MRB3009Q2

Technical Report No. 2

to the

Office of Naval Research
and
Advanced Research Projects Agency
ARPA Order No. 299, Amend. 6
Contract Nonr 4511(00)
Task NR 356-464

CHEMILUMINESCENT SYSTEMS

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY

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15 December 1964

ABSTRACT

Major emphasis has been placed upon the screening program for chemiluminescent autoxidation reactions. Weak chemiluminescence was observed for almost all base-catalyzed reactions in aprotic solvents. The brightest visible emissions observed thus far have been the oxidations of benzoin and of 2-benzylimidazoline.

The luminescence of lucigenin in alkaline peroxide oxidation in mixed solvents was studied as a function of THF concentration. Within the bounds determined by product precipitation, the peak intensity, total emission "figure-of-merit", and decay rate increase with THF concentration. Striking correlation has been observed between the decay half-lives of the chemiluminescence of the lucigenin solution and of the lucigenin-free solution at the same reagent levels.

TABLE OF CONTENTS

I. INTRODUCTION

The first phase of the present program for the development of practical chemiluminescent systems has been directed toward the exploration of solvent and sensitizer effects on chemiluminescence and the empirical screening of promising chemiluminescent reactions. In the previous report (ref. 1), a bright (visible) chemiluminescence was noted associated with the alkaline peroxide reaction with tetrahydrofuran (THF) and with acetone (sensitized). It was also shown that THF was the most efficient of the reagents tested in increasing the total chemiluminescence output of the lucigenin reaction.

The present report discusses the continuation of this work and the results of the initial screening of autoxidation chemiluminescence in strongly basic solution in aprotic solvents.

II. INSTRUMENTATION

The "batch" photometer (ref. 1) was modified by the addition of a gas purification and handling system to permit total luminescence measurements during addition of nitrogen or oxygen gas. Another such instrument has been assembled to increase the screening rate.

The Bass-Kessler spectrometer was essentially completed and is being tested. The Spex scanning spectrometer has been received and is being assembled. A sample compartment is being designed to permit determination of standard spectral brightness (ref. 2).

The data presented in this report are relative measurements of total emission as determined by the geometry of our apparatus and response of the phototubes. The photo currents may be only crudely related to brightness measurements under standard conditions by comparison to the photocurrent observed for a "reference" luminol solution (ref. 1).

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. ALKALINE PEROXIDE OXIDATIONS

The dependence of the peak emission, decay half-life, and "figure-of-merit" product of those quantities upon the volume per cent THF in the mixed solvent is presented in Figures 1-3.

