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The Chemiluminescence of 3-Aminophthalhydrazide

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The oxidation of 3-aminophthalhydrazide in alkaline solution is accompanied by considerable light emission.[1] A knowledge of the quantum efficiency under various conditions may assist in interpreting the mechanism of this light emission. Measurements of the quantum efficiency have been reported for certain chemiluminescent reactions,[2,3] and while conclusions have been drawn from measurements with dilute flames, data for condensed phases are meager. In this investigation, measurements were made to determine the maximum quantum efficiency of the chemiluminescence of 3-aminophthalhydrazide and the effect of various factors on this efficiency.

A thermopile offers a more direct measure of the chemiluminescent energy than photometric measurements, but is usually too insensitive. However, if the light reaction zone is made to approach a point source, a larger fraction of the emitted light energy may be focused on the thermopile surface. A number of preliminary measurements indicated that if a solution of sodium luminol[4] containing hydrogen peroxide was thoroughly mixed with a large excess of strong oxidizing agent (alkaline hypochlorite), the light reaction could be confined to a small volume. Accordingly, a suitable reaction chamber was designed and the energy measurements effected with a thermopile.

Materials.—1. **Sodium luminol** was prepared according to directions.[5]

2. **Hydrogen peroxide** (3% U. S. P.) was analyzed before its addition to the sodium luminol solutions.

3. **Sodium hypochlorite** was prepared by bubbling commercial (tank) chlorine slowly through a solution *N* in sodium hydroxide and 2 *N* in sodium carbonate, with continuous stirring until the solution contained about 5% (by weight) available chlorine (as Cl_2). This solution was diluted to a chlorine content of 0.5 or 1.0%, and sodium carbonate added to bring the alkali concentration to 0.350 *N* (carbonate).

Any other chemicals used were of C. P. quality and distilled water was employed throughout.

Apparatus.—A number of reaction chambers were tested; that illustrated in Fig. 1 proved the most satisfactory. This chamber could be so operated that a brilliant spherical spot of light (2 mm. in diameter; slightly larger for the concentrated solutions) appeared at the point where the reactants met, with no residual light in the effluent. The chamber was constructed of standard size glass tubing with quartz tubing around the reaction zone. The sodium luminol plus hydrogen peroxide feed nozzle was 0.483 mm. in diameter. Stopcocks in the connecting lines from two 18-liter aspirator bottles, containing the reactants, regulated the gravity flow. The spot of light was focused by a quartz lens, 3.8 cm. in diameter and 19.1 cm. away, on the sensitive surface of a Kipp (micro) thermopile. (The image of this spot, formed by the lens, was slightly smaller than the active surface of the pile which was 28.26 sq. mm.) The thermopile was connected to a Leeds and Northrup H. S. type galvanometer. The thermopile–galvanometer system was calibrated with two standard lamps (Bureau of Standards).

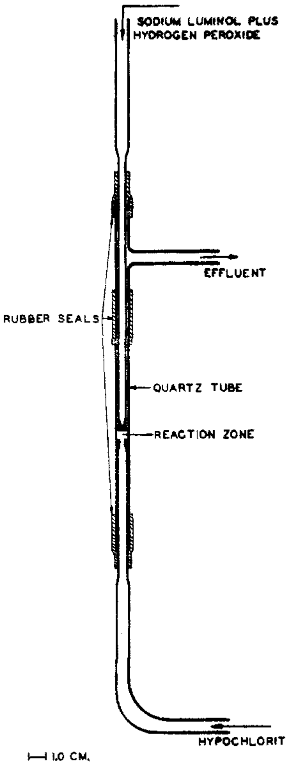

Fig. 1.—Reaction chamber.

Experimental Procedure

It was necessary to determine what part of the galvanometer deflection was due to heat of mixing or to any other extraneous effects. Proper shielding of the system prevented stray light from entering the thermopile. Preliminary measurements showed that it was advisable to store the bottles containing the reactants for twenty-four hours, before making measurements, in a thermally insulated room (24 to 25°) with the thermopile–galvanometer system. When sodium luminol solution (in the absence of hydrogen peroxide) was mixed in the chamber with the hypochlorite, the galvanometer deflection obtained was less than 1% of the maximum deflection when hydrogen peroxide was present. Likewise, when hydrogen peroxide solution alone was mixed with the hypochlorite, the deflection obtained was a negligible fraction of that obtained under normal conditions of operation.

