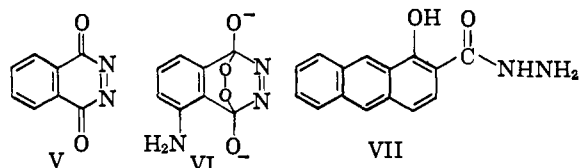


pression for the rate of photon emission becomes $(k_1 k_2 / k_{-1} [\text{H}_2\text{O}]) [\text{III}] [\text{OH}^-] [\text{O}_2] = k [\text{III}] [\text{OH}^-] [\text{O}_2]$. Experimentally, in the presence of an excess of base, and kept saturated with oxygen at 35° ($[\text{III}] \approx$ concentration of luminol = $4.0 \times 10^{-4} M$, $[\text{OH}^-] = 6.0 \times 10^{-2} M$, $[\text{O}_2] = 1.6 \times 10^{-3} M$), the reaction was strictly pseudo-first order, $k' = 2.5 \times 10^{-3} \text{ sec.}^{-1}$. Changing the concentration of luminol 10-fold, the concentration of base 40-fold, and the concentration of oxygen 10-fold (independently) showed that the reaction was first-order in each of these reactants.

Intermediates have not been detected to date (by e.p.r., for example) in the oxidation step (eq. 3), which proceeds at a reasonable rate even at -60° . An oxidation of dinegative ion IV to the azo state is unlikely since 1,4-phthalazinedione (V) is nonchemiluminescent under conditions which lead to the production of considerable light from phthalic hydrazide. Cyclic intermediates⁹ such as VI are attractive from the standpoint of visualizing the formation of nitrogen and the aminophthalate ion (II). We have found, however, that certain acyclic hydrazides such as 1-hydroxy-2-anthroic acid hydrazide (VII)¹⁰ are practically as



chemiluminescent as luminol (quantum yield = *ca.* $1/3$ that of luminol); cyclic adducts or intermediates, therefore, are not necessary features of the reaction. Evidence is being sought at present for multistep reaction paths which lead to the aminophthalate ion (II), the emitter of light in the chemiluminescence of luminol.⁵

(9) P. C. Wilhelmson, R. Lumry, and H. Eyring, "The Luminescence of Biological Systems," F. H. Johnson, Ed., American Association for the Advancement of Science, Washington, D. C., 1955, p. 96.

(10) We thank Mr. David F. Roswell for preparing this compound.

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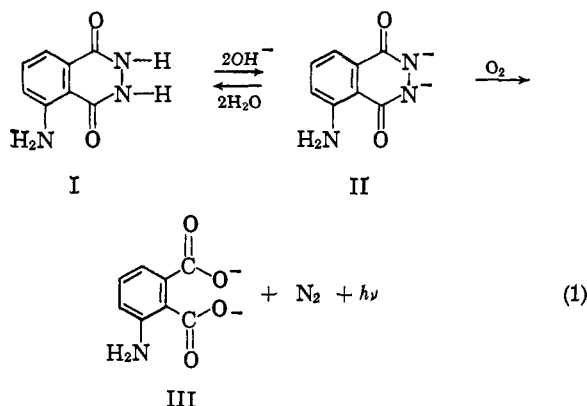
EMIL H. WHITE
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RECEIVED NOVEMBER 1, 1963

Chemiluminescence of Luminol and Related Hydrazides: The Light Emission Step

Sir:

The chemiluminescence of luminol (I) in relatively nonacidic solvents has been shown to involve the following chemical reactions.¹



(1) E. H. White, O. Zafriou, H. H. Kägi, and J. H. M. Hill, *J. Am. Chem. Soc.*, **86**, 940 (1964).