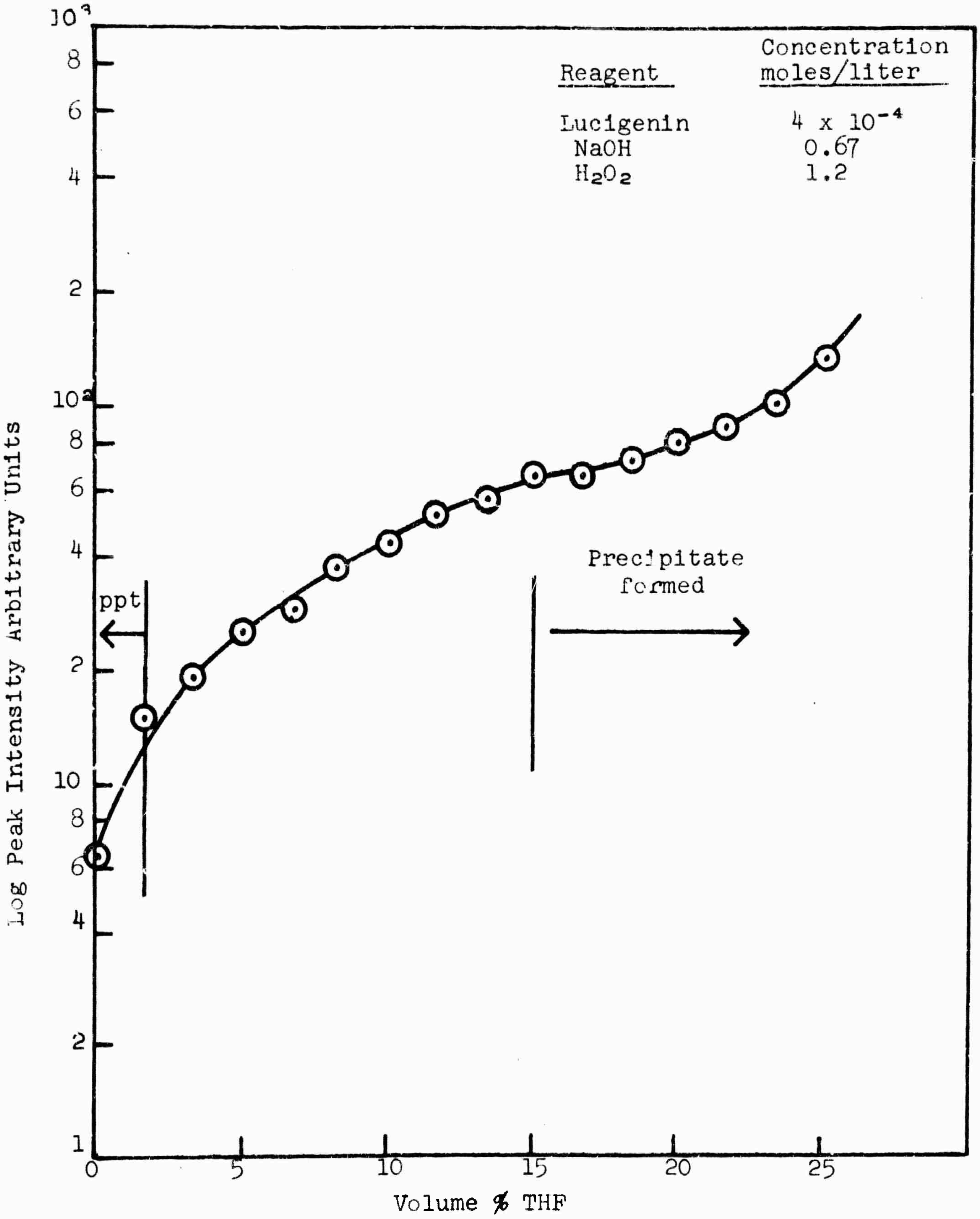

Figure 1. Peak Emission of Lucigenin as a Function of THF Concentration

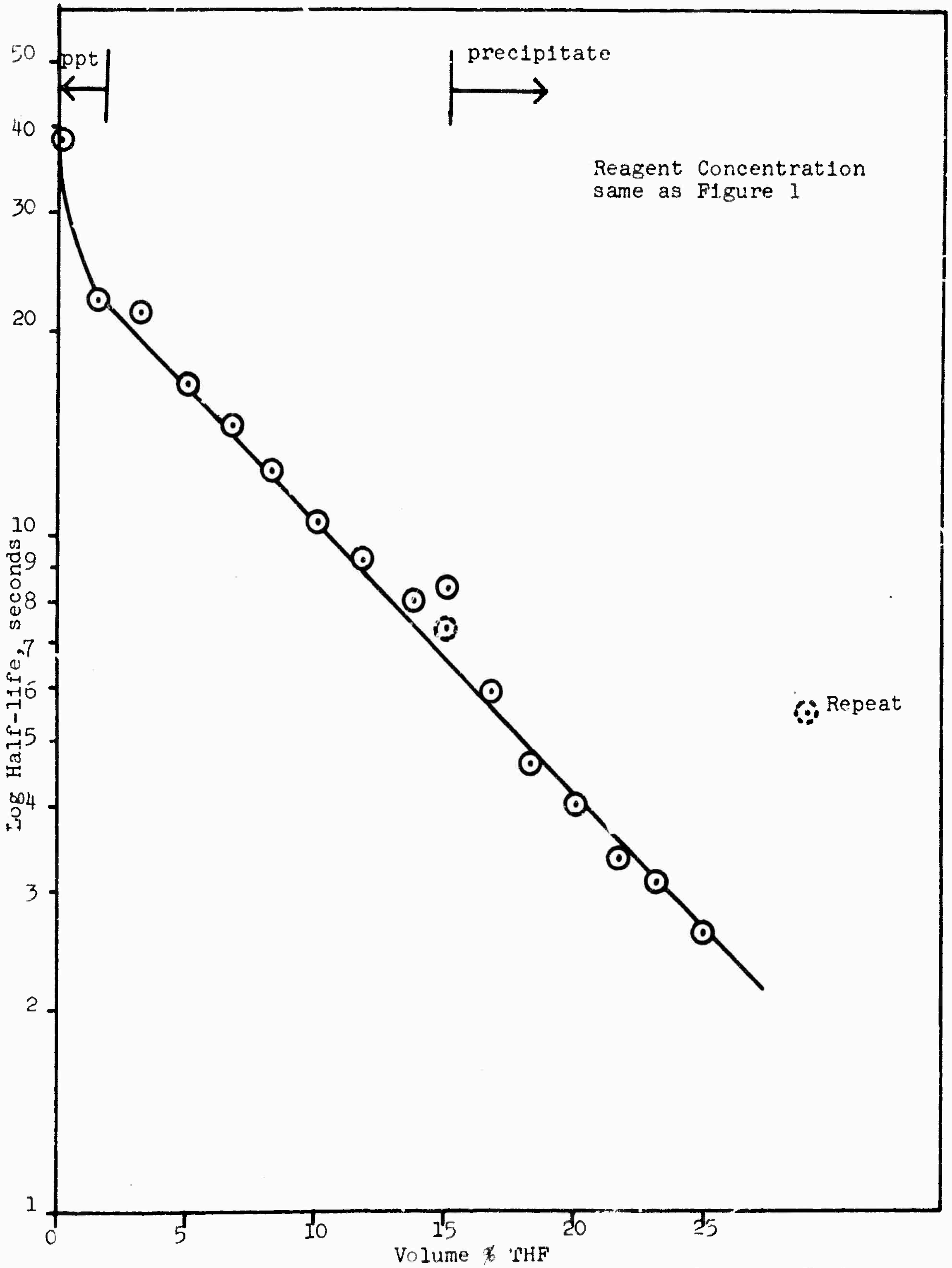

Figure 2. Half-life of Lucigenin Emission as Function of THF Concentration

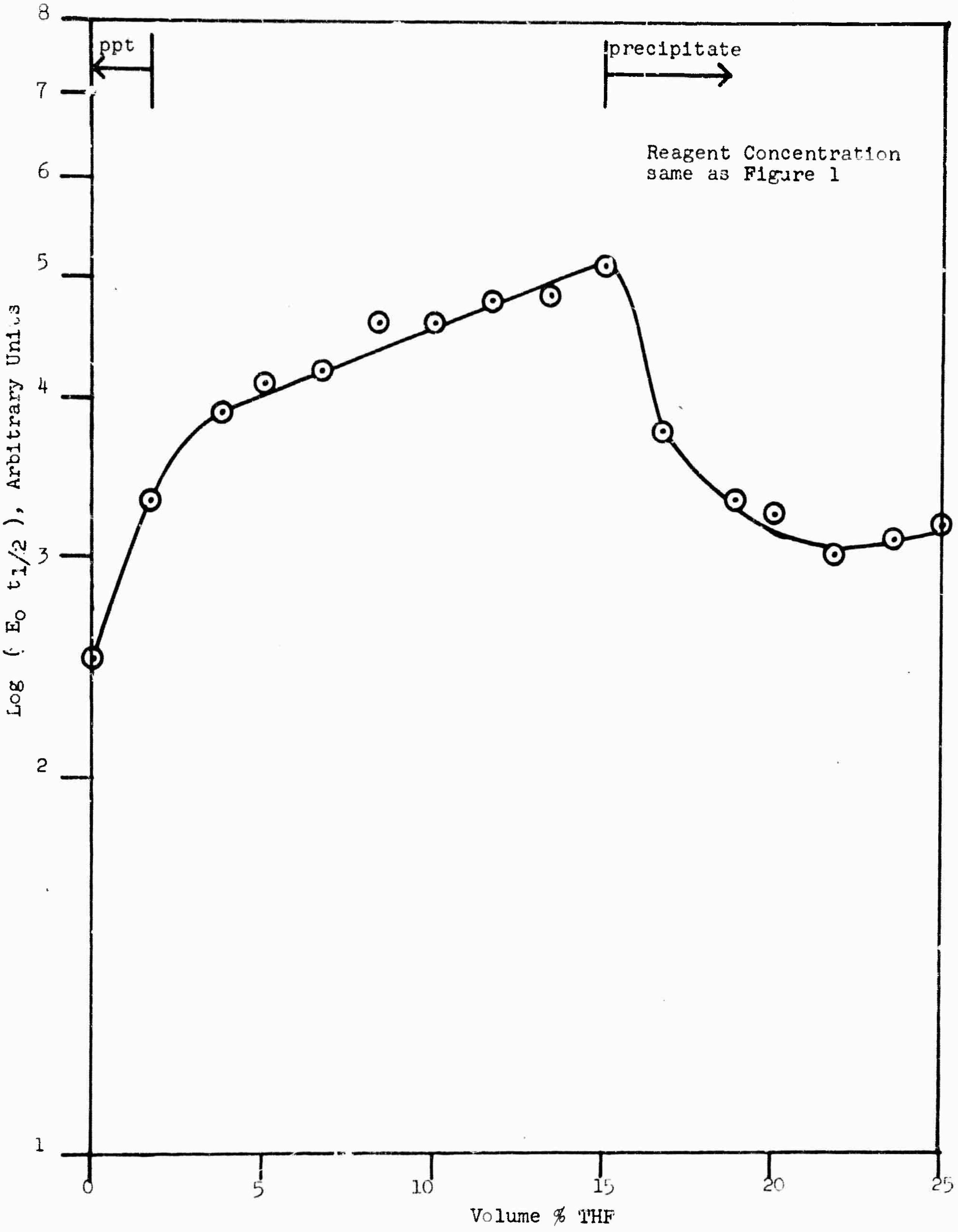

Figure 3. Variation of $E_o(t_{1/2})$)"figure of merit") of Lucigenin with Addition of THF

Both emission peak intensity and decay half-life are monotonic functions of the THF concentration; the product, related to the integrated output, is a simple, increasing function of the THF concentration only within the region defined by absence of product precipitation.

Within the limitations of the simple "figure-of-merit" product (rather than the integrated emission), the efficiency of the emission appears to increase by a factor of about two until reduced by turbidity, assuming that the emission spectrum is unchanged. The logarithmic dependence of the decay half-life upon the THF concentration over a rather wide range is striking. For a pseudo first-order reaction (ref. 3), this relationship is formally that due to a decrease in activation energy. This may, of course, be determined by measurement of the reaction rate temperature coefficient at various THF concentrations. It would clearly be of interest to investigate this apparent efficiency increase for additional solverts in which greater product solubilities may exist.

In the course of determination of the background emission from alkaline peroxide solutions, it was observed that the decay half-life of the presumably lucigenin-free aqueous solutions was strikingly similar to that of the lucigenin-containing solutions (Table 1).

Table 1

DECAY HALF-LIVES OF ALKALINE PEROXIDE SOLUTIONS

(H_2O_2 conc. = 1.2 mole/liter)

