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Reaction Rates, Quantum Yields, and Partial Mechanism for the Chemiluminescent Reaction of 3-Aminophthalhydrazide with Aqueous Alkaline Hydrogen Peroxide and Persulfate[1]

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The chemiluminescent reaction of 3-aminophthalhydrazide with aqueous alkaline hydrogen peroxide and persulfate was found to be first order in 3-aminophthalhydrazide (APH), first order in persulfate, zero order in hydrogen peroxide, and zero order in base. Allyl alcohol, an efficient sulfate ion radical trap, is without effect. Unlike other APH systems the reaction and consequent light emission is capable of extended lifetimes. The quantum yield increases with increasing hydrogen peroxide and approaches 1%. A mechanism is discussed in terms of this and other evidence.

Although light emission has been observed from a large number of chemical reactions,[2] the most prominent example of nonbiological, liquid-phase chemiluminescence has long been the oxidation of 3-aminophthalhydrazide (APH) and its analogs.[2–5] More than 200 papers relating to the reaction conditions, hydrazide structure, spectral distribution, and mechanism have appeared. While many oxidants generate light from APH in aqueous alkaline solution,[3] particularly in the presence of oxygen,[4,6,7] the specific use of hydrogen peroxide and a co-oxidant in aqueous solution or oxygen in strongly alkaline organic media[4,8] appears necessary for reasonably strong emission. Under these conditions, which suggest the involvement of a key peroxide intermediate,[6] quantum yields on the order of 1% have been reliably reported,[9] an efficiency which has been exceeded[10] only in recent times.

Inquiries into the mechanism of phthalhydrazide chemiluminescence have proven difficult because of the complex, multistep processes involved and because of the low light yield. Thus, the identity of the light-producing step is obscured by early mechanistic steps and by competing nonluminescent reactions. E. H. White and co-workers, however, have recently provided considerable insight into the mechanism of the APH-oxygen reaction in strongly alkaline dimethyl sulfoxide. Under these conditions, the reaction was shown to be first order in APH, oxygen, and base, and to provide the 3-aminophthalate dianion, V, as product in over 90% yield.[11] One-half of the oxygen in V was shown to be derived from the oxygen reactant,[11] and chemiluminescence and fluorescence spectral comparisons suggested that the singlet excited state of V was the emitting species.[12] The results were consistent with the involvement of transannular peroxide III proposed by Drew[13,14] and others[6] as a key intermediate, although, as White has pointed out,[11] certain noncyclic hydrazides are also moderately chemiluminescent.

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(1) Presented in part at the "Symposium on Chemiluminescence," U. S. Army Research Office, Durham, N. C., March 31–April 2, 1965.

(2) E. N. Harvey, "A History of Luminescence," The American Philosophical Society, Philadelphia, 1957; K. D. Gundermann, *Angew. Chem., Intern. Ed. Engl.*, **4**, 566 (1965); R. S. Anderson, *Ann. N. Y. Acad. Sci.*, **49**, 337 (1948); C. Reid, "Excited States in Chemistry and Biology," Butterworth and Co. (Publishers) Ltd., London, 1957, p 136.

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(6) P. C. Wilhelmse, R. Lumry, and H. Eyring, in "The Luminescence of Biological Systems," F. H. Johnson, Ed., American Association for the Advancement of Science, Washington, D. C., 1955, p 75.

(7) J. R. Totter, W. Stevenson, and G. E. Philbrook, *J. Phys. Chem.*, **68**, 752 (1964).

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(10) K. D. Gundermann and M. Drawert, *Chem. Ber.*, **95**, 2018 (1962); E. H. White and M. M. Bursey, *J. Am. Chem. Soc.*, **86**, 941 (1964); K. D. Gundermann, W. Horstmann, and G. Bergmann, *Ann.*, **684**, 127 (1965); M. M. Rauhut, B. G. Roberts, and A. M. Semsel, *J. Am. Chem. Soc.*, in press.

(11) E. H. White, O. Zafiriou, H. M. Kagi, and J. H. M. Hill, *ibid.*, **86**, 940 (1964).

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(13) H. D. K. Drew, R. F. Garwood, *J. Chem. Soc.*, 791 (1938).

