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Technical Report No. 1

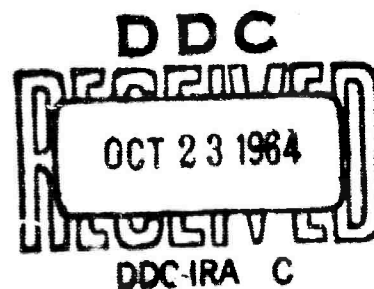
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ARPA Order No. 299, Amend. 6
Contract Nonr 4511(00)
Task NR 356-464

CHEMILUMINESCENT SYSTEMS

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CHEMILUMINESCENT SYSTEMS

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13 October 1964

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SUMMARY

The objective during the first quarter has been to design and procure the photometric instrumentation and to investigate empirically the response of typical known chemiluminescent reactions to solvent variation, catalysis, and, to a lesser extent, the addition of sensitizers.

For this purpose, representative "bright" and "feeble" chemiluminescent reactions were chosen. The major effort in the first class was devoted to the oxidation of lucigenin, extending the work of Weber (ref. 1, 2). As a result of checks for "background" radiation, it was confirmed that the observations of Vassil'ev (ref. 3) and Stauff (ref. 4) of widespread feeble chemiluminescence accompanying oxidation reactions applied to many presumably quite pure organic solvents. It has also been found that Vassil'ev's (ref. 5) and Chandross' (ref. 6) observations of sensitized increase of emission of many orders of magnitude apply to one system investigated (acetone). Tetrahydrofuran (THF) is a more efficient "catalyst" for lucigenin chemiluminescence than previously investigated organic substances. Furthermore, the chemiluminescent decomposition of alkaline peroxide in the presence of THF is extraordinarily bright, being readily visible to the eye, in the absence of sensitizers.

An intriguing feature of many of the solvent system oxidations investigated is a post-peak emission recovery phase that, in some cases, results in a two-fold rise in the post-peak luminescence. This result suggests that the search for and isolation of reaction intermediates in these systems would be fruitful.

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I. INTRODUCTION

The ultimate applied goal of this research is the development of chemiluminescent systems for field use. Since present knowledge of fundamental mechanisms in chemiluminescent reactions is fragmentary, only rather inadequate guiding principles are available for such a development program. Thus, the first phase of the program is exploratory; it is designed to screen promising chemiluminescent reactions, particularly for the influence of non-aqueous solvents and energy trapping substances in addition to the usual reaction variables.

II. INSTRUMENTATION

The research program has been initiated with the construction of the two simple photometers, illustrated in Figures 1 and 2, for batch mixed and steady-state flow conditions, respectively. Jacketed reaction chambers have been constructed for both photometers for temperature control by closed loop circulation. The major objectives for the flow system are, first, to determine the time-resolved emission spectra at low light levels and, second, to permit convenient evaluation of optimum reagent and solvent ratios.

Major hardware for the modified Bass-Kessler spectrograph (ref.7) has been completed, and most of the components received. Components for the Spex 3/4-meter Czerny-Turner scanning spectrometer are on order. Both instruments will be adapted for the determination of fluorescence as well as chemiluminescence spectra.

The several spectra discussed in the present report have been obtained with our Bausch and Lomb $f/4.5$, 0.5-meter monochromator coupled to a conventional RCA IP28 photomultiplier and oscilloscope readout (ref. 8).

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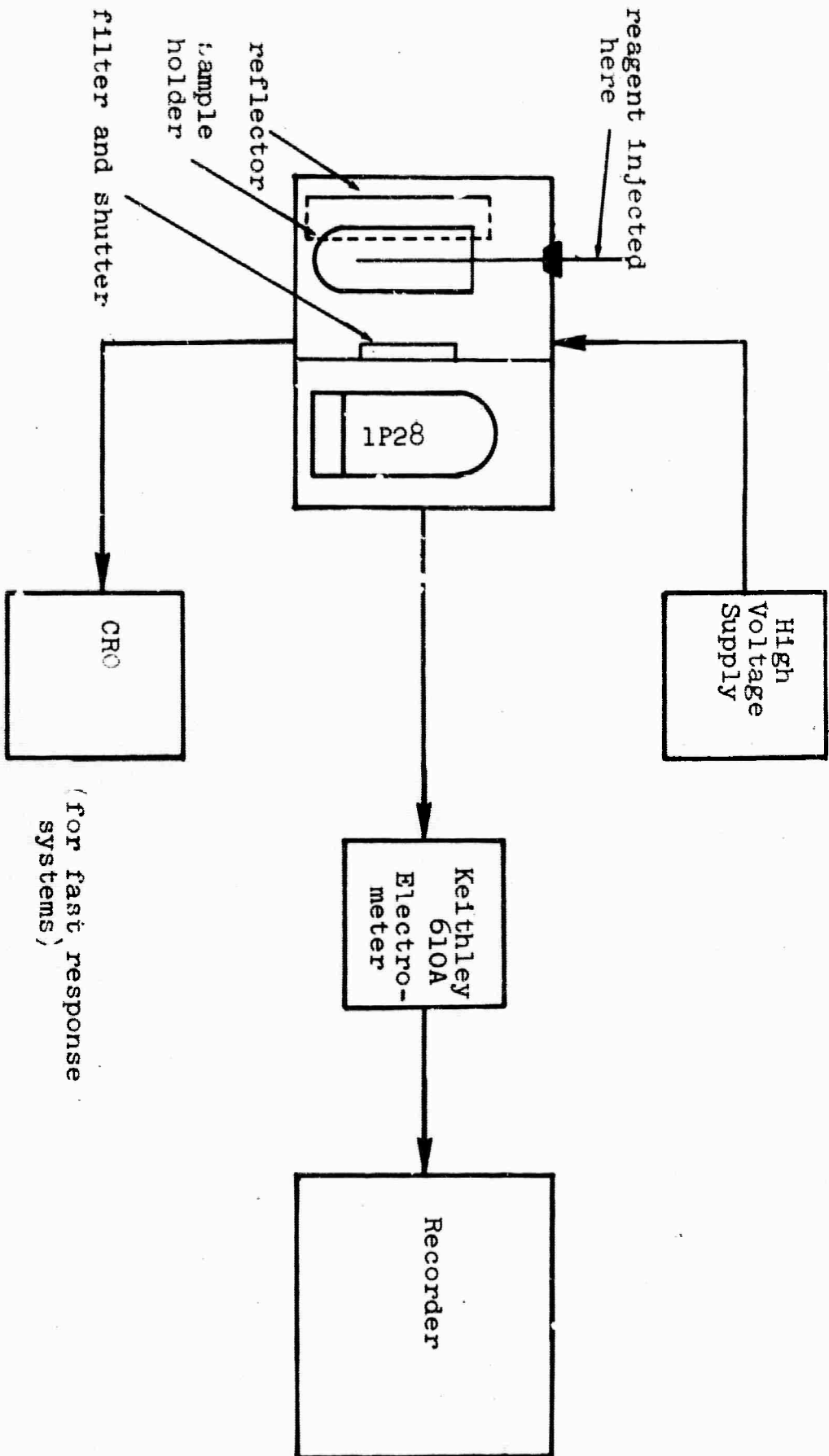