Reagent Level		Decay Half-Life, sec.*	
NaOH, M	THF, vol-%	Lucigenin, 4 x 10^{-3}M	Lucigenin-free
0.38	0	115	90
0.67	0	38	38
0.67	13	8.0	8.2
0.67	24	3.8	3.1

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*Note that the peak intensity ratios for the decays compared above are greater than 10^4.

It is not clear at this point whether this striking correlation is a trivial result of contamination of the lucigenin-free solutions. If the observations prove reproducible under various conditions it would strongly suggest that the luminescence of lucigenin is a sensitization, or energy transfer phenomenon.

B. AUTOXIDATION REACTIONS

The noteworthy result of the autoxidation work to date is that the observation of chemiluminescence is the usual rather than the exceptional phenomenon for base-catalyzed reactions in aprotic solvents.

The compounds screened and the results obtained are given in Table 2. To relate these results to the previous work with alkaline peroxide oxidant, we may consider the autoxidation of acetone. The peak chemiluminescence after the initial flash observed for 30% acetone and 0.5 M NaOH with O_2 addition is quite feeble (10^{-11} amp), roughly three orders of magnitude below the alkaline peroxide value. For 5×10^{-3} M acetone in dimethylsulfoxide (DMSO)(with 0.1 M potassium t-butoxide) the peak photo current rises to the order of 5×10^{-10} amp. This latter value may crudely be used for comparison of the efficiency of the present autoxidation reactions to the previous peroxide results; i.e. the total luminescence for acetone under the chosen conditions for autoxidation is roughly twenty fold below the observed values for oxidation with alkaline peroxide*. (This is not the case for luminol, however. See following).