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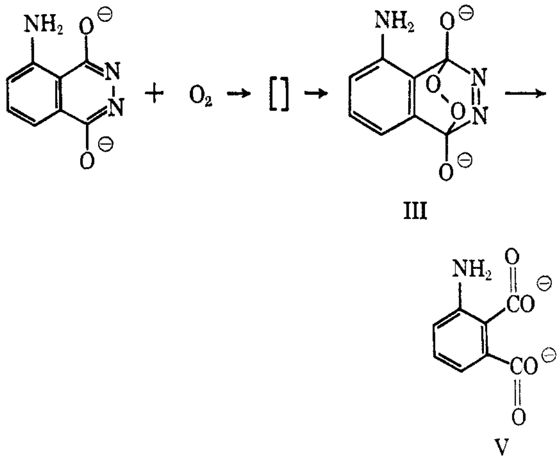

Under aqueous conditions with hydrogen peroxide, where the co-oxidant has typically been ferricyanide,[3,15,16] hypochlorite,[3,16–18] or the hydroxyl radical (derived from hydrogen peroxide and a metal salt[3,19] or complex[20–22]), the reaction products are complex, and light emission is generally brief. Attempts to relate the kinetics of such reactions to the chemiluminescent mechanism have been hampered by the speed of the reactions and by complicating side reactions between hydrogen peroxide and the co-oxidant.[15,22]

During a search for improved chemiluminescent reaction conditions in these laboratories, Dr. J. M. W. Scott and Mr. R. F. Phillips discovered that the use of persulfate as a co-oxidant with hydrogen peroxide for APH chemiluminescence provided a reasonably strong and long-lived light emission, a result which was unexpected in terms of the published literature.[23] The persulfate–hydrogen peroxide reaction thus appeared to be particularly suitable for kinetic studies relating to the reaction mechanism.

Results

Reaction Rates from APH Disappearance.—Rates of APH reactions with potassium persulfate in 0.1 M aqueous potassium carbonate were determined at 29.2° in the presence and absence of hydrogen peroxide by following the disappearance of APH absorption at 346 mμ, where the other components and products do not absorb. The reactions were carried out with a large excess of reactants relative to APH so that pseudo-first-order kinetics were anticipated, and plots of log absorbance *vs.* time were in fact linear. Data from a typical experiment are summarized in Table VII which appears in the Experimental Section, p 2436. Reasonably constant second-order rate constants were calculated by dividing the pseudo-first-order constants by the persulfate concentration; the results are summarized in Table I.

TABLE I

REACTION RATES FROM APH DISAPPEARANCE[a]

Expt	APH, $M \times 10^4$	$K_2S_2O_8$, $M \times 10^2$	H_2O_2, $M \times 10^2$	k_2, M^{-1} sec^{-1} $\times 10^2$
1	2.5	3.0	0	1.44
2	2.5	6.0	0	1.43
	2.5	6.0	0	1.41
3	2.5[b]	6.0	0	1.37
4	2.5[c]	6.0	0	1.35
5	2.5[b,c]	6.0	0	1.15
	2.5[b,c]	6.0	0	1.15
6	2.5	6.0	1.5	1.38
7	0.25	6.0	3.0	1.44
8	2.5	6.0	3.0	1.45
9	2.5	6.0	3.0	1.31
10	2.5[c]	6.0	3.0	1.30
11	2.5	3.0	3.0	1.30

[a] Reactions in 0.1 M K_2CO_3 at 29.2°. [b] Deoxygenated by nitrogen bubbling. [c] Allyl alcohol (0.030 M) was present.

It is evident from the table that the data fit the second-order rate expression

$$\frac{d[APH]}{dT} = -k_2[APH][S_2O_8^{2-}]$$

and that hydrogen peroxide is not involved in a rate-determining step. The related (but nonchemiluminescent) oxidation of hydrazobenzene by persulfate has also been shown to follow second-order kinetics.[24]

Many persulfate oxidation reactions are essentially first order in persulfate alone.[25] Such reactions have been interpreted in terms of a free-radical chain process involving the sulfate ion radical, $SO_4\cdot^-$, as an essential chain carrier.[26] Indeed this free-radical chain mechanism has been suggested to apply to the reaction of 3-methylaminophthalhydrazide with persulfate.[7] Allyl alcohol, however, is known to strongly inhibit such reactions by trapping $SO_4\cdot^-$.[27]

The results in Table I show that allyl alcohol has no effect on APH–$S_2O_8^{2-}$ reactions, even with an allyl alcohol–APH ratio of 120. These results, along with the second-order kinetics observed, make it unlikely that a free-radical chain process involving $SO_4\cdot^-$ is involved.

