0.75	10.2	9.0	4.2
5	1.0	5.0	5.0 "	10.0	1.71	2.0	1.7	1.8
6	1.0	10.0	5.0 "	3.3	0.86	7.5	6.4	3.5
7	1.0	5.0	6.0 Rubrene	3.3	38.0	8.4	8.9	15.2
8	1.33	3.33	5.0 "	2.7	26.2	15.8	16.4	15.6

B. In the Presence of Oxalic Acid

9	1.0	5.0	5.0 DPA	3.3	0.16	57.8	57.0	4.8
10	1.0	5.0	5.0 "	3.3[e]	0.11	89.0	74.2	6.3
11	1.0	5.0	5.0 "	3.3[f]	0.32	17.3	23.7	3.5
12	1.0	5.0	6.0 Rubrene	3.3	9.72	30.4	55.8	15.2

C. In the Presence of Trifluoroacetic Acid

13	1.0	5.0	5.0 DPA	0.33	0.54	10.0	13.4	3.7
14	1.0	5.0	5.0 "	0.33[e]	0.08	100.8	75.0	3.1
15	1.0	5.0	5.0 "	3.3	Reaction is too fast to measure			

a) Reaction in dimethyl phthalate at 25°. DPA is 9,10-diphenylanthracene.

b) Maximum brightness measured in a 1.0 cm thick cell.

c) $T_{1/4}$ is the time required for the light intensity to decay to one-quarter of its maximum value. $T_{3/4L}$ is the time required for the emission of three-quarters of the available light

d) Based on PG.

e) The acid was added in several aliquots during the course of the reaction.

f) 6.7 x 10^{-2} M Tetrabutylammonium perchlorate was added.

D. Quantitative Chemiluminescence Experiments with Bis(1-[1H]-5-nitro-2-pyridonyl)glyoxal (NPG)

The results of a series of experiments with NPG under varying conditions are summarized in Table D-1. The fluorescers rubrene and 9,10-bis(phenylethynyl)anthracene gave similar quantum yields and lifetimes (Experiments 6 and 8). Only a slight loss in efficiency was observed when the NPG concentration was increased from 0.010 M to 0.014 M (Experiments 6 and 9). Increasing the hydrogen peroxide concentration from a 1:1 H_2O_2:NPG ratio to a 5:1 ratio increased the efficiency by 62% and had little effect on the lifetime (Experiments 2 and 6). While significant light emission was obtained in the absence of acid or base (Experiment 3), increasing acid concentration substantially increased quantum yields, while decreasing lifetimes, (Experiments 3, 5, and 6). Triethyl amine also greatly increased the quantum yield and decreased the lifetime relative to the uncatalyzed experiment (Experiments 3 and 4), but base catalysis was less effective than acid catalysis under the limited conditions studied (Experiments 4 and 6). Gradual addition of acid increased the lifetime as expected but decreased the quantum yield (Experiments 6 and 7). Addition of tetrabutylammonium perchlorate under acidic conditions moderately decreased both the quantum yield and lifetime.

TABLE D-1

Quantum Yield and Lifetime of Chemiluminescence from the Reaction of Bis(1-[1H]-5-nitro-2-pyridonyl)glyoxal (NPG), Hydrogen Peroxide and Fluorescer in Acidic Media[a]

No.	NPG (Mole l^{-1} x 10^2)	H_2O_2 (Mole l^{-1} x 10^2)	Methanesulfonic Acid (Mole l^{-1} x 10^2)	I_{max}[b] (Ft. Lambert)	Lifetimes (Min)[c] T1/4	T3/4L	Quantum Yield[d] (Einstein $Mole^{-1}$ x 10^2)
1	0.1	1.0	0.5	0.07	206.2	154.0	7.0
2	1.0	1.0	5.0	3.65	37.1	28.5	6.1
3	1.0	5.0	None	0.19	53.0	80.3	0.6
4	1.0[e]	5.0	None	34.4	2.1	6.3	4.6
5	1.0	5.0	1.0	1.51	91.0	69.1	6.6
6	1.0	5.0	5.0	5.49	39.4	27.8	9.9
7	1.0	5.0	5.0[f]	1.31	131.3	89.9	6.9
8	1.0[g]	5.0	5.0	6.72	31.1	22.5	10.3
9	1.4	5.0	5.[illegible]	7.62	36.6	25.3	9.2
10	1.4[h]	5.0	5.0	8.72	26.5	18.6	7.8

a) Experiments with 6 x 10^{-4} M rubrene in dimethyl phthalate at 25°.