It should be noted that no chemiluminescence is observed for O_2 plus pure DMSO. However, addition of potassium t-butoxide (t-BuOK) produces a pulse at 7×10^{-11} amp†, which drops quickly (one minute) to a steady level of $\approx 4 \times 10^{-11}$ amp. Addition of O_2 leads to a slow rise to 8×10^{-11} amp (at a flow rate of ≈ 0.35 cc/sec) in about 15 minutes. This base line behavior must be kept in mind in discussion of subsequent reactions.

The chemiluminescence output is generally a complex function of time, paralleling the DMSO behavior; i.e., an initial mixing pulse is followed by decay and gradual buildup with O_2 addition. Of the reactions thus far investigated, the brightest autoxidations are with fluorene and 9-fluorenone (both in DMF), $>10^{-8}$ amp; benzoin, 4×10^{-8} amp; and 2-benzylimidazoline, $3 + 1 \times 10^{-7}$ amp (initial pulse). The luminescence of benzoin and 2-benzylimidazoline is visible to the eye.

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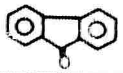
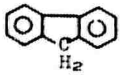
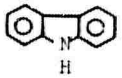
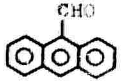
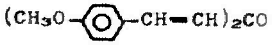
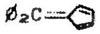
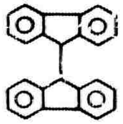
* These values are still far below the luminol output of $\approx 8 \times 10^{-5}$ amp (Ref. 1).

† Data for batch photometer with P28 photomultiplier at 500 volts.

Table 2

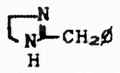
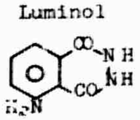
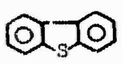
AUTOXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitization* or Reaction Condition	Conc.*~ t-BuOK, molar	Initial Pulse,†,‡ amp	Peak‡,§,†† O_2 Current, amp	Time to O_2 Peak	Appearance Before O_2 Add.	Appearance After O_2 Add.	Comments
1	Dimethyl Sulfoxide (DMSO) $(CH_3)_2SO$	a			-	$8x10^{-11}$	15 min	light yellow		≈$4x10^{-11}$amp before O_2 add (Spectro).
		b			(3)10^{-9}	(3)$2.9x10^{-11}$	29 min			(3)$1.2x10^{-11}$ before O_2 add (Reagent).
		c	DPA		(3)$3x10^{-10}$	(3)$8.7x10^{-11}$ (3)$3x10^{-10}$	4 sec 31 min			Note ten-fold increase of luminescence with DPA.
2	Dimethyl formamide (DMF) $(CH_3)_2NCHO$	a		0.2	-	10^{-t}	50 r'n	precipitate		solvent decomposition with precipitation
		b	6.5M in DMSO			10^{-9}	7 min	pink	yellow	
3	9-Fluorenone 	a				$2.4x10^{-8}$	4.5 min	red-brn		Note luminescence and increase in DMF with precipitate.
		b	$2.5x10^{-3}M$ In DMF			10^{-9}	4.5 min			
		c				$1.8x10^{-8}$	1 min	pink	yellow	
4	Benzophenone ø CO ø					$9x10^{-11}$	13 min	yellow		No increase in luminescence over solvent system.
5	Fluorene 	a				$8x10^{-9}$	9 min	red-brn	color deepens	Fairly bright luminescence.
		b	In DMF			10^{-8}	2 min	orange		With precipitate.
6	Carbazole 					$9x10^{-10}$	3 min	yellow		
7	9-Anthraldehyde 					$3x10^{-9}$	[illegible] min	brown solution		
8	Dianisidene acetone 	a				$1.5x10^{-10}$	5 min	brown solution		weak luminescence
		b		0.05		$1.5x10^{-10}$	9 min	solution red-brn		
		c	TPB	0.05		$2.7x10^{-10}$	3.5 min			sensitized emission
		d	TP	0.05		$1.5x10^{-10}$	5 min			
9	Diphenylfulvene 	a		0.05	10^{-9}	-	-			No O_2 effect.
		b				$5x10^{-10}$	30 sec	dark solution		
		c	TPB			$5x10^{-10}$	30 sec	dark solution		No sensitization.
10	9,9'-Bifluorene 					$1.2x10^{-9}$ $1.5x10^{-9}$	4 min 16 min	red solution		Secondary buildup.

NOTES: See end of Table.

Table 2 (Continued)