Oxygen is also without effect on the reaction, although oxygen has been shown to inhibit $SO_4\cdot^-$ chain reactions.[28] The somewhat low rate constant obtained with allyl alcohol in deoxygenated solutions (expt 5), however, suggests that oxygen does inhibit the direct reaction between persulfate and allyl alcohol.[27] Thus, the loss of persulfate resulting from its reaction with allyl alcohol in deoxygenated solution would produce an erroneously low rate constant for APH disappearance.

Reaction Rates and Quantum Yields from Light Intensity Decay.—A radiometer–spectrofluorimeter, de-

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(17) L. Harris and A. S. Parker, *J. Am. Chem. Soc.*, **57**, 1939 (1935).

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(25) D. A. House, *Chem. Rev.*, **62**, 185 (1962).

(26) I. M. Kolthoff, E. J. Meehan, and E. M. Carr, *J. Am. Chem. Soc.*, **75**, 1439 (1953); K. B. Wiberg, *ibid.*, **81**, 252 (1959).

(27) E. J. Behrman, *ibid.*, **85**, 3478 (1963).

(28) D. L. Ball, M. M. Crutchfield, and J. O. Edwards, *J. Org. Chem.*, **25**, 1599 (1960).

signed by R. C. Hirt,[29] was used to measure light intensity in absolute units as a function of time at constant wavelength and as a function of wavelength at constant time. The spectral distribution of emission (Figure 1) was independent of time and reactant concentrations and was essentially constant for all the experiments.

Most of the rate experiments were carried out under pseudo-first-order conditions with an excess of persulfate and hydrogen peroxide relative to APH. Under these conditions only APH changes significantly in concentration during a run so that variations in quantum yield (einsteins of light per mole of APH) with time within an experiment which might be caused by decreases in hydrogen peroxide or persulfate concentrations are avoided. Thus, under pseudo-first-order conditions, the intensity should be proportional to the APH concentration providing that the disappearance of APH and the formation of products do not effect the quantum yield. This experimental design allows the first-order rate equation (1) to be replaced by eq 2 for the measurement of reaction rates.[30]

$$\ln \frac{(\mathrm{APH})_0}{(\mathrm{APH})} = k^1T \qquad (1)$$

$$\ln \mathrm{I}_0/\mathrm{I} = k^1T \qquad (2)$$

Aside from a short induction period, plots of ln intensity *vs.* time were found to be linear during at least two half-lives for experiments carried out under these conditions. Second-order intensity decay rate constants were calculated by dividing the slope of each linear plot by the persulfate concentration. Good agreement was obtained between the second-order rate constants measured by absorption and emission procedures, under most reaction conditions indicating that the requirement for constant quantum yield within an experiment was met under pseudo-first-order conditions, and that the intensity accurately monitors the APH concentration under such conditions. Data from a typical experiment are summarized in Table VIII in the Experimental Section.

The effect of APH concentration on the intensity decay rate and quantum yield are summarized in Table II. It is seen that up to 8.00 × 10^{-3} *M* APH, the second-order rate constants are in good agreement with those obtained by measurement of APH disappearance. At higher APH concentration, the light decay rates are more rapid, reflecting a decreasing quantum yield as the reaction proceeds. The quantum yield decreases with time at low hydrogen peroxide–APH ratios as a result of hydrogen peroxide consumption (see below) and as a result of color formation and consequent light absorption.

It is evident from Table II that allyl alcohol is without substantial effect on the reaction rate or quantum yield. The quantum yield decreases at higher APH concentrations, an effect evidently common to APH chemiluminescence.[15,17,31]