Figure 1. "Batch" Photometer

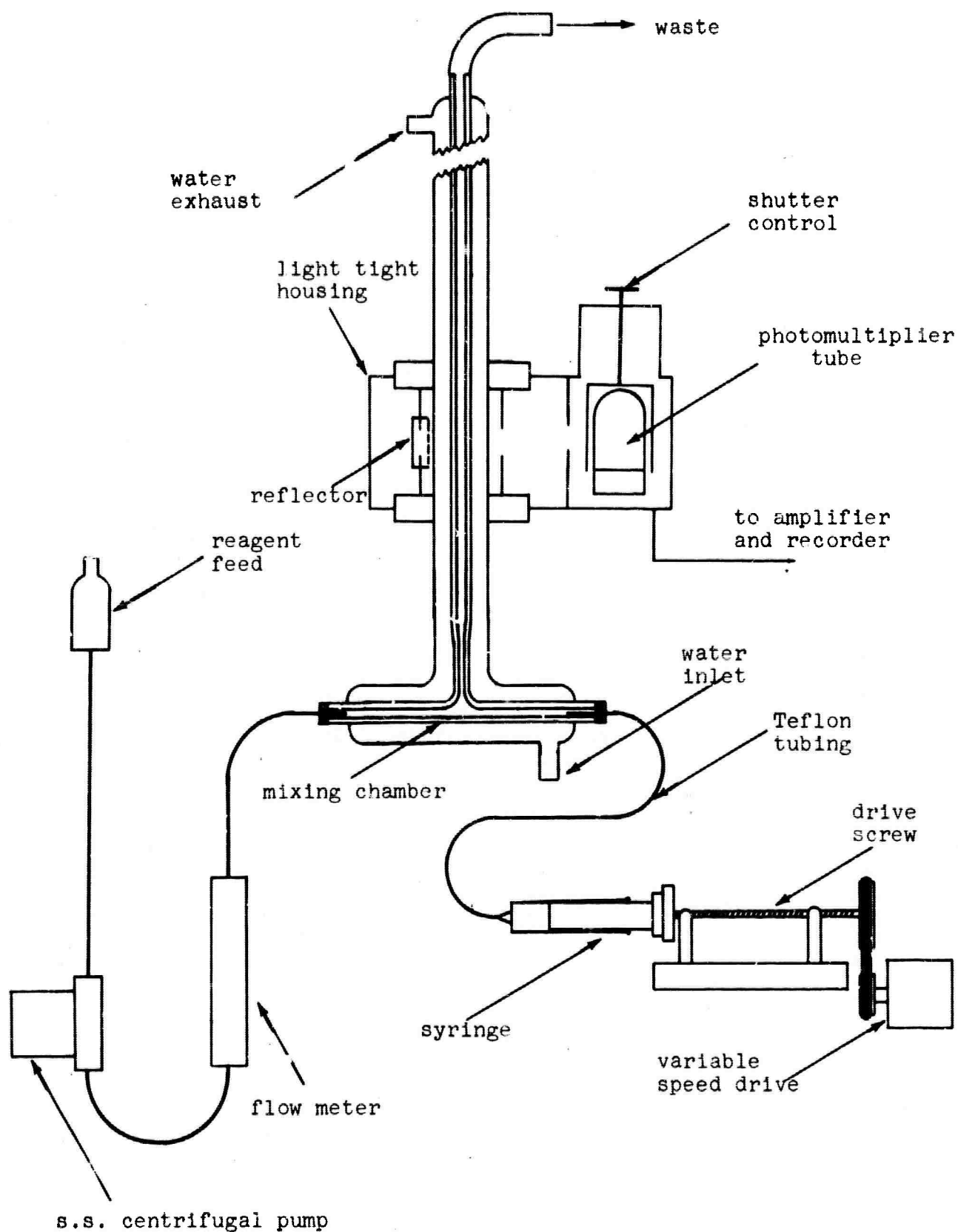


Figure 2. "Flow" Photometer

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. REAGENTS

All organic solvents were "Spectro" grade (except as noted). Inorganic reactants were all "A.R." grades. Both were used without further purification. A number of sensitizers ordinarily prepared as high purity components of scintillators were also used without further purification†. Melting point determinations and thin layer chromatographic separations were carried out for the reducing (organic) reactants. The observed and literature data are compared in Table 1.

Table 1

MELTING POINTS OBSERVED FOR REACTANTS

<u>Compound</u>	<u>Literature, °C</u>	<u>Observed, °C</u>
Luminol	332-333	312-314 (dec.)
Lucigenin	410*	400 (dec.)
Hydroquinone	170	172-173
Pyrogallol	132-133	117-122
Rhodamine B	210	210

* Tetrahydrate

The observed values did not match reported melting points too well, in general. However, since no impurity separations were observed for any of the above materials in T.L.C. analysis, they were also used as supplied for this phase of the work, except for the luminol and lophine standards, which were prepared from freshly recrystallized material (ref.11).

† Obtained from Pilot Chemical Co., Watertown, Mass.

It is of major importance to note that the results reported must be regarded as tentative until confirmed with high purity reagents prepared in the laboratory under known standard conditions. This will, of course, be one of the objectives of future work.

B. "BRIGHT" CHEMILUMINESCENCE

1. Lophine

Preliminary studies were begun on the peroxide-hypochlorite oxidation of lophine in mixed alcohol-acetone-water solvent. Great difficulty was encountered in obtaining reproducibility, and the study was abandoned (for the preliminary phase). Although part of the reproducibility problem was later traced to instrumental instabilities, it was observed that relatively rapid decomposition of lophine occurred in a variety of solvents. The "half-life" of a $10^{-4}M$ solution of lophine in dimethylsulfoxide (DMSO) or dimethylformamide (DMF) appeared to be about one hour, as determined by ultra-violet spectrophotometry.*

The following qualitative observations are included for completeness.