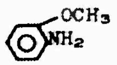
AUTOXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitization* or Reaction Condition	Conc.** t-BuOK, molar	Initial Pulse,†,‡ amp	Peak‡,§,†† O_2 Current, amp	Time to O_2 Peak	Appearance Before O_2 Add.	Appearance After O_2 Add.	Comments
11	Acetone CH_3COCH_3					$6x10^{-10}$	2 min	yellow	dark brn	
12	Benzoin  $\overset{H}{øCOCOø}$	a				$(5±1)10^{-8}$	3.5±0.5min	dark red-brn	yellow	Dark green → blue intermediate.
		b	DPA			$6x10^{-8}$	4 min			Peak luminescence in blue → yellow transition (visible luminescence).
		c				10^{-7}	50 sec			O_2 flow rate ≈0.7 cc/sec.
		d		0.016		10^{-7}	2 min	dark green	yellow	
		e		0.0035		$2x10^{-11}$	40 sec			Addition of same conc. base → pulse >10^{-7} amp.
13	2-Benzylimidazoline 				$(3±1)10^{-7}$				yellow	Addition of O_2 or N_2 decreased luminescence (visible luminescence).
14	Benzil øCOCOOø	a			$5x10^{-9}$			yellow		No sensitization - no effect with O_2
		b	DPA		$5x10^{-9}$					
		c	TP		$5x10^{-9}$					
		d	TPB		$5x10^{-9}$					
15	Benzaldehyde ø CHO	a			10^{-8}			yellow		Not distilled - no O_2 effect.
		b			10^{-8}	10^{-9}	15 sec			Freshly distilled.
		c			$3x10^{-9}$					Distilled and aged 24 hr (also d,e).
		d	DPA		$3x10^{-9}$					No O_2 effect.
		e	TPB		10^{-8}					Initial pulse sensitized.
16	Luminol 	a				$5x10^{-6}$		dark brown		Note sensitivity to base concentration.
		b		0.008	$9x10^{-6}$			yellow		
		c		0.015	$6.4x10^{-4}$	$5.8x10^{-4}$	30 sec	yellow		Decay to 10^{-4} before O_2 addition.
17	Thiourea H_2NCSNH_2	a			$6.4x10^{-9}$	$4.5x10^{-10}$	2 sec	yellow	orange	Water and H_2O_2 injection effect minor.
		b	DPA		$7.6x10^{-9}$	$4x10^{-10}$	2 sec			
18	Anisonitrile 	a			$3x10^{-9}$	$1.5x10^{-10}$	10 sec	yellow	orange	
		b	DPA		$2.3x10^{-9}$	$1.4x10^{-10}$ $2.4x10^{-10}$	5 sec 28 min			Note long slow rise.
		c	TP		$6.5x10^{-9}$	$8x10^{-11}$	5 sec			
		d	TPB		$9x10^{-9}$	$7x10^{-10}$	25 sec			Weak sensitization.
19	Dibenzothiophene 	a			$3.6x10^{-9}$	$4x10^{-10}$	3 min	colorless	red-brn	O_2 peak is three-fold greater than background.
		b			$(3)2.7x10^{-9}$	$(3)1.1x10^{-10}$	30 sec			
		c	DPA		$(3)5x10^{-9}$	$(3)5x10^{-11}$	10 sec			Time to peak variable.
		d	TPB		$(3)5x10^{-9}$	$(3)10^{-10}$	50 sec			No sensitization.
		e	TPB + rubrene		$(3)10^{-9}$	-	-			

NOTES: See end of Table.

Table 2 (Continued)

AUTOXIDATION REACTIONS

No.	Compound and Structure	Run	Sensitization* or Reaction Condition	Conc.** t-BuOK, molar	Initial Pulse,†,‡ amp	Peak‡,§,†† O_2 Current, amp	Time to O_2 Peak	Appearance		Comments
								Before O_2 Add.	After O_2 Add.	
20	Benzalazine ø CH=N-N=CH ø	a			$3.7x10^{-10}$	$8x10^{-11}$	15 min			Oscillation in output during O_2 addition - aee text. Average is DMSO base.
		b	TPB		$5.3x10^{-10}$	$2.6x10^{-10}$	11 min			Oscillations and average amplified by TPB
21	Acetonitrile CH_3CN	a			$8x10^{-10}$	$6x10^{-11}$	13 min			
		b	TPB		10^{-9}	$6x10^{-11}$	5 min			O_2 peak is DMSO base.
		c	TP		$3x10^{-9}$	$6x10^{-11}$	-			
		d	DPA		10^{-9}	$9x10^{-10}$	21 min			Compares to sensitization in pure DMSO.
22	Azobenzene ø N=N ø	a			(3)6.5x10	(3)1.5x10	5 min	orange	dark red-brn	Steady state signal independent of O_2. Note inhibition of DMSO luminescence.
		b		0.025	$(3)10^{-10}$	zero	-	orange	lt brn	
23	o-Anisidine 	a			$(3)10^{-9}$	$(3)5x10^{-11}$	20 sec	colorless	deep red-brn	Luminescence and aensitization effects both small.
		b		0.05	$(3)10^{-9}$	$(3)2.4x10^{-11}$	2 min			
		c	TPB	0.05	$(3)3x10^{-9}$	$(3)7.2x10^{-11}$	15 sec			
		d	DPA	0.05	$(3)10^{-9}$	$(3)5.3x10^{-11}$	40 sec			
		e	TP	0.05	$(3)2.6x10^{-9}$	$(3)4.4x10^{-11}$	5 sec			
		f	TP + rubrene	0.05	$(3)2.4x10^{-9}$	$(3)3.8x10^{-11}$	40 sec			
		g	rubrene + fluorescein	0.05	$(3)1.7x10^{-9}$	$(3)6.2x10^{-11}$	50 sec			
24	Phthaldiamide 	a			$(3)1.2x10^{-9}$	$(3)6x10^{-11}$	1 min	clear	turbid	
		b	DPA		$(3)1.2x10^{-9}$	-	-			No increase with O_2.
		c	TPB		$(3)2x10^{-9}$	$(3)7.5x10^{-11}$	20 aec			Marginal sensitization.
25	U-dimethylhydrazine $(CH_3)_2NNH_2$	a			$>(3)3x10^{-9}$	$(3)4.8x10^{-11}$	15 sec	lt yellow	dk yellow	Luminescence weak.
		b	TPB		$(3)1.4x10^{-9}$	$(3)4.5x10^{-11}$	14 sec			No sensitization.

NOTES TO TABLE 2:

* Sensitizers at 10^{-4} mole/liter. Reactant $5x10^{-3}M$; solvent DMSO unless otherwise noted.
TP ≡ p-terphenyl
TPB ≡ 1,1,4,4-tetraphenylbutadiene
DPA ≡ 9,10-diphenylanthracene
POPOP ≡ 2,2'-p-phenylene-bis-(5-phenyloxazole)
** Concentration 0.1 mole/liter unless otherwise noted.

† Initial or mixing pulse values are given where they exceed the current observed with addition of O_2.
‡ The parenthetical factors given in some current values are required for equivalent sensitivity of different photometers. Thus the current value $(3)2.9x10^{-11}$ is to be read as $8.7x10^{-11}$.
§ At standard flow rate of 0.35 cc/sec, unless otherwise noted.
†† Photomultiplier current maintained $<10^{-8}$ amp by attenuation filters where required.