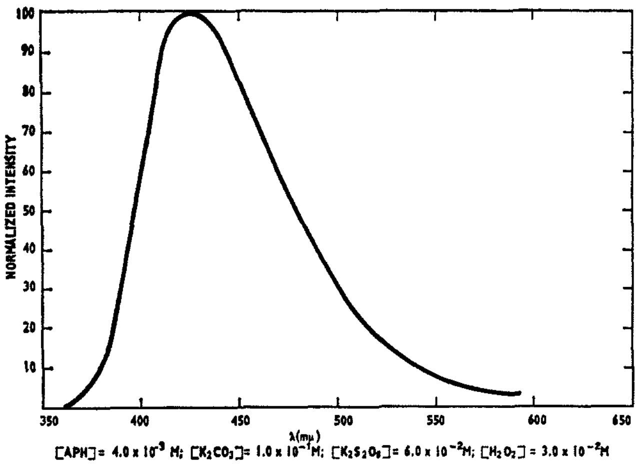

Figure 1.—Spectral distribution of APH chemiluminescent emission

Table II

Effect of 3-Aminophthalhydrazide Concentration on Reaction Rate and Quantum Yield[a]

APH, *M* × 10^3	Second-order intensity decay constant, M^{-1} sec^{-1} × 10^2	Quantum yield, einsteins mole^{-1} × 10^3
0.10	1.66	8.1
1.00	1.34	7.2
1.00[b]	1.29	7.1
4.00	1.57[c]	6.0[d]
8.00	1.63	4.4
12.00	[2.08][e]	2.8
20.00[f]	[2.62][e]	2.0

[a] The reactions were carried out with 0.060 *M* $K_2S_2O_8$ and 0.030 *M* H_2O_2 in 0.10 *M* aqueous K_2CO_3 (except note *f*) at 29.2°. [b] The reaction contained 0.030 *M* allyl alcohol. [c] Average of 11 experiments; average deviation ±0.066 × 10^{-2}. [d] Average of 11 experiments; average deviation ±0.190 × 10^{-3}. [e] Calculated from initial rate. The first-order plot deviated somewhat from linearity. [f] Reaction with 0.10 *M* $K_2S_2O_8$ and 0.10 *M* H_2O_2 in 0.20 *M* K_2CO_3.

The effect of base strength on reaction rate and quantum yield is summarized in Table III. The results indicate that the effect of pH on rate is minor, but, as reported for other APH reactions,[17,20,22,32] the quantum yield decreases at high pH.

Table III

Effect of pH on Reaction Rate and Quantum Yield

APH, *M* × 10^3	Base	Base concn, *M*	pH	Second-order intensity decay constant, M^{-1} sec^{-1} × 10^2	Quantum yield, einsteins mole^{-1} × 10^3
4.00[a]	K_2CO_3	0.100	11.60	1.57	6.0
4.00[b]	NaOH	0.049	12.69	1.28	3.9
4.00[b]	NaOH	0.098	12.91	1.38	3.0
4.00[b]	NaOH	0.196	13.29	1.85	1.4
8.00[a]	Et_3N	0.100	11.87	1.63	4.2
8.00[a]	K_2CO_3	0.100	11.60	1.63	4.4
8.00[b]	NaOH	0.098	12.91	1.57	2.5

[a] $K_2S_2O_8$ and H_2O_2 were 0.060 and 0.030 *M*, respectively. [b] $K_2S_2O_8$ and H_2O_2 were 0.059 and 0.027 *M*, respectively.

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[29] B. G. Roberts and R. C. Hirt, Research Service Department, American Cyanamid Co. The instrument was described at the 19th Annual Instrument Society of America Conference, New York, N. Y., Oct 12–15, 1964 (preprint no. 2.2-2-64).

[30] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p 28.

[31] B. Tamamushi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **41**, 166 (1943); *Chem. Abstr.*, **41**, 6157*h* (1947).

[32] B. Y. Sveshnikov, *Compt. Rend. Acad. Sci. URSS*, **35**, 278 (1942); *Chem. Abstr.*, **37**, 1931 (1943); K. Weber, M. Krajcinovic, *Ber.*, **75B**, 2051 (1942).

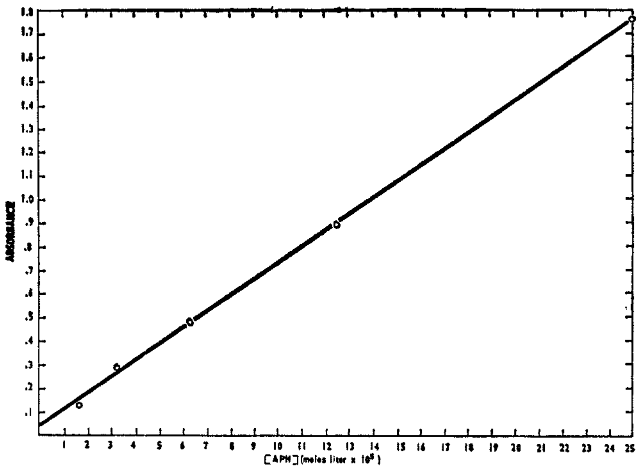

Figure 2.—Absorbance at 346 mμ *vs.* APH concentration.