The dependence of the peak emission (E_0) and emission decay half-life ($t_{1/2}$) upon hydroxide ion concentration is shown in Figure 3. The product $E_0 \times t_{1/2}$, which may be taken as a crude figure of merit for total output, decreases monotonically from the lowest hydroxide ion concentration examined.

The gross emission spectrum (not corrected for photomultiplier response) is plotted in Figure 4 with commercial bleach as hypochlorite ion source. The values given are for the peak response at the given wavelength.

Chemiluminescent oxidation of lophine in DMSO and DMF was observed for t-butyl peroxide in the presence of t-butyl alcoholate. The luminescence was much weaker than for the aqueous alcohol-acetone solvent. However, the concentrations employed were probably very far from optimum.

2. Lucigenin

a. Catalysis by Organic Solvent Addition

The work of Weber (ref. 1, 2) on "catalysis" of the lucigenin-alkaline peroxide reaction by organic solvents was extended.

* All experiments performed during the last quarter were carried out in a laboratory environment at $20 \pm 2^\circ C$, but were not otherwise temperature controlled.

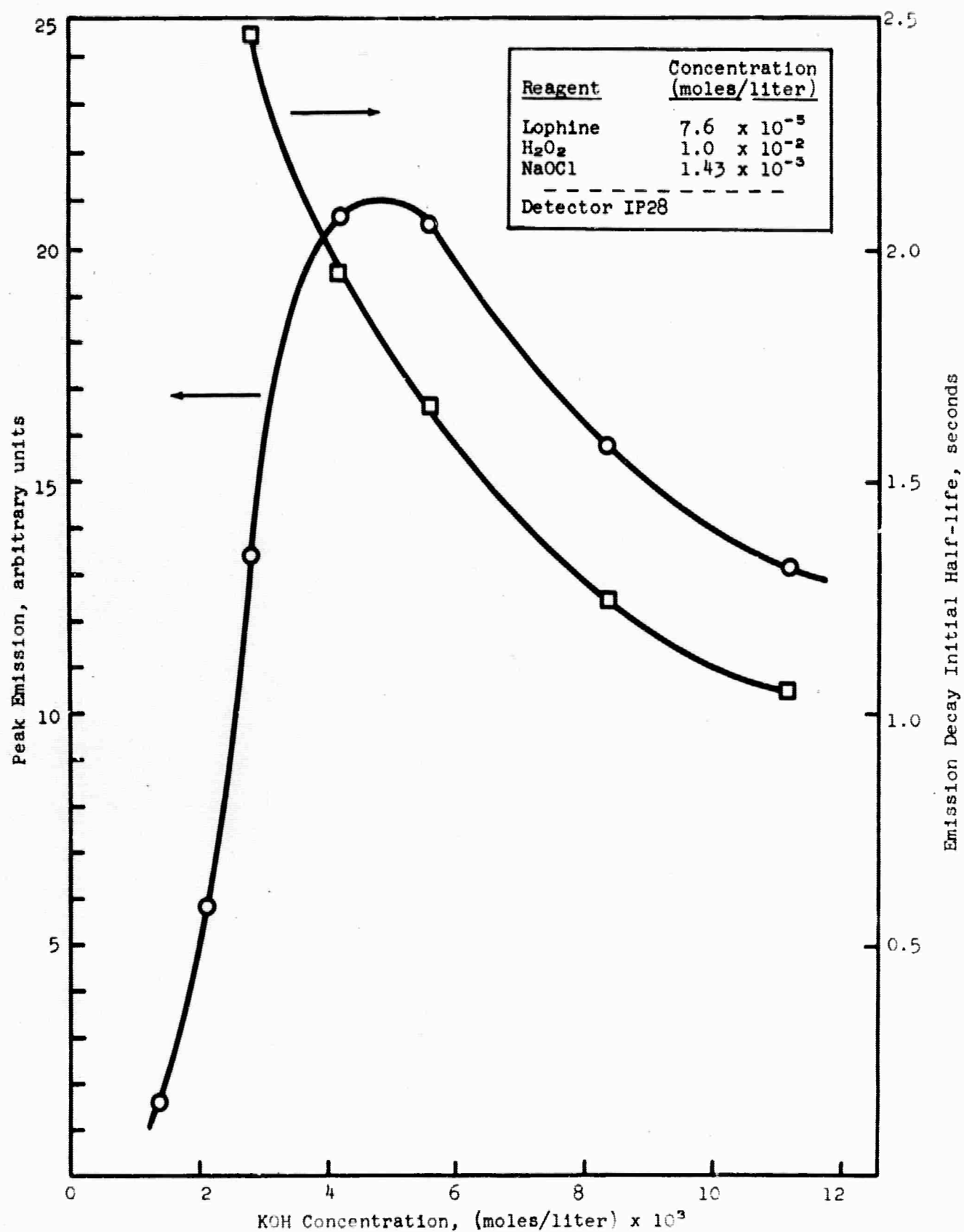
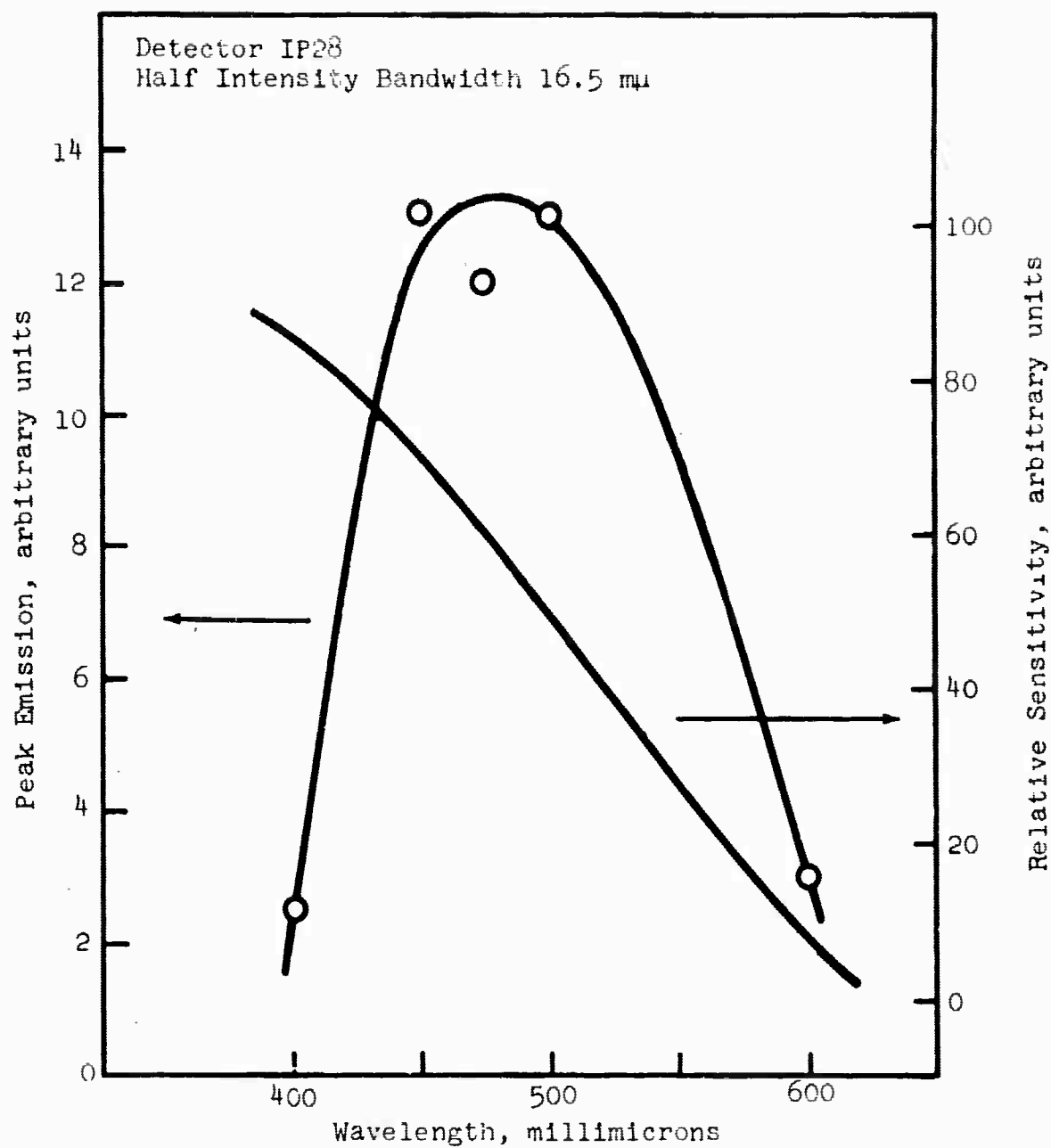