The great complexity of these reactions is well illustrated by the results for benzalazine. In this case, the buildup of the photocurrent was accompanied by an increasing but very regular oscillation at one cycle/10 seconds (which does not correlate with the bubble rate of $\approx$2-3/second. The peak amplitude of the oscillation was approximately equal to the value of the photocurrent at the minimum. Addition of 1,1,4,4-tetraphenylbutadiene increased both the oscillation amplitude and the average value of the photocurrent, but did not affect the oscillation frequency.

The azobenzene results are noteworthy in that they show inhibition of the base chemiluminescence attributable to the solvent-base combination. For the stronger base solution, the observed luminescence is down fivefold. For the 0.025M t-BuOK solution, no luminescence is detectable; i.e., the photocurrent is the dark current value. This contrasts with the behavior of benzophenone which is inert, the observed photocurrent corresponding to the base line emission.

The critical nature of the reaction conditions is well brought out by the observations for luminol, first studied in this system by White (ref. 4). With the "standard" base concentration used in the bulk of this work, a strongly absorbing solution is produced with emission an order-of-magnitude below the "reference" luminol (ref. 1) alkaline peroxide-persulfate solution. In more dilute base (0.015M), the solution remains clear and the emission is two orders of magnitude greater.

The benzoin reaction clearly reveals a quite complex chemistry. Addition of the compound to a solution of t-BuOK in t-butanol (t-BuOH) produces a dark purple solution, presumably the benzoin anion. The color is discharged with oxygen with weak chemiluminescence. In DMSO solution, a dark brown solution is formed with 0.1M t-BuOK. Upon addition of oxygen, the chemiluminescence increases immediately by more than an order of magnitude ($\approx 5 \times 10^{-9}$ amp) and rises steadily for 4 minutes. The optical density is seen to decrease after 2-3 minutes of O_2 addition and the solution undergoes a sequence of color changes (transmitted light) from red-brown, to dark-green, to blue, and finally to the yellow characteristic of the base-DMSO solution. The peak luminescence occurs with the appearance and destruction of the fairly transparent blue solution.

The luminescence output for this reaction is extremely "noisy". In the strongly absorbing solutions existing during the first few minutes of the oxidation, rapid fluctuations of the output from 20-50% of the average value are observed that appear to be of the frequency of the bubble formation rate. These observations suggest that the system may be a strong emitter under properly optimized conditions. Qualitative experiments with the same reaction in t-BuOH solvent suggest that the first step is the formation, presumably, of the resonance-stabilized benzoin anion.*

The brightest reaction observed in this series was that associated with the oxidation of 2-benzylimidazoline. This reactant is related to amarine, a triphenyl-substituted imidazoline, so that the chemiluminescence observed is not unexpected. It is not known whether the luminescence of the 2-benzyl compound has been reported, however. The peak luminescence was observed for the air-saturated solution upon mixing. The luminescence peak was reduced by addition of either O_2 or N_2.

In DMF/t-BuOK and in DMF in DMSO/t-BuOK, the chemiluminescence is an order of magnitude greater than the "background" in DMSO/t-BuOK. It is clear from the instability of the solutions that extensive decomposition of DMF occurs. Comparison of the emission from fluorene and 9-fluorenone in DMF and DMSO, however, reveals enhanced emission in DMF, again emphasizing the importance of solvent variation in optimization.

The preliminary results on sensitization in the autoxidation reactions generally indicate only modest increases (≈50%) for a few specific sensitizer-reactant combinations. The initial pulse for (aged) benzaldehyde is, however, increased by an order of magnitude in the presence of p-terphenyl, although 9,10-diphenylanthracene is inert. These highly specific interactions will require careful isolation of the (spectroscopic) energy transfer mechanisms from possible chemical reaction effects for meaningful interpretation.

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*A citation [CA, 55, 12055g (1961); E. A. Bozhevalnov, Trudy Vsesoyuz, Nauch - Issledovatel, Inst. Khim. Reactivov, 1958, No. 22, 60-4] to an analytical method for zinc and antimony ions has been found which is based on a reported catalysis of (chemi?)luminescent oxidation-reduction (sic) of benzoin, apparently in aqueous solutions.

IV. FUTURE WORK

The chemiluminescence screening program will be continued. In the appendix a tentative classification of compounds to be investigated and a discussion of the rationale for selection is given. It is proposed to broaden the listing by computer search for available substituted compounds for those classes that appear of interest in the screening phase. At the present time, for example, various α-hydroxy ketones would be of interest for comparison to benzoin. The influence of catalysts, selected from the class showing activity for the oxygen electrode, will be investigated.

The spectrometers will be calibrated during the coming quarter, and spectral output for the systems of interest will be obtained as will fluorescence quantum efficiences. It is suggested that work begin on the detailed analysis of the benzoin reaction, at least until a more promising candidate appears. For this purpose flow reactor studies will be convenient for both emission and absorption spectra.

V. REFERENCES

1. Monsanto Research Corporation, Technical Report No. 1, ONR-ARPA, "Chemiluminescent Systems", 13 October 1964.

2. Conference on Chemiluminescence Measurements at RCA-Lancaster, Pa., 4 November 1964, and private communication, G. Warren Kennerly.