b) Maximum brightness in a 1 cm. thick cell.

c) T1/4 is the time when the light intensity remains above one-quarter of its maximum value. T3/4L is the time required for the emission of three-quarters of the available light.

d) Based on NPG.

e) 3.3 x 10^{-4} M triethylamine was added.

f) Methanesulfonic acid was added in five equal protions at 0, 90, 117, 135, and 144 minutes to maintain the light intensity above 25% of I_{max}.

g) The fluorescer was 1.6 x 10^{-3} M 9,10-bis(phenylethynyl)anthracene.

h) 3.3 x 10^{-2} M tetrabutylammonium perchlorate was added.

E. Reaction Product Studies

Gaseous products of the PG-hydrogen peroxide-trichloroacetic acid reaction have been determined under reduced pressure ($\lesssim$ 0.1 mm Hg) in dimethyl phthalate solution. The results are shown in Table E-1. The major reaction product is carbon dioxide which accounts for 81.1% of the glyoxal carbon. Although carbon monoxide and oxygen are also produced in minor amounts, their low yields rule them out as chemiluminescent products. The absence of rubrene showed no substantial effect on product distribution or yield.

A control experiment was carried out under an argon atmosphere to check the effect of pressure on light emission. The results in Figure 1 compare light emission at 1 atm. argon and in vacuum. No substantial effect of pressure was observed.

The effect of rubrene on the rate of evolution of gaseous products is indicated by Figure 2. Rubrene produced no observable change in evolution rate during the first sixty minutes of the reaction, but appeared to increase the rate slightly in the later dim period of reaction.

The light emission and gas evolution rates are compared in Figure 3. The results indicate that the maximum gas evolution rate follows the maximum intensity by about 4 minutes. This may reflect in part the initial saturation of the solution by carbon dioxide. Following the maximum in the gas evolution rate at 5 minutes the intensity decay and gas evolution rates become similar, although the intensity decay is clearly more rapid. This may result from a decrease in quantum yield (light per unit reaction) at longer reaction times caused by product quenching.

In the absence of trichloroacetic acid the reaction proceeded rather slowly and produced somewhat higher oxygen yield.

TABLE E-1

Gaseous Products of the PG Chemiluminescent Reaction[a]