Figure 3. Peak Emission Intensity and Emission Decay Half-life as a Function of (KOH) for Lophine Oxidation



Reagent	Concentration, moles/liter
Lophine	9.6×10^{-4}
H ₂ O ₂	1.0×10^{-2}
NaOCl	6.2×10^{-2}
KOH	1.15×10^{-2}

Figure 4. Approximate Peak Emission Spectrum of Lophine (uncorrected)

In Figure 5 we present a plot of the peak emission vs half-life "figure-of-merit" for a number of organic solvents plotted as a function of the dielectric constant of the mixed solvent (at constant volume fraction for the organic phase). It is seen that a small increase is suggested for decreasing dielectric constant for a majority of the compounds. The dielectric constant has been chosen here as a convenient "stretch-out" parameter. It is not suggested that dielectric constant is indeed a significant reaction variable.

The three solvents (dioxane, pyridine, and dimethylformamide) in this presentation are seen to be an order of magnitude greater, and tetrahydrofuran appears to be two orders of magnitude greater in "figure-of-merit" than the average value. The stratification of the organic "catalysts" may be seen more clearly in Figure 6, where the peak intensity is shown as a function of half-life. It must be emphasized that these are preliminary results from work in progress and are not corrected for possible spectral shifts. The data presented for this run were not well replicated subsequently in both total intensity and intensity ratio. Thus, although THF is clearly a more efficient catalyst than any other solvent found, it is not clear, at present, that the large ratio, $E_{\text{THF}}/E_{\text{Diox}}$, for example, is as great as an order of magnitude.

b. Catalysis by Dioxane

(1) Batch System

In Figure 7, we present preliminary data on the "catalysis" of the lucigenin reaction by dioxane as a function of volume per cent dioxane. The logarithmic plots of both the half-life and peak emission appear quite linear at high dioxane concentrations. Indeed, the $E_{0t_{1/2}}$ product is constant to $\pm 3\%$. The results in pure water are, however, disconcerting since, first, there is an apparent initial decrease in the peak emission intensity with increasing dioxane concentration. Secondly, there is an apparent discrepancy with the data in Figure 5, which indicate an order of magnitude increase with $E_{0t_{1/2}}$ product at 19% dioxane over the value in pure water. Since it is known that the emission spectra are functions of the time and concentration (ref. 9), it is possible that the initial decrease in Figure 7 is associated with an initial red shift of the spectrum. Comparison with Figure 5 is made difficult by the different response curves of the IP21 and IP28 photomultipliers. Finally, the NaOH concentration change also affects the total emission (ref. 10) and therefore the $E_{0t_{1/2}}$ product. Further work is required to clear up these points.

The emission spectrum for the 16.7 vol-% solution is given in Figure 8. This emission curve was corrected for photomultiplier response by calibration against a luminol reference standard (ref. 11) in the 450-500 m μ region, and by fairing in the IP28