The maximum flow of sodium luminol plus hydrogen peroxide was limited by the liquid head (about 1.5 m.) and the capillary feed nozzle (Fig. 1). After the rate of sodium luminol plus peroxide had been fixed, the flow of

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[1] Albrecht, *Z. physik. Chem.*, **136**, 321 (1928).

[2] Polanyi and co-workers, *ibid.*, **B1**, 3–73 (1928).

[3] Thomas and Dufford, *J. Opt. Soc. Am.*, **23**, 251 (1933).

[4] The sodium salt of 3-aminophthalhydrazide will be designated as sodium luminol.

[5] Huntress, Stanley and Parker, THIS JOURNAL, **56**, 241 (1934).

hypochlorite was adjusted to give a small spot of light on the lens-side of the reaction zone. Under these conditions, moderate variations (as high as 15%) in the rate of flow of hypochlorite had no influence on the galvanometer deflection. When potassium ferricyanide plus sodium hydroxide was tried as the oxidizing agent, in place of hypochlorite, the light was no longer confined to a spot but filled the reaction zone and appeared dimmer than before.

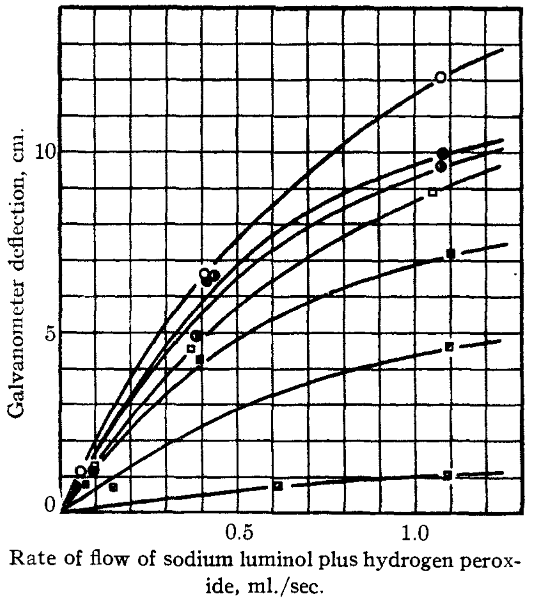

Fig. 2.—Variation of galvanometer deflection with rate of flow of sodium luminol plus hydrogen peroxide.

Curve	Conc. sodium luminol, g. mole/liter	Conc. hydrogen peroxide, g.mole/liter	Conc. hypochlorite, % Cl_2	Conc. alkali, *N*
○	0.0251	0.0434	1.0	0.350
●	.0251	.0215	0.5	.350
◑	.0126	.0215	1.0	.350
□	.0251	.0215	1.0	.350
■	.0050	.0215	1.0	.350
◩	.0025	.0215	1.0	.350
◪	.00050	.0215	1.0	.350

Data.—The data are presented in Figs. 2 and 3. Each of the galvanometer deflections plotted is the average of ten observations. The average deviation was 3%. Different batches of the reactant solutions gave the same deflections within 5%. The change in galvanometer deflection with varying rate of flow of sodium·luminol plus hydrogen peroxide is shown in Fig. 2. By interpolation of these data, it was found possible to express all data for other rates of flow. The data, interpolated in this way, are presented in Fig. 3, which also shows how variations in the hydrogen peroxide concentration affect the galvanometer deflections.

Quantum Efficiency

It was assumed that the chemiluminescent intensity was equal in all directions and that the source might be considered as a point. The latter assumption was validated by measurements with a larger lens. Therefore, the galvanometer deflections were an easily calculated fraction of the total energy emitted.

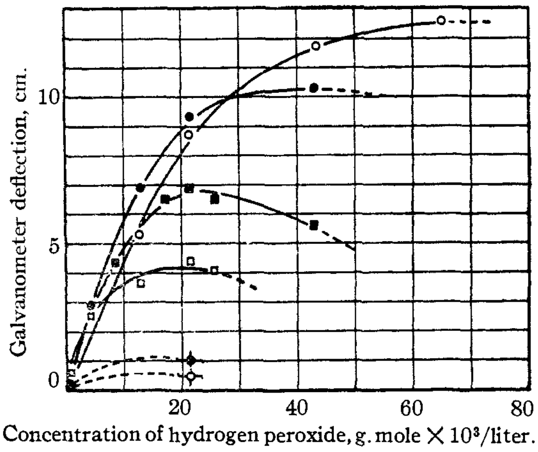

Fig. 3.—Variation of galvanometer deflection with hydrogen peroxide concentration; hypochlorite, 1% Cl_2; alkali, 0.350 *N;* rate of flow of sodium luminol plus hydrogen peroxide, 1 ml./sec.; rate of flow of hypochlorite, 3 ml./sec. (approx).