3. B. J. Sveshnikov and P. P. Dikun, Acta Physicochimica U.R.S.S., 17, 173 (1942).

4. E. White in "Light and Life", W. D. McElroy and B. Glass, eds., The Johns Hopkins Press, Baltimore, 1961, p. 183.

APPENDIX I

COMPOUNDS FOR CHEMILUMINESCENCE SURVEY

Acids

fumaric
formic
benzoic
naphthoic (α and β)
cinnamic

Aldehydes

formaldehyde
acetaldehyde
benzaldehyde
cinnamaldehyde
acrolein
anisaldehyde
naphthaldehyde (α and β)
9-anthraldehyde
salicylaldehyde
furfurylaldehyde

Aliphatic amines

methyl amine
pyrrolidine
dimethyl amine
trimethyl amine
n-butyl amine
ethylene diamine
ethanol amine
triethanol amine
allylamine
piperidine

Amides

2-furamide
formamide
2-pyrrolidone
oxamide
N-vinylpyrrolidone
benzamide

Aromatic amines

benzidine
o- and p-anisidine
pyrrole
o-, m-, and p-toluidine
o-, m-, and p-nitroaniline
aniline
diphenylamine
triphenylamine
anthranilic acid
o-, m-, and p-chloroaniline
o-, m-, and p-phenylenediamine

Di-Ketones

2,3-butanedione
2,4-pentanedione
benzil

Heterocyclics

quinoline and isoquinoline
amarine
tetraphenylpyrrole
carbazole
dibenzothiophene
thiophene
9-fluorenone
benzimidazole
pyrrole
imidazole
indole
benzimidazoline
2-benzylimidazoline
indene
furan
dihydropyran
tetrahydropyran

Hydrazines

phenylhydrazine
hydrazine
nitrophenylhydrazine
formohydrazide
1,1-dimethylhydrazine
tetrakis(p-octylphenyl)hydrazine
tetraphenylhydrazine

Hydrocarbons

conjugated olefins
acetylenes
difluorene
diphenyl fulvene
fluorene

Hydroxyl Compounds

methanol
isopropyl alcohol
benzyl alcohol
α and β-naphthol
furfuryl alcohol
allyl alcohol
ethylene glycol
diacetonylalcohol
pyrocatechol
glycerol
hydroquinone
phloroglucinol
pyrogallol

Imides

phthalimide
succinimide

Ketones

acetophenone
acetone
benzophenone
methyl ethyl ketone
methyl isopropyl ketone

Olefinic Ketones

methyl vinyl ketone
furfuryl acetone

Quinones

p-benzoquinone
naphthoquinones
anthraquinone

Sulfur analogues of oxygenated compounds

thioacetic acid
thiourea
ethylene thiourea

α,β-Unsaturated Ketones

chalcone
dibenzalacetone
benzalacetone
dianisylidene acetone

Miscellaneous compounds

porphyrin-catalyzed decomp. of hydroperoxides
azobenzene
phenylhydrazone
cyclohexadiene sulfone
phenyl sulfone
salicylhydrazide
2-mercaptobenzothiazole
2-nitrofluorene
duroquinone
acetonitrile
benzonitrile
benzoin
anisonitrile

APPENDIX II

GUIDELINES FOR SELECTION OF CHEMILUMINESCENT REACTIONS

A general criterion for visible chemiluminescent reaction is that the transient metastable species possess energy at least 40 kcal per mole greater than that of the products in order to satisfy the minimum energy required for emission in the red region of the spectrum. If for any reason the excited molecules cannot radiate, addition of molecules capable of receiving this energy that are themselves efficient fluorescence emitters is necessary.

Recent work has shown that in addition to peroxidation reactions, two other major classes of chemiluminescent reactions, independent of oxygen, exist. These are processes in which the excited state is formed directly, either by removal or addition of an electron (refs. A-1, A-2, A-3). We discuss below examples of possible chemiluminescent reactions chosen from these classes and from possible additional classes. In principle, excitation may result from quite general addition or dissociation reactions meeting the minimum energy requirements for visible radiation.

A. ELIMINATION OF SMALL MOLECULES

During the course of dissociative reactions, at least two species are formed. The structural complexity of the fragments will determine the type and amount of excess energy each receives from the bond-breaking and bond-forming processes. If a molecular fragment has many functional groups that are interbonded in a manner such that many resonance structures can be written, the probability exists of many intersecting potential energy surfaces. This would facilitate the ease of thermalization of excess energy through intersystem crossings.

On the other side of the structural scale, a small molecule will have fewer paths for thermalization, and radiation probability will increase. The small molecules eliminated during reaction that would be of interest to study are CO_2, CO, N_2, O_2, and H_2CO. The emission spectra of these molecules are well known. It is quite possible that these molecules do not take up excess energy since their lowest excited electronic energy levels may be greater than the energy available in the bond-forming and breaking process. In this case, the organic species may accept a larger share of the energy as opposed to the situation where its dissociation partner is also a large molecule. The organic species should be a small, conjugated system. The well-known chemiluminescences of the luminol and the oxalyl chloride plus H_2O_2 systems justify this approach.

1. Deamination

A reaction class meeting these requirements is the deamination of aliphatic primary amines with nitrous acid. Classically, the reaction is pictured as follows:

$$ArR'CHNH_2 + HONO \longrightarrow ArR'CHOH + N_2 + H_2O \qquad (1)$$

However, other products may result through elimination and rearrangement of the carbon skeleton. The mechanism has been extensively studied, and it is generally agreed that the active species is an aliphatic diazonium ion that further participates with loss of nitrogen (ref. A-4).

$$ArR'CH\overset{+}{N}\equiv N \xrightarrow{H_2O} ArR'CHOH + N_2 + H^+ \qquad (2)$$

2. Oxidation of Wittig Reagents

Another class of reactions that formally meets the requirements is the oxidation of Wittig reagents (ref. A-5). For example,

$$\phi_3P{=}CH_2 + O_2 \longrightarrow \phi_3PO + [H_2O + CO_2] \qquad (3)$$

The brackets in the equation indicate ultimate products of oxidation. Possible intermediates such as formaldehyde and formic acid are also of interest for excitation processes.

B. PEROXIDATION REACTIONS

1. Correlation of Reactivity in Autoxidation with Chemiluminescence

The autoxidation of many hydrocarbons can be accelerated by addition of activators. This increase in oxidation rate will, in turn, increase the number of occurrences of the chemiluminescent reactions and hence the brightness of the emission. It has been shown by Stauff (ref. A-6) that the recombination of two peroxy radicals yielding an excited oxygen molecule is a light-producing mechanism.