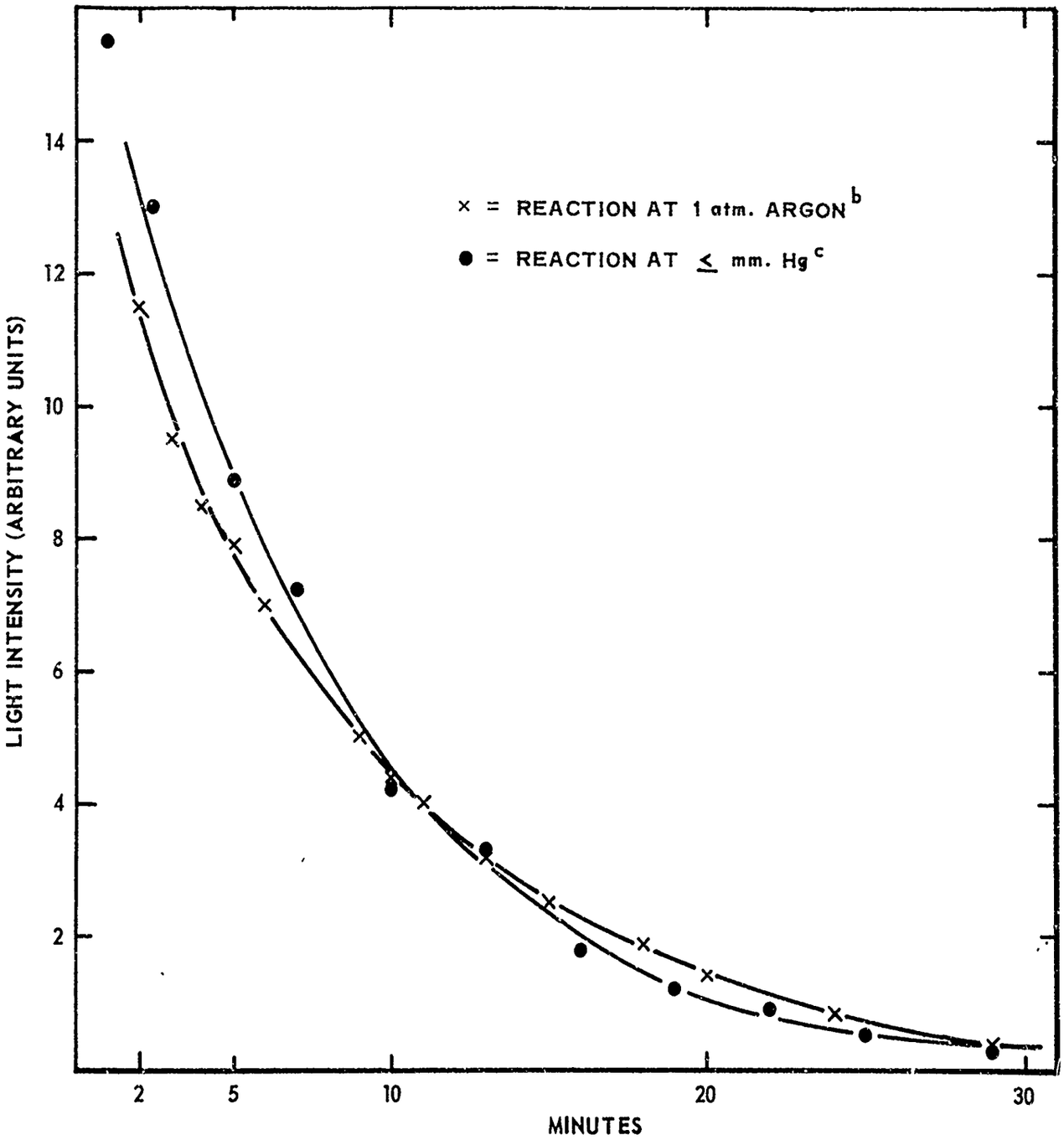
Reactant Concentrations (Mole l^{-1})				Chemiluminescent Quantum Yield	Products (Mole/Mole PG)				Glyoxal Carbon Balance (%)
PG	H_2O_2	CCl_3CO_2H	Rubrene	(Einstein $Mole^{-1} \times 10^2$)	CO_2	CO	$CO_2 + CO$	O_2	$CO_2 + CO$
1.33×10^{-2}	3.33×10^{-2}	None	5×10^{-4}	-	1.598	0.075	1.673	0.095	83.7
1.33×10^{-2}	3.33×10^{-2}	2.7×10^{-2}	None	-	1.510	0.080	1.590	0.009	79.5
1.33×10^{-2}	3.33×10^{-2}	2.7×10^{-2}	5×10^{-4}	15.6	1.621	0.061	1.682	None[b]	84.2

a) In dimethyl phthalate at 25° at 0.1 mm mercury as described earlier.[13]

b) Less than 0.005 mole/mole PG.

Figure 1

THE EFFECT OF PRESSURE ON LIGHT EMISSION OF THE PG CHEMILUMINESCENT REACTION[a]



Footnotes for Figure 1

a) The reactions were carried out in identically cleaned Pyrex glass ware using identical reagent stock solutions in dimethyl phthalate at 25°. Concentrations were : 1.33×10^{-2} M PG, 3.33×10^{-2} M H_2O_2, 2.7×10^{-2} M CCl_3CO_2H, 5.0×10^{-4} M rubrene.