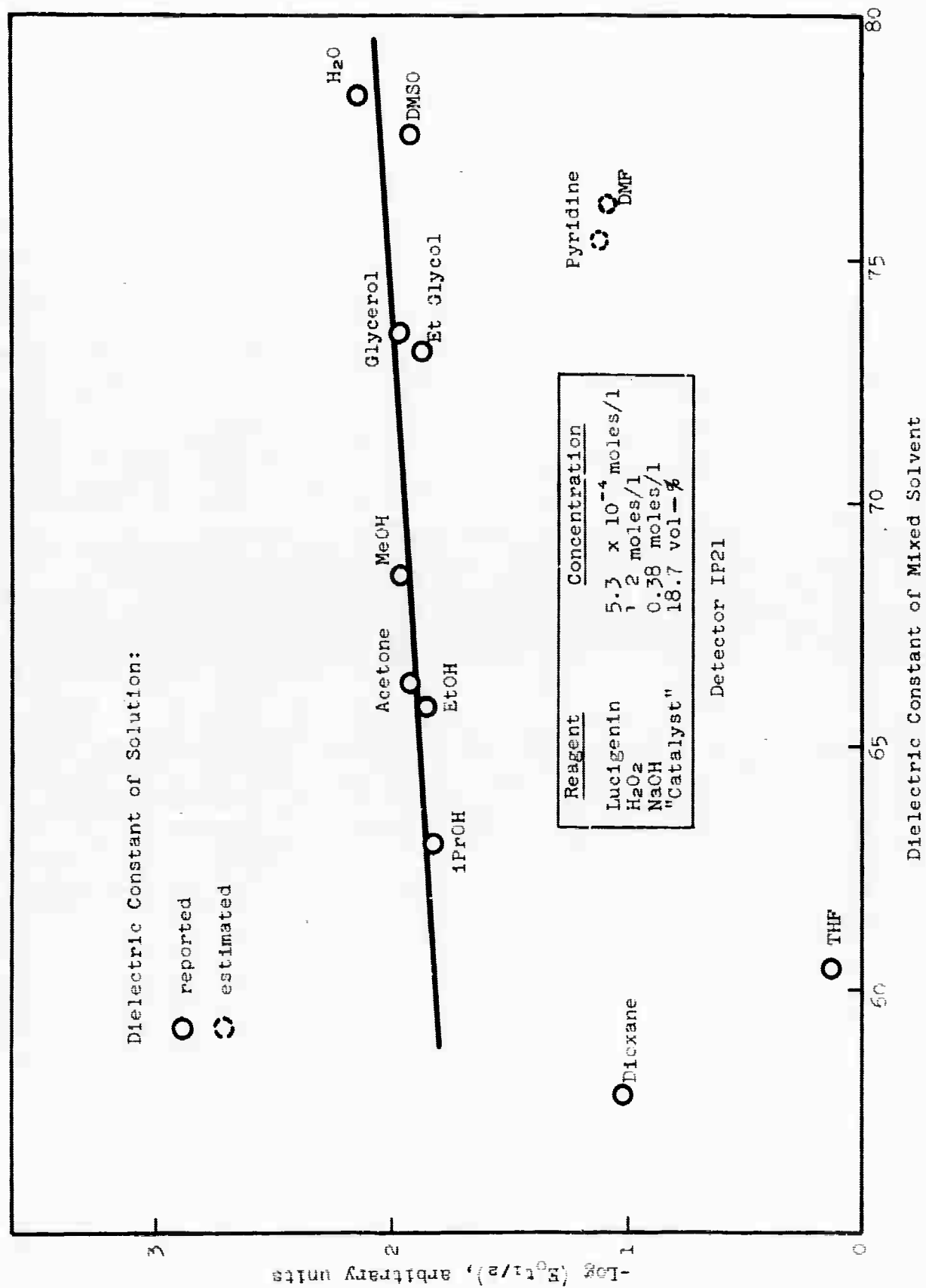


Figure 5. Peak Intensity x Half-life Product as a Function of Dielectric Constant of Mixed Solvents for Lucigenin Oxidation (at 18.7 vol-% organic phase)

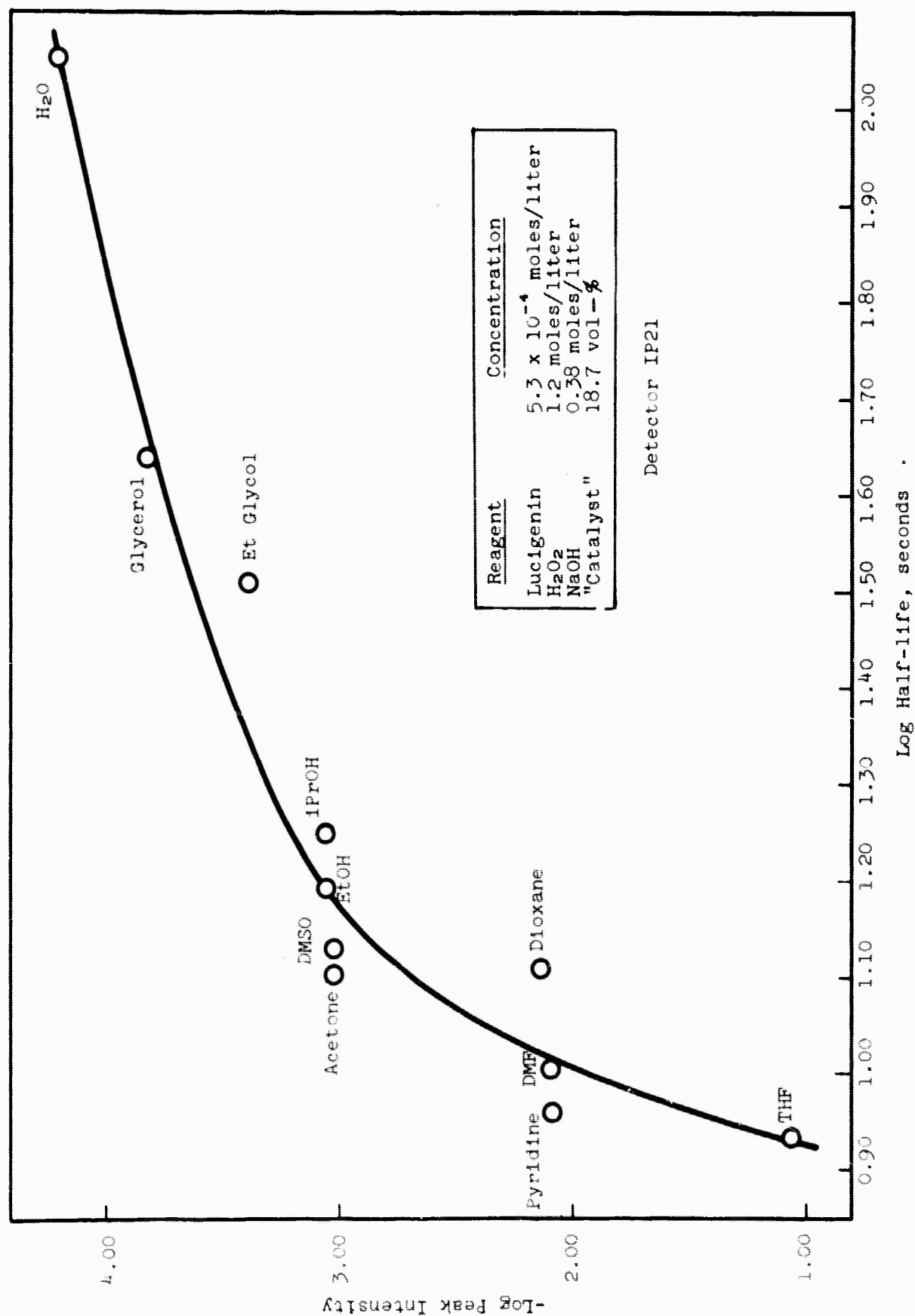


Figure 6. Peak Intensity for Lucigenin Oxidation in Mixed Solvent vs Half-life for Emission Decay