Results indicating the effect of persulfate concentrations on reaction rate and quantum yield are summarized in Table IV. The trend toward increasing rate constant with increasing persulfate is probably within the experimental error. The quantum yield decreases at high persulfate concentration.

TABLE IV

EFFECT OF PERSULFATE CONCENTRATION ON REACTION RATE AND QUANTUM YIELD[a]

$K_2S_2O_8$, $M \times 10^2$	Second-order intensity decay constant, M^{-1} sec^{-1} $\times 10^2$	Quantum yield, einsteins mole^{-1} $\times 10^3$
2.95	1.48	3.2
5.90	1.59	3.0
11.80	1.72	2.3

[a] The reactions were carried out with 1.00 $\times$ 10^{-3} M APH and 0.027 M H_2O_2 in 0.098 M aqueous NaOH.

Results indicating the effect of hydrogen peroxide on quantum yield and reaction rate are summarized in Table V. As observed in other APH systems,[15,17,31] at low hydrogen peroxide levels, the quantum yield increases substantially with increasing hydrogen peroxide, with the increase leveling off when high hydrogen peroxide concentrations are reached. At low hydrogen peroxide concentrations, intensity decay is more rapid than the over-all reaction rate as a consequence of the decreasing quantum yield with decreasing hydrogen peroxide within an experiment. The minor trend toward increasing rate at high hydrogen peroxide concentrations may result from persulfate consumption in a side reaction with hydrogen peroxide, although this reaction is relatively slow compared to the reactions reported here.[33] It is evident that hydrogen peroxide increases the quantum yield of the APH–$S_2O_8^{2-}$ reaction by a factor of 100. Moreover, the fast light decay observed in the absence of hydrogen peroxide demonstrates that the intensity under such conditions is not determined by the rate of the APH–persulfate reaction. The commonly used expedient of attempting to relate maximum intensity at different reactant concentrations to the overall mechanism is clearly invalid for such systems. In the absence of hydrogen peroxide, the light may result from a reaction of persulfate with a trace impurity, possibly derived from photooxidation of the APH during storage, although oxygen is also a factor in the absence of hydrogen peroxide.

TABLE V

EFFECT OF HYDROGEN PEROXIDE CONCENTRATION ON REACTION RATE AND QUANTUM YIELD[a]

H_2O_2, $M \times 10^3$	Second-order intensity decay constant, M^{-1} sec^{-1} $\times 10^2$	Quantum yield, einsteins mole^{-1} $\times 10^3$
0[b]	25.03	0.078
2	6.20	1.0
5	2.98	2.9
10	1.97	4.7
20	1.47	6.1
30	1.40	6.9
50	1.34	7.5
100	1.28	7.9

[a] Reactions carried out with 1.0 $\times$ 10^{-3} M APH, 0.060 M $K_2S_2O_8$ in 0.10 M aqueous K_2CO_3 at 29.2°. [b] The APH concentration was 8.0 $\times$ 10^{-3} M. Emission could not be detected at low concentrations.

Results showing the effect of temperature on reaction rate and quantum yield are summarized in Table VI. The quantum yield decreases with increasing temperature. The activation energy and frequency factor calculated from an Arrhenius plot of the rate data were 12.8 kcal mole^{-1} and 3.2 $\times$ 10^7 M^{-1} sec^{-1}.

TABLE VI

EFFECT OF TEMPERATURE ON APH CHEMILUMINESCENCE[a]

Temp, °C	k_2,[b] M^{-1} sec^{-1}	Quantum yield, einsteins mole^{-1}
13	4.37 $\times$ 10^{-3}	0.915 $\times$ 10^{-2}
29	1.42 $\times$ 10^{-2}	0.69 $\times$ 10^{-2}
40	3.03 $\times$ 10^{-2}	0.57 $\times$ 10^{-2}
52	6.69 $\times$ 10^{-2}	0.44 $\times$ 10^{-2}

[a] Reactions carried out with 0.001 M luminol, 0.06 M $K_2S_2O_8$, and 0.03 M H_2O_2 in 0.1 M K_2CO_3. [b] Second-order rate constant.