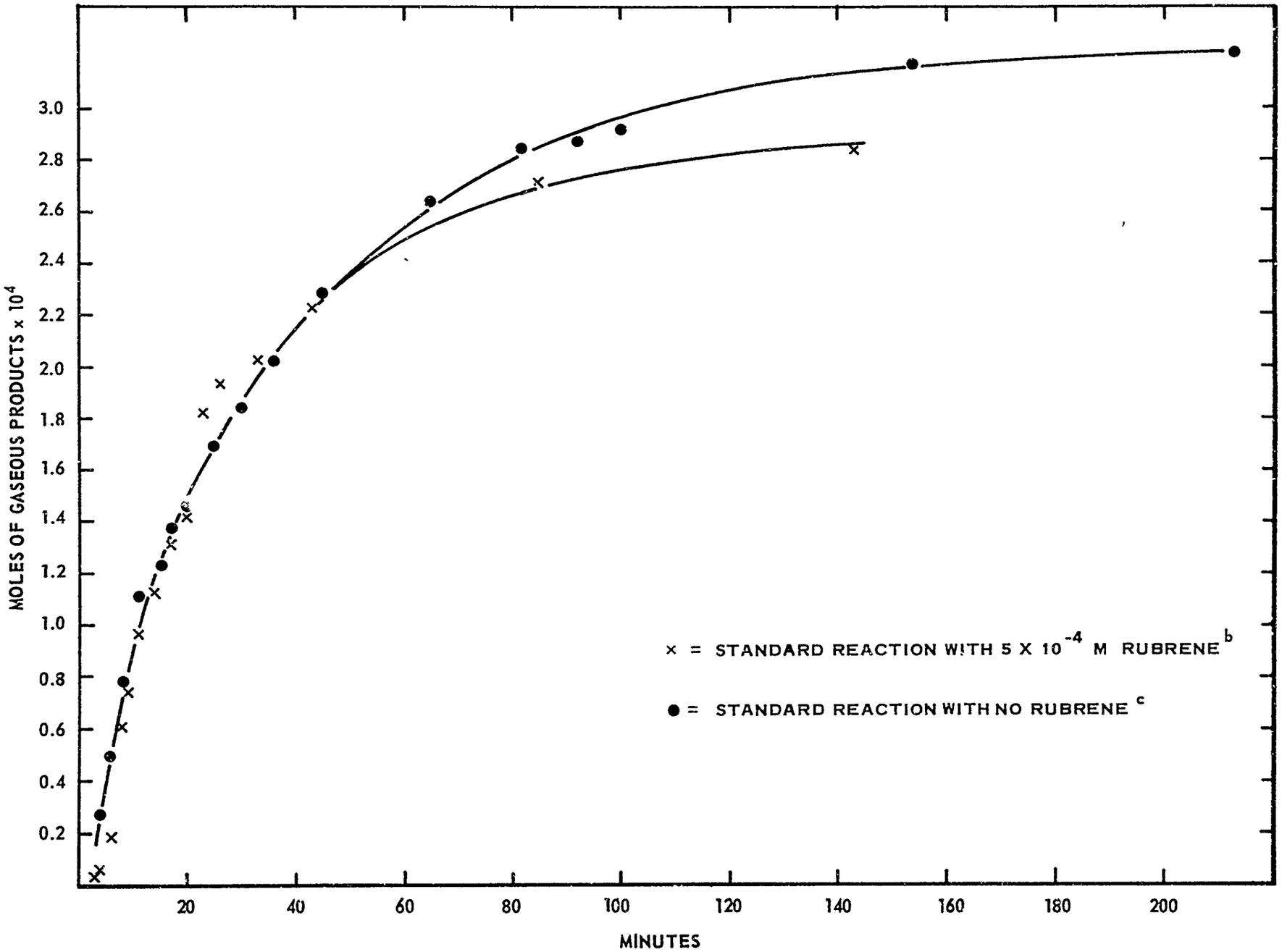
b) X = The solutions were degassed under vacuum and argon was added to produce 1 atm. pressure. The degassing was repeated and the reaction carried out 1 atm. argon pressure.

c) • = The solutions were degassed under vacuum using good agitation. When no pressure change was observed after 30 minutes standing the reactor flask was isolated from the vacuum pump. The reaction was carried out at ≤ 0.1 mm Hg initial pressure.

Figure 2

Figure 2

THE EFFECT OF RUBRENE ON GASEOUS PRODUCTS OF THE PG CHEMILUMINESCENT REACTION [a]