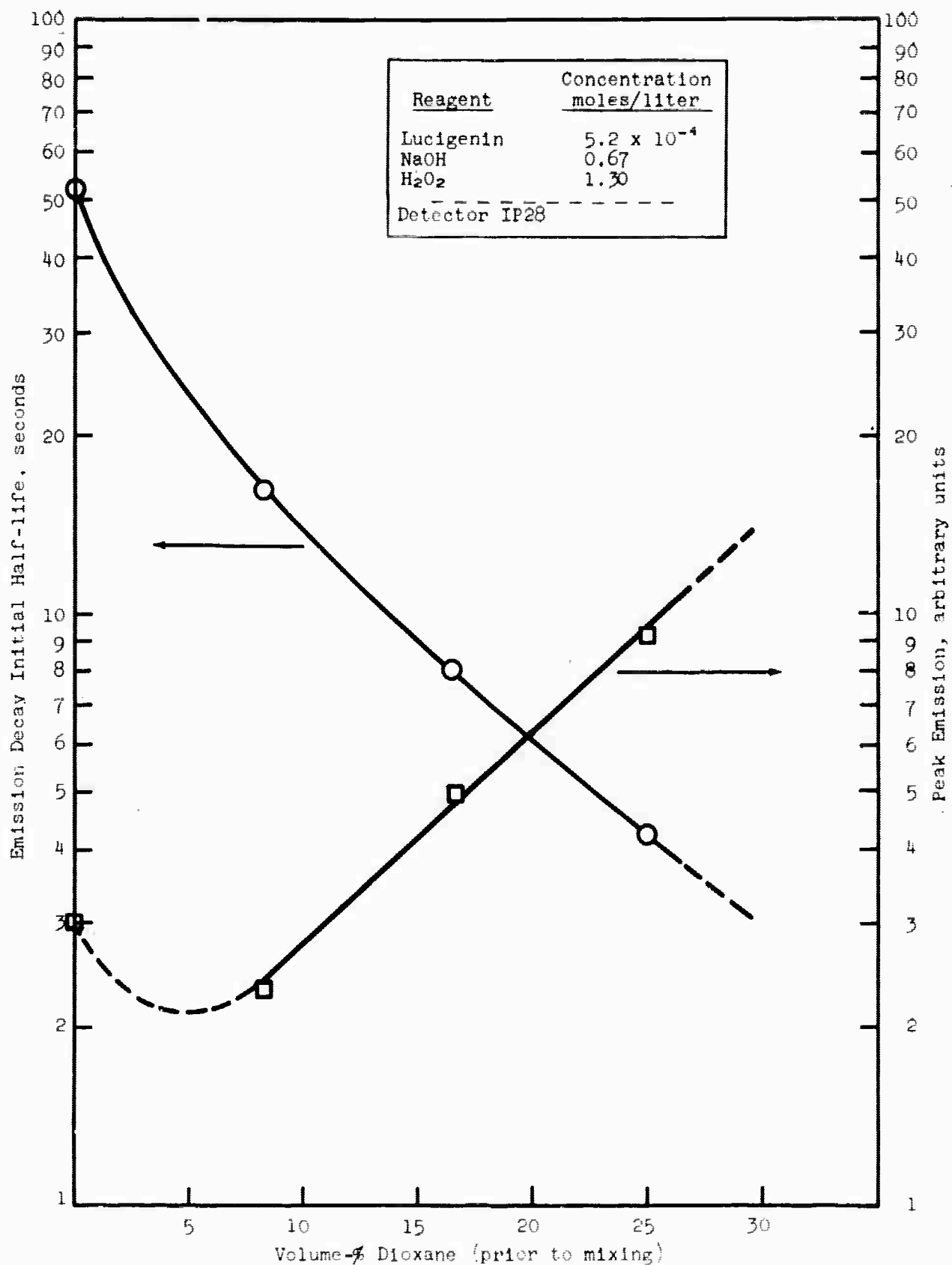


Figure 7. Peak Emission and Half-life for Dioxane "Catalyzed" Lucigenin Oxidation