Curve	Conc. sodium luminol, g. mole/liter	Curve	Conc. sodium luminol, g. mole/liter
○	0.0251	□	0.0025
●	.0126	-●-	.00050
■	.0050	-○-	.00025

A spectroscope showed that the chemiluminescence extended from the violet, deep into the red. A quartz cell filled with distilled water, placed between the reaction zone and the thermopile, reduced the galvanometer deflections by about 10%. Jena filter OG2b, which transmits nearly 100% from 5780 to 20,000 Å., reduced the galvanometer deflection by about 98%, showing that only 2% of the chemiluminescent energy was of wave lengths longer than 5780 Å.

Photographs of the chemiluminescence and of the emission from a standardized lamp, taken with a Hilger E315 spectrograph and III-L Eastman Kodak plates, assisted in evaluating the energy distribution of the chemiluminescence. Most of the chemiluminescent radiation was in the wave length region 3800 to 5000 Å. with a flat maximum from 4100 to 4400 Å.

Inasmuch as the sodium luminol, hypochlorite and the product of the chemiluminescence each absorbs light of wave lengths shorter than 3700 Å., the energy observed may be only a fraction of the total produced.

The following constants and variables were used in the calculation of the quantum efficiency (Eff).

Eff = quanta emitted per molecule of sodium luminol introduced.
d = galvanometer deflection (cm.).
v = rate of flow of sodium luminol plus hydrogen peroxide (ml. per sec.).
a = concentration of sodium luminol (g. mole per ml.).
f = galvanometer calibration factor (8.556 ergs per sec. per cm. deflection).
λ = wave length of the maximum chemiluminescent intensity (4250×10^{-8} cm.).
l = fraction of the total emitted light focused on the thermopile (0.00246) (calculated from the geometry of the system).
t = fraction of light transmitted by lens and chamber wall (0.9).
h = Planck's constant (6.554×10^{-27} erg. sec. per quantum).
c = velocity of light (3.00×10^{10} cm. per sec.).
N = Avogadro's number (6.063×10^{23}).

$$\mathrm{Eff} = \frac{d}{v \times a} \times \frac{f \times \lambda}{l \times t \times c \times h \times N}$$

Figure 4 shows how the quantum efficiency varies with the concentration of sodium luminol and with the rate of flow of sodium luminol plus hydrogen peroxide. The numerical value for the quantum efficiency, from the maximum of the lowest curve of Fig. 4. was calculated to be 2.8×10^{-3} quanta per molecule of sodium luminol introduced. At lower rates of flow of sodium luminol plus hydrogen peroxide the efficiency increased but never more than doubled.

Fluorescence Experiments

Even though the chemiluminescence extended over a rather broad band in the spectrum, it seemed of interest to study the emission of light from aqueous solutions of sodium luminol when they were illuminated by an external source. Most of the experiments were performed under daylight illumination with window glass interposed between the light and the solutions ($\lambda >$ 3400 Å.). The fluorescence was found to be much stronger when hydrogen peroxide was added to the sodium luminol. The fluorescence intensity was a maximum for concentrations of sodium luminol between 0.00025 and 0.00005 molal. Although the maximum quantum efficiency is also in this concentration range, no correlation between the two is implied. It is more likely that the dependence of the fluorescence on concentration is determined by the molal absorption coefficient (ϵ = 8000 approx. for wave lengths shorter than 3700 Å.).