Footnotes to Figure 2

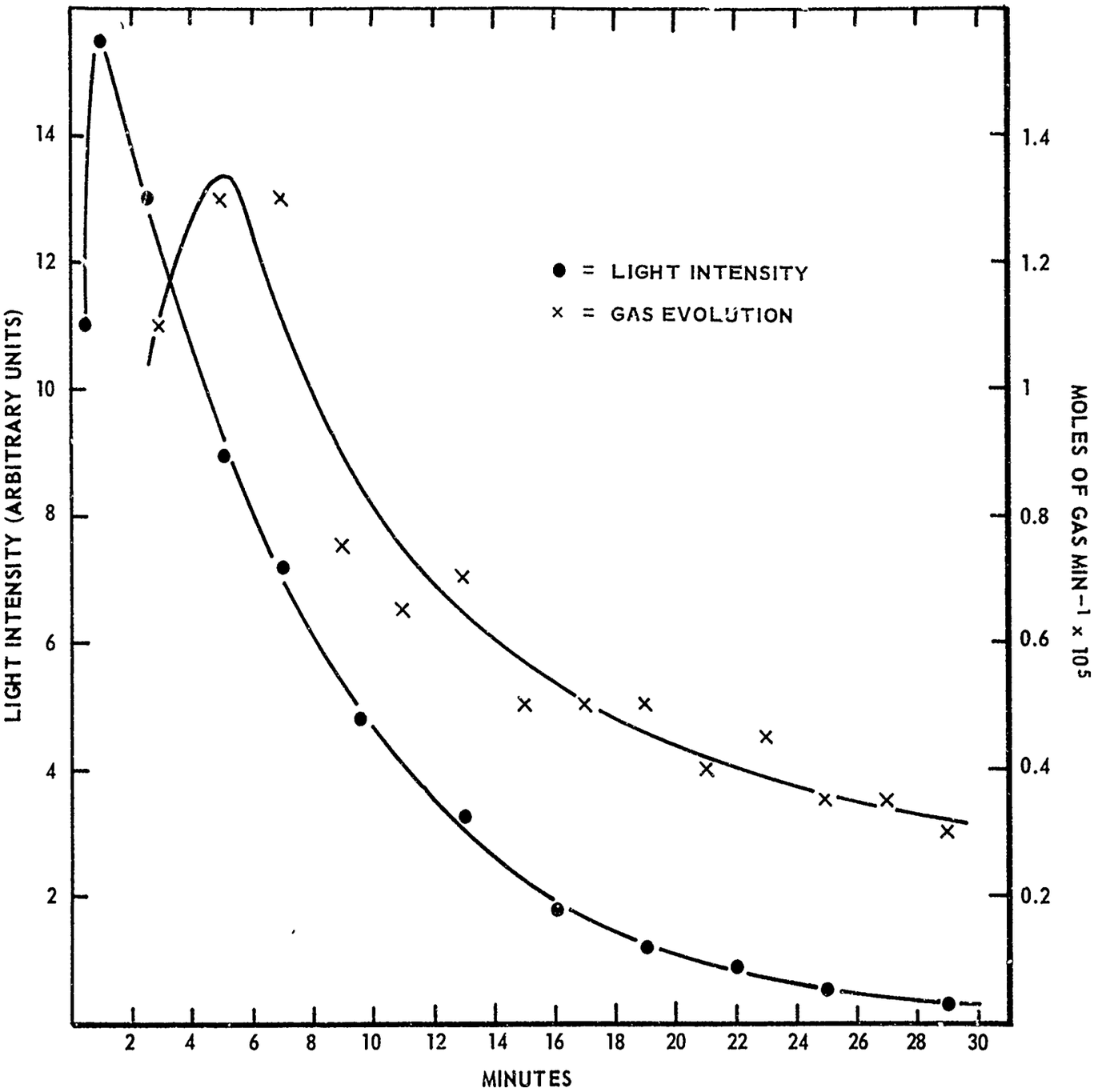
a) Reactions were in identically cleaned glass ware using identical reagent stock solutions in dimethyl phthalate under $\leq$ 0.1 mm Hg pressure at 25°.

b) • = Concentrations were : 1.33×10^{-2} M PG, 3.33×10^{-2} M H_2O_2, 2.7×10^{-2} M CCl_3CO_2H, 5.0×10^{-4} M rubrene.

c) X = Identical to b except no rubrene was present.

Figure 3

COMPARISON OF LIGHT INTENSITY AND RATE OF GAS EVOLUTION IN THE PG CHEMILUMINESCENT REACTION[a]



Footnotes for Figure 3

a) Concentrations were : 1.33×10^{-2} M PG, 3.33×10^{-2} M H_2O_2, 2.7×10^{-2} M CCl_3CO_2H, 5×10^{-4} rubrene. The reaction was carried out in dimethyl phthalate under 0.1 mm Hg pressure at 25°.

b) • = Light intensity.

c) X = Gas evolution.