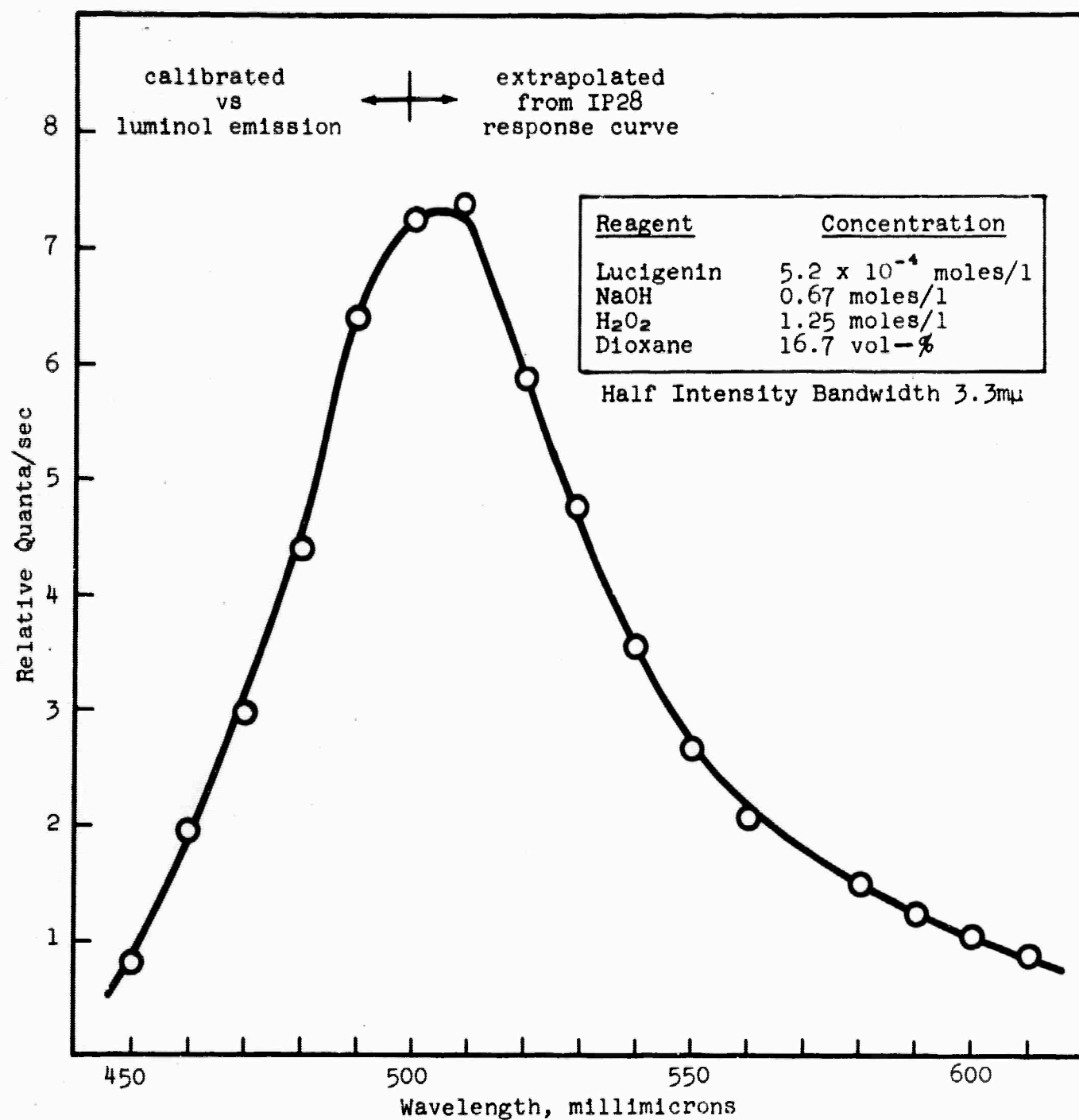


Figure 8. Lucigenin Peak Emission Curve
(corrected for system response)

response curve (ref. 12) from 500 to 610 mμ. Each data point represents a fresh sample at the emission peak for the wavelength measured; at about 5 sec from the beginning of injection. However, this time is not entirely constant as a function of wavelength. The spectrum is generally similar to that reported by Ryzhikov (ref. 9) and Kariaki (ref. 13), but has not yet been compared with the aqueous solution under our conditions. More meaningful comparisons may, perhaps, be made with the flow system.

(2) Flow System

Preliminary data have been obtained for total emission in the flow system for 24 vol-% dioxane solutions (other reagent concentrations approximately as above). The intensity vs time plot is shown in Figure 9. The initial half-life (from the linearly extrapolated zero time emission) is about three seconds, in reasonable agreement with the batch-mixed sample value of four seconds.

c. Nonaqueous Solutions of Lucigenin

Comparison was made of the total emission from air-saturated lucigenin solutions in absolute methanol in the presence of alkali alcoholates to the aqueous alkaline solutions. The results are shown in Table 2.

Table 2

LUMINESCENCE OF AIR-SATURATED LUCIGENIN SOLUTION

(1.3×10^{-3} m/l)

<u>Solvent</u>	<u>Base</u>	<u>Base Molarity</u>	<u>Peak Photocurrent (amp)</u>
MeOH	NaOMe	0.33	2.6×10^{-7}
MeOH	KO(t-Bu)	0.10	3.1×10^{-7}
H ₂ O	NaOH	0.67	6.7×10^{-8}

The results are sufficiently encouraging to warrant further investigation.