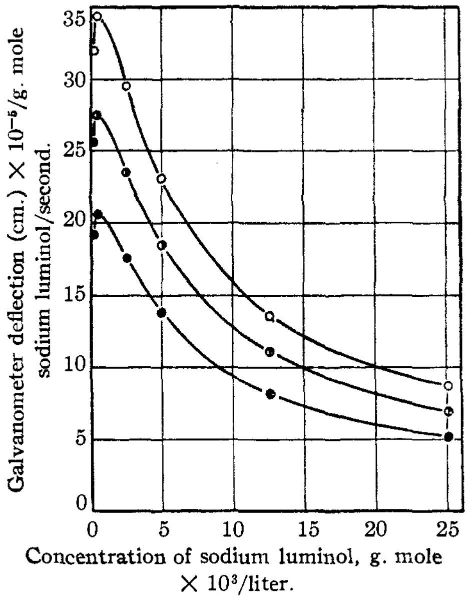

Fig. 4.—Variation of energy emitted per mole of sodium luminol, with its concentration. Concentration of hydrogen peroxide: maxima of Fig. 3. Concentration of hypochlorite, 1% Cl_2: concentration of alkali, 0.350 N.

Curve	Rate of flow of sodium luminol plus hydrogen peroxide
○	0.1 ml./sec.
◑	0.5 ml./sec.
●	1.0 ml./sec.

Absorption Spectra Measurements

Quantitative measurements of the absorption spectra were made, in order to obtain further information concerning the reactants and products. The absorption of aqueous solutions of sodium luminol, and of mixtures of sodium luminol with hydrogen peroxide, extended from 3970 to 2400 Å. Each solution showed absorption maxima at 3500 and 2900 Å., and evidence of another maximum at shorter wave lengths than 2500 Å. Below 3600 Å. the absorption by sodium luminol is slightly but definitely different from that of solutions containing hydrogen peroxide, the necessary corrections having been made for absorption by hydrogen peroxide alone. Absorption by aqueous solutions of the product from the chemiluminescence extends from 5000 to below 2300 Å. The amount and character of the absorption depended upon the manner in which the reactants were brought together. The results indicate that the internal absorption, by the final products, and possibly by the intermediate products, reduces the light emission, especially for concentrated solutions. In evaluating the quantum efficiencies, however, the internal absorption has been neglected.

Discussion of Results

The change in energy emission with changing hydrogen peroxide concentration (Fig. 3) indicates that hydrogen peroxide plays a major role in the chemiluminescence. The fluorescence and the absorption spectra point to the same conclusion. Figure 3 indicates that each molecule of sodium luminol is associated with about four molecules of hydrogen peroxide. This, in conjunction with the other results, suggests a compound between sodium luminol and hydrogen peroxide. The binding between the two types of molecule is probably a loose one and the molecular ratio in the compound itself is not necessarily four to one.

The quantum efficiency, though low, is about 10,000 times higher than any thus far reported for condensed systems.[3] The comparatively high efficiency is, no doubt, assisted by the successful mixing. The prolonged chemiluminescence customarily observed seems to indicate that in those instances, the rate of reaction is limited by the rate of diffusion. The fact that the rate observed with potassium ferricyanide is less than with hypochlorite, indicates that a smaller concentration of the active oxidizing agent is produced in the former case. Recently,[6] there was reported an intense chemiluminescence in the oxidation of alkaline solutions of dimethyldiacridylium nitrate by hydrogen peroxide. The luminescent interval was shortened from hours to seconds and the light intensity increased considerably by the addition of a catalyst, osmium tetroxide, which decomposed the hydrogen peroxide. A similar result is obtained in the oxidation of sodium luminol by physical rather than chemical means.

Mechanism of Chemiluminescence

It seems fairly definitely established that sodium luminol plus hydrogen peroxide is the light-emitting molecule or its parent substance. The light-emitting molecule is brought to its energized state by reactions of the parent with some oxidizing substance. The relatively low quantum efficiency would then be explained by one or more of the following non-light producing processes: (a) simultaneous reactions of the reactants to form other substances; (b) reactions of the excited molecule with the oxidizing substance; (c) collisions "of the second kind" involving the excited molecules or the oxidizing substance. In addition, if transitions corresponding to the ultraviolet occur, the quantum efficiency is reduced, due to internal absorption.

Since the light-emitting process may consist of several steps, where the excited molecules do not fall directly to the ground level, it is difficult to draw conclusions concerning the energetics of the over-all reaction.

Summary

The oxidation of the sodium salt of 3-aminophthalhydrazide has been carried out under conditions to give a maximum light intensity. The quantum efficiency was found to be about 0.3%. Evidence for compound formation between hydrogen peroxide and the sodium salt has been presented. The mechanism of the chemiluminescence has been discussed.

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[6] Gleu and Petsch, *Z. angew. Chem.*, **48**, 57 (1935).