EXPERIMENTAL

Bis(1-[1H]-5-nitro-2-pyridonyl)glyoxal (NPG) - To a stirred solution of 7.0 g. (0.05 moles) of 5-nitro-2-hydroxypyridine in 125 ml. of distilled 1,2-dimethoxyethane under argon, was added 3.2 g. (0.025 moles) of oxalyl chloride then 5.1 g. (0.05 moles) of triethylamine. The reaction was stirred one hour at 25° then evaporated to dryness under reduced pressure. The reaction residue was washed with chloroform to remove triethylamine hydrochloride and crystallized twice from benzene to obtain 2.1 g. (25%) of pale orange crystals, m.p. 186.5-188° dec.

Anal. Calcd. for $C_{12}H_6N_4O_8$: C, 43.13; H, 1.81; N, 16.77. Found: C, 43.99; H, 1.84; N, 17.99.

Procedures for Light Measurements[9] and Gaseous Product Analyses - have been described previously.[13]

SECTION III

OXALIC ANHYDRIDE CHEMILUMINESCENCE

The Effect of Hydrogen Peroxide Concentration on Quantum Yield

Four mixed anhydrides of oxalic acid were prepared earlier.[7-9] Although two of them, triphenylacetic oxalic anhydride (TPAOA) and acetic oxalic anhydride (AOA), produced efficient long lived chemiluminescent light emission, the study of oxalic anhydride chemiluminescence was not completed because of the general thermal and hydrolytic instability of these anhydrides and the apparent superiority of oxalic esters. Most of the earlier quantitative measurements were carried out with the relatively stable TPAOA. However, the effect of hydrogen peroxide concentration on TPAOA chemiluminescence was not studied in the important equimolar and lower than equimolar concentration range. The quantum yield might be expected to depend strongly on the anhydride: hydrogen peroxide ratio in this range if the reaction requires 1:1 stoichiometry.

The effect of hydrogen peroxide-TPAOA molar ratio on the chemiluminescent quantum yield is shown in Table I.

The light yield per mole of hydrogen peroxide added to the system appears to decrease in a more or less regular manner with increasing hydrogen peroxide even at quite low hydrogen peroxide: anhydride ratios where complete consumption of hydrogen peroxide would be expected. It would thus appear that a non-chemiluminescent process, which is favored by higher hydrogen peroxide: anhydride ratios, competes with the process leading to light emission. This view is reinforced by the observation that the light yield per mole of added anhydride decreases with increasing hydrogen peroxide above a H_2O_2: anhydride ratio of

about 5:1 rather than at a 1:1 or 2:1 ratio which would represent a simple reaction stoichiometry. It is not presently known whether anhydride consumption is complete at H_2O_2: anhydride ratios less than 5:1, although it is likely that consumption would be complete at a 1:1 ratio. The results observed could be a consequence of hydrogen peroxide consumption by a side reaction (perhaps a free radical chain decomposition), or a consequence of anhydride consumption by a competing non-chemiluminescent reaction (perhaps a free radical chain process or reaction with water) wherein excess hydrogen peroxide would convert a larger fraction of anhydride to chemiluminescent intermediates, or both. The effect of increasing H_2O_2 concentration on anhydride chemiluminescence clearly differs substantially from its effect on oxalyl chloride chemiluminescence (where the quantum yield based on oxalate increases to an asymptotic limit)[9] and from its effect on oxalic ester chemiluminescence (where the quantum yield based on oxalate increases up to a 1:1 ratio and then remains essentially constant.[12]

TABLE I

The Effect of Hydrogen Peroxide Concentration on the Quantum Yield of Bis(triphenylacetic) Oxalic Anhydride (TPAOA) - Hydrogen Peroxide - DPA Reaction

H_2O_2[a] (Moles l^{-1} x 10^2)	Molar Ratio $\frac{H_2O_2}{TPAOA}$	Quantum Yield [Einstein (Mole TPAOA)$^{-1}$ x 10^2]	Quantum Yield [Einstein (Mole H_2O_2)$^{-1}$ x 10^2]
0.12	0.21	3.6	17.0
0.24	0.42	4.7	11.1
0.42	0.71	6.8	9.2
0.60	1.06	7.4	7.0
0.80	1.40	10.4	7.3
1.40	2.48	11.1	4.5
2.80	4.95	13.3	2.7
5.61	9.90	9.4	0.95
27.70	40.0	5.9	0.15

a) The concentrations of other reagents were: 5.67×10^{-3} mole l^{-1} TPAOA and 5.2×10^{-4} mole l^{-1} DPA and the reaction was carried out in DMP at 25°.

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