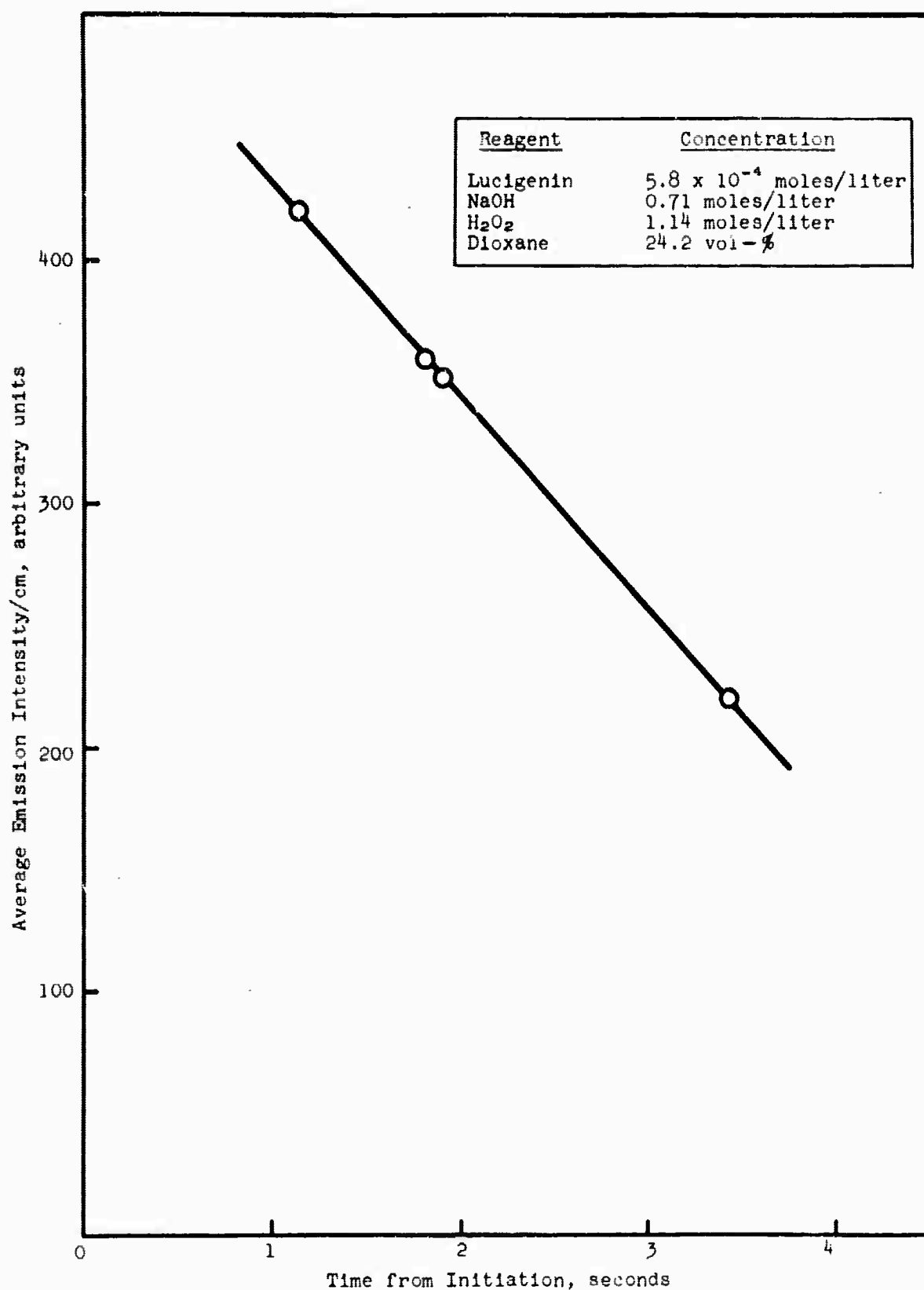


Figure 9. Gross Emission vs Time for Lucigenin Oxidation in Flow Reactor

C. "WEAK" CHEMILUMINESCENCE

During the course of the work on organic solvent catalysis of the lucigenin reaction it was observed that occasionally the emission began to increase after the "bright" initial pulse had decayed. Initial screening of the solvents employed revealed significant emission levels for acetone and dioxane when added to alkaline hydrogen peroxide. "Weak" chemiluminescent systems have been investigated by Stauff (ref. 4) for metal-catalyzed decompositions of peroxide and by Vassil'ev (ref. 3, 5) for organic systems. Recently, we have found that THF produces a very bright (visible) emission.

Preliminary work has shown that the weak emission of the acetone reaction may be increased by several orders of magnitude by addition of POPOP, tetraphenylbutadiene or p-terphenyl. These sensitizers produce a visible pulse in the acetone-peroxide system.

The results are summarized in Table 3. Since the data were obtained without special precautions to insure high purity, they must be treated with a great deal of caution. This is particularly important for the very weak luminescence associated with the decomposition of "pure" peroxide and that attributed to methyl alcohol. Clearly, however, THF solutions are relatively powerful emitters, compared with the other unsensitized "pure" solvents. Similarly, the effect of sensitizers on the reaction in acetone is unambiguous.

Comparison of the "solvent" oxidation results of Table 3 with the lucigenin "catalysis" data (Figures 5 and 6) suggests that a correlation may exist.

We have also investigated the weak chemiluminescence associated with the peroxide oxidation of pyrogallol. Pyridine and heavy metal salts are found to increase the emission sequentially. The results are given in Table 4.

Table 3

SOLVENT OXIDATION*

No.	Reactant	Vol-%	H ₂ O ₂ m/liter	NaOH m/liter	Detector	Peak Photocurrent amp	Remarks
1	MeOH	29.2	1.5	0.58	1P28	1.2×10^{-10}	
2	1-PROH	16.7	1.2	1.0	1P28	7×10^{-10}	Spectrograde compare No. 3
3	1-PROH	27.3	1.6	0.55	1P28	3×10^{-8}	Solvent grade
4	Dioxane	33.3	1.5	0.5	1P28	$>10^{-8}$	
5	Acetone	33.3	1.2	0.67	1P28	8.7×10^{-9}	Two-phase
6	Pyridine	50.0	1.2	0.33	1P28	3×10^{-9}	Two-phase
7	THF	21.6	1.2	0.5	1P21	2×10^{-8}	Visible flash
8	Acetone plus saturated p-terphenyl	33.3	1.2	0.67	1P21	8×10^{-8}	Visible flash Two-phase
9	Acetone plus saturated tetraphenyl- butadiene	33.3	1.2	0.67	1P21	$>10^{-8}$	Visible flash Two-phase
10	None	-	1.2	0.67	1P21	5×10^{-10}	
11	Acetone	33.3	1.2	0.67	1P21	8.1×10^{-9}	
12	Luminol†				IP28	7.75×10^{-5}	

* All reagents are "high purity" grades except as marked (No. 3).

† Standard Luminol reference solution (ref. 11) concentrations in mole/l:
luminol, 4×10^{-3} ; K₂S₂O₈, 6×10^{-2} ; H₂O₂, 3×10^{-2} ; Na₂CO₃, 0.1.

Table 4
PYROGALLOL OXIDATION*

No.	Reactant	Catalyst	Remarks	Peak Photo-current, amp
1	Pyrogallol $3 \times 10^{-3}M$	FeSO ₄	Phosphate buffer, pH 6	2.4×10^{-10}
2	Pyrogallol $3 \times 10^{-3}M$	Pyridine, $1.6 \times 10^{-2}M$	Acetate buffer, pH 6.5	2.4×10^{-9}
3	Pyridine $1.6 \times 10^{-2}M$	None	-	7.2×10^{-11}
4	Pyrogallol $3 \times 10^{-3}M$	Pyridine 8×10^{-3} CrAA $2 \times 10^{-4}M$	Acetate buffer	$7.1 \times 10^{-9}***$
5	Pyrogallol $3 \times 10^{-3}M$	Pyridine 8×10^{-3} Cu Phthalocyanine	Acetate buffer	7.1×10^{-9}

*H₂O₂ ≈ 0.3M for all reactions; detector 1P28

**AA is the acetylacetonate complex

***Similar results with FeAA. CoAA peak photocurrent 2.5×10^{-9} amp

IV. FUTURE WORK

During the next quarter, the spectrometers for this research will become available. A quantitative study of the solvent effect in the lucigenin reaction and in peroxide decomposition luminescence will be made. High purity reagent preparations will be undertaken for comparison with earlier results. Relative fluorescence yields in the reactions of interest will be determined for aid in the reaction analysis and optimization. Additional chemiluminescent reactions will be screened. The isolation or identification of reaction intermediates will be attempted for cases which appear of interest in the search for new chemiluminescent reactions.

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