Discussion

The mechanism of the chemiluminescent reaction between APH, persulfate, and hydrogen peroxide must be consistent with the observations summarized below. (a) The reaction is first order in APH, first order in persulfate, zero order in hydrogen peroxide, and zero order in base. (b) The reaction rate and quantum yield are not affected by added allyl alcohol. (c) The quantum yield increases substantially with increasing hydrogen peroxide up to a limiting value. (d) The quantum yield decreases at high APH concentrations and at high persulfate concentrations.

A mechanism in agreement with these results and with the results of previous work is tentatively suggested in Chart I.

The rate-determining two-electron oxidation of the phthalhydrazide monoanion (I) in step 1 is indicated by the second-order kinetics and by our failure to trap the sulfate ion radical, a necessary product of any one-electron oxidation process.[25] Even a nonchain process involving $SO_4\cdot^-$ would be substantially re-

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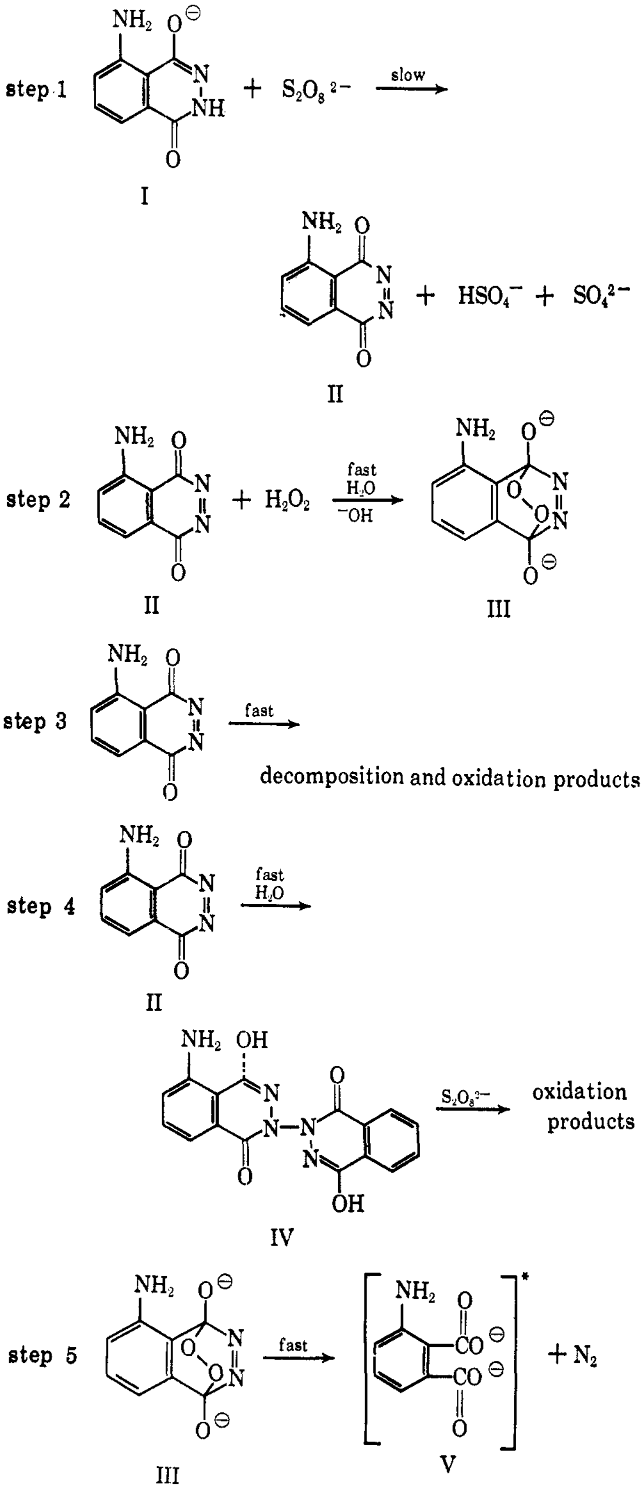
CHART I