The rate of occurrence of this recombination depends on the concentration of peroxy radicals. The peroxy radicals are formed in the catalytic decomposition of hydroperoxides, ROOH, and the recombination of $R\cdot$ with C_2 to yield $RO_2\cdot$. By maximizing the concentration of $R\cdot$, the concentration of $RO_2\cdot$ is also increased. The reactivity of an aralkyl hydrocarbon to autoxidation can be assessed as its reactivity toward peroxy radicals to form $R\cdot$ (propagation step). It has been shown by Russell (ref. A-7) that the most reactive hydrocarbons are those whose corresponding radicals are stable. Substituents have a pronounced effort. Electron-supplying groups increase and electron-withdrawing groups decrease the rate of the propagation step. Stauff proposes the mechanism of the chemiluminescent reaction as:

$$RO_2\cdot + O_2R \longrightarrow [ROO\cdots OOR] \longrightarrow R + O_2\cdots O_2^{*} + R\cdot \qquad (4)$$

$$O_2\cdots O_2^{*} \longrightarrow 2\ O_2 + h\nu \qquad (5)$$

Electron-supplying groups would aid in the cleavage of the $R\text{-}O_2\cdot$ bond in this complex, and also increase the reaction of hydrocarbon parent toward peroxy radicals. Cleavage regenerates R· to participate in the formation of RO_4R complexes. Ultimately, radical R· is destroyed by oxidation to a product molecule.

Trace amounts of compounds such as indan, fluorene, cyclohexene, styrene, and tetralin have strong inhibition effects on the oxidation of cumene. We have observed that the oxidation of fluorene is chemiluminescent. However, at this time it is not certain whether the emission observed is due to oxygen or the oxidation product fluorenone. Comparisons of the appropriate spectra will elucidate which mechanism is important.

Of the compounds studied by Russell, the following appear to warrant investigation as a possible luminescent system: indan, allylbenzene, cyclohexene, and dibenzyl ether. Tetralin, which has an equivalent reactivity, has been shown to be chemiluminescent through an intermediate similar to the diperoxy complex (ref. A-8).

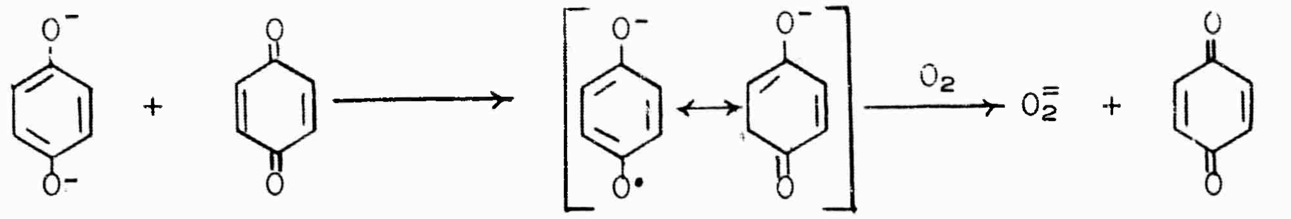
2. Polarization of Olefinic Double Bonds and Chemiluminescence

The partial ionic character and hence reactivity of an olefinic double bond will be determined by the inductive effect of the substituents. The class of compounds to be considered are $R_2C{=}CR_2$, $R\text{-}N{=}N\text{-}R$, and $R_2C{=}N\text{-}R$ These substrates will be investigated in conjunction with both the peroxy radical attack mechanisms discussed in the previous section and the anion attack mechanism discussed in the following section.

3. Hydroquinone Catalyzed Peroxidations

The peroxide dianion is often postulated as an intermediate in direct attack on reactive sites such as olefinic double bonds. This reactive intermediate is formed in the oxidation of hydroquinones. In this system, the chemical process of interest is the conversion of molecular oxygen to the peroxide dianion. The dianion thus formed can be utilized to oxidize reactive groups.

In strong alkaline solutions, substituted hydroquinones are autoxidized to their corresponding quinones and hydrogen peroxide (ref. A-9). The rates of oxidation depend strongly on the extent of decomposition. This suggested that a product autocatalyzes the oxidation. It has been shown that the rate-determining step is not the oxidation of the hydroquinone double anion but rather the reaction between quinone dianion and the quinone to form the radical anion (I). The sequence of reactions may be written as:



(6)

By adding the quinone (at the proper concentrations) to the hydroquinone, the catalytic effect of the quinone will be maximized and hence so will the production of $O_2^=$. As a result, relatively large reaction rates of $O_2^=$ attack on oxidizable olefinic linkages can be attained.

The increased rate of attack will enhance the brightness of the chemiluminescent system. Whether a given molecule will possess luminescent properties will depend on the nature of the substituents attached to the oxidizable site.

C. EXCITATION BY ELECTRON TRANSFER

1. Reductive Excitation

The class of N-halo secondary amines has recently been shown to be readily oxidized to the stable free radical (ref. A-10).

$$R_2NCl + Fe^{+2} \longrightarrow R_2N^{\cdot} + FeCl^{+2} \qquad (7)$$

This electron transfer process may lead directly to an excited radical, $R_2N\cdot^*$, itself luminescent, or the radical may react with another species, such as an olefin, to form excited or autoxidizable products. Possible analogous reactions with N-halo amides and C- and N-nitroso compounds will also be considered.

2. Oxidative Excitation

Alkali metal salts of organic compounds, i.e., active methylene compounds, amines, etc., will be investigated for possible oxidative excitation.

Specific examples are:

$$[RCOCHR]^-Na^+ + O_2 \longrightarrow \qquad (8)$$

and

$$[R_2N]^-Li^+ + O_2 \longrightarrow \qquad (9)$$

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