tarded by added allyl alcohol or hydrogen peroxide, since less $SO_4\cdot^-$ would then be available to oxidize I and the stoichiometry would be altered. The mechanism may be related to that of the Elbs oxidation of phenols, which has also been shown to be second order and unaffected by allyl alcohol.[27] The phthalazinedione II is the probable product of a one-step two-electron oxidation. The competition among steps 2, 3, and 4 seems required by the increase in quantum yield with increasing hydrogen peroxide. Thus increasing hydrogen peroxide would favor the formation of chemiluminescence precursor III in step 2 relative to nonchemiluminescent steps 3 and 4. Step 3 is necessary to account for the effect of hydrogen peroxide at low APH concentrations where the essential constancy of quantum yield with APH concentration indicates that step 4 is unimportant. In the absence of a competing nonluminescent reaction increasing hydrogen peroxide might influence the reaction rate but not the quantum yield. Step 4 seems necessary, however, to account for the decrease in quantum yield at high APH concentrations and is strictly analogous, moreover, to the known coupling of phthalazinedione itself in aqueous solutions.[34] The suggestion that transannular peroxide III is the key intermediate whose decomposition produces the emitting excited state V in step 5 is consistent with the oxygen 18[11] and spectral studies[4,12] by White. Moreover, concerted multiple bond cleavage decomposition of V would accommodate the substantial and simultaneous energy release essential to excitation.[35]

The evidence at hand does not permit us to specify the detailed mechanism of step 2. Both a nucleophilic attack by HOO^- and a free-radical reaction involving $HOO\cdot$ are possibilities. It should be noted that the free-radical inhibition results reported for a number of phthalhydrazide systems[4] do not necessarily point to the latter since systems involving one-electron oxidants[15,36] and aqueous systems requiring oxygen,[7] would necessarily involve a free-radical process, in any event.

The involvement of phthalazinedione II in APH chemiluminescence has been suggested previously. Its excited state has been suggested to be the emitting species,[37] it has been suggested as a nonchemiluminescent side product,[15] it has been suggested to react with diimide to generate excited I in the chemiluminescent process,[3,38] and it has been suggested to form transannular peroxide III, which can then decompose to excited I and oxygen[13] or to excited V and nitrogen.[6,14] Mechanisms requiring excited I, however, can be ruled out because I is not fluorescent under the alkaline chemiluminescent conditions.[17,39] Since even short-lived excited singlets equilibrate with a liquid phase medium,[40] the ability of an excited singlet to emit in a given environment must be independent of the mechanism of its formation. Mechanisms requiring excited II are also inconsistent with the marked effect of hydrogen peroxide. Similarly, mechanisms involving a dimeric product such as IV as a chemiluminescence precursor[15] are inconsistent with the decrease in quantum yield with increasing APH concentration.

It has also been argued that intermediate II cannot be involved in APH chemiluminescence because chemiluminescence is not observed from phthalazinedione, itself, under conditions where chemiluminescence was observed from phthalhydrazide.[11] However, in

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(34) T. J. Kealy, *J. Am. Chem. Soc.*, **84**, 966 (1962).

(35) M. M. Rauhut, D. Sheehan, R. A. Clarke, and A. M. Semsel, *Photochem. Photobiol.*, **4**, 1097 (1965).

(36) K. Weber, Z. Prochazka, and J. Spoljaric, *Croat. Chem. Acta*, **28**, 25 (1956); *Chem. Abstr.*, **50**, 1640*f* (1956).

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our hands appreciable chemiluminescence has not been seen from freshly recrystallized phthalhydrazide under a variety of conditions, including the aqueous persulfate–hydrogen peroxide system. Thus, the present evidence while not conclusive is best interpreted in terms of intermediates II and III as indicated in Chart I.

Experimental Section

Materials.—The sodium salt of 3-aminophthalhydrazide[41] (APH) was recrystallized (35 to 0°) four times from distilled water and dried under vacuum over P_2O_5. Allyl alcohol and triethylamine were redistilled. Other reagents were of analytical grade obtained commercially and were not further purified. Recrystallization of potassium persulfate or the inclusion of ethylene–diaminetetracetic acid in experiments did not influence the results.

Appropriate stock solutions were prepared from weighed quantities of sodium APH, potassium persulfate, potassium carbonate, triethylamine, and distilled water. Sodium APH solutions were always freshly prepared prior to use. Stock solutions of hydrogen peroxide were prepared from the 30% reagent and were standardized iodometrically. Standard sodium hydroxide solutions were standardized potentiometrically.

Rates of APH Disappearance.—Aliquots of thermostated standard solutions were pipetted into a 10.0-mm-thick quartz cell contained in a thermostated housing attached to a Beckman model DU spectrophotometer. The order of addition was not critical provided that potassium persulfate was added last. The temperature was maintained at 29.2°. The absorbance at 346 mμ, a maximum in the sodium APH spectrum, was recorded as a function of time. Preliminary experiments showed that only sodium APH absorbed at this wavelength under the conditions used. A Beer's law plot for 346-mμ absorbance of sodium APH in 0.10 *M* aqueous K_2CO_3 is shown in Figure 2. Typical data for an experiment are summarized in Table VII. Pseudo-first-order rate constants were calculated from the linear plots of log absorbance *vs.* time and divided by the persulfate concentrations to obtain the second-order rate constants summarized in Table I.

TABLE VII

APH ABSORBANCE AT 346 mμ *vs.* TIME[a]

Time, sec	Absorbance	$k^1 \times 10^4$ sec^{-1}
200	1.517	10.20
400	1.304	8.89
600	1.090	8.91
800	0.927	8.71
1000	0.777	8.73
1200	0.654	8.71
1300	0.585	8.89
1400	0.548	8.73
1500	0.496	8.82
1600	0.457	8.77
1700	0.418	8.77
1800	0.393	8.64
1900	0.351	8.80
2000	0.321	8.80

[a] [APH] = 2.5×10^{-4} *M*; [$K_2S_2O_8$] = 6.0×10^{-2} *M*; [H_2O_2] = 3.0×10^{-2} *M*; [K_2CO_3] = 1.0×10^{-1} *M* at 29.5°.

Light Decay Rates and Quantum Yields.—The instrumentation, a combination spectroradiometer–fluorimeter, consisted essentially of a Bausch and Lomb grating monochromator, a 1P21 photomultiplier tube, an Aminco photomultiplier power supply and amiplifier, and a Leeds and Northrup integrating recorder. The instrument and its absolute calibration have been described elsewhere.[42] Early experiments were carried out in a 10-mm-thick, 3-ml, rectangular quartz cell contained in a thermostated housing attached to the monochromator. Later experiments were carried out in a 10-mm-deep, 3.0-ml cylindrical cuvette to permit reference to the absolute calibration. The cuvette was blackened on the rear face to minimize reflection.

Aliquots of the reaction components were combined in the cuvette, with the persulfate added last. The recorder was started with persulfate addition. The intensity of a 5-mm-wide emission band, usually centered at 430 mμ, was followed for at least two reaction half-lives. Results from a typical experiment are summarized in Table VIII.

TABLE VIII

APH LIGHT EMISSION *vs.* TIME[a]

Time, sec	Intensity,[b] einsteins sec^{-1} ml^{-1} $\times 10^{11}$	$k^1 \times 10^4$ sec^{-1}
0	1.928	...
60	1.838	7.97
120	1.749	8.12
180	1.656	8.45
240	1.564	8.72
300	1.500	8.37
360	1.430	8.30
420	1.363	8.26
480	1.292	8.34
540	1.226	8.39
600	1.162	8.44
660	1.107	8.41

[a] [APH] = 4.0×10^{-3} *M*; [$K_2S_2O_8$] = 6.0×10^{-2} *M*; [H_2O_2] = 3.0×10^{-2} *M*; [K_2CO_3] = 1.0×10^{-1} *M* at 29.2°. [b] Integrated over the spectral distribution.

Emission spectra were determined manually at several decay times throughout selected experiments by intermittent rotation of the monochromator wavelength drum over 5-mμ intervals. The spectra appeared as a step function on the recorder chart. The scan time was short relative to the rate of intensity decay, but a small correction for intensity decay was made. The chemiluminescence spectrum (Figure 1) was invarient with time and reaction conditions under the conditions studied.

Quantum yields in einsteins mole^{-1} were calculated as previously described,[42] and refer to the total quanta of light emitted over the spectral distribution and reaction time divided by the moles of APH introduced.

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