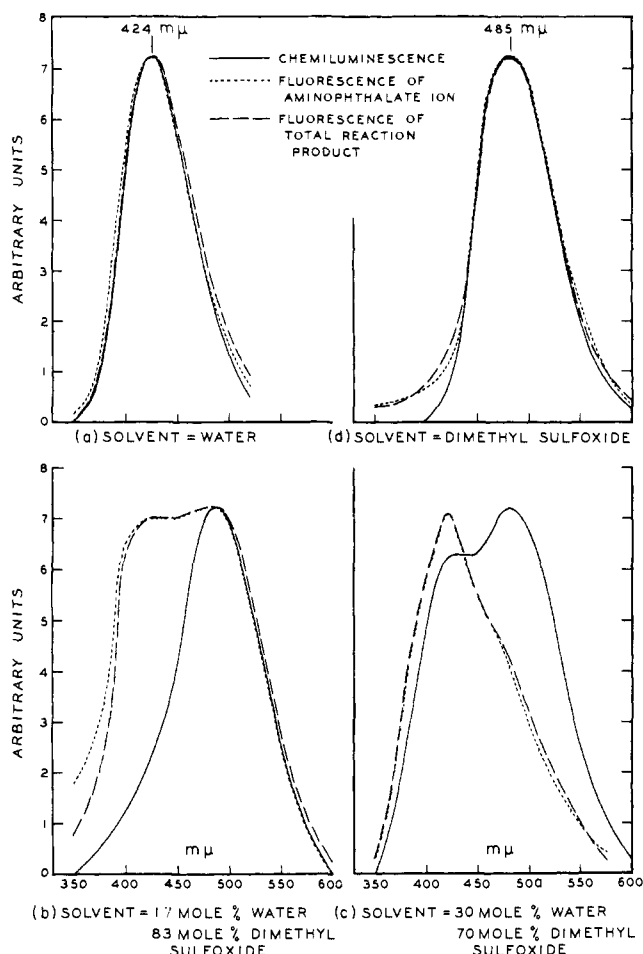


Fig. 1.—Fluorescence and chemiluminescence emission spectra.

In this communication, we will consider the production of light in the reaction and show that the aminophthalate ion (III) is the light emitting species.

In the chemiluminescence of liquid solutions, the conversion of chemical energy into light energy involves the formation of a reactant, intermediate, or product molecule in an excited electronic state (directly or by energy transfer), and the emission of a photon by that species.² Since excited states are also reached by the absorption of light, it should be possible to correlate the wave length distribution in chemiluminescence with that in phosphorescence, if a triplet state were the emitter, or in fluorescence,^{3a} if a singlet state were involved.

In the chemiluminescence of luminol in dimethyl sulfoxide and also in water,⁴ a good match has been found for the wave length distribution in chemiluminescence, the fluorescence of the total reaction product, and the fluorescence of sodium aminophthalate (Fig. 1a and d). In mixtures of dimethyl sulfoxide and water (or other protic solvents), furthermore, a double emission occurs in *both* chemiluminescence and fluorescence (Fig. 1b and c), with peak positions unchanged from the values in the pure solvents. The occurrence of two emission peaks is attributed to the formation of two different kinds of excited state molecules: an excited aminophthalate ion hydrogen bonded to water—

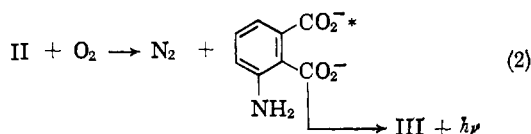
(2) Certain of these steps have been established for gas phase reactions: (a) M. G. Evans, and M. Polanyi, *Trans. Faraday Soc.*, **35**, 178, (1939), also pp. 185-226; (b) M. G. Evans, H. Eyring, and J. F. Kincaid, *J. Chem. Phys.*, **6**, 349 (1938); (c) F. Kaufman and J. R. Kelso, *ibid.*, **27**, 1209 (1957).

(3) "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961: (a) H. Linschitz, p. 173; (b) E. H. White, p. 183.

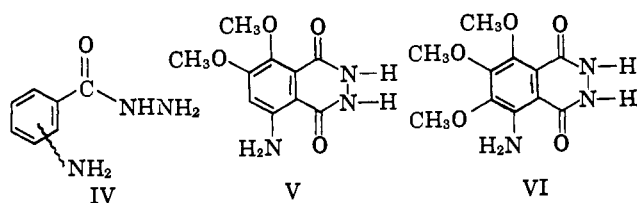
(4) The system used was luminol, NH_3 , H_2O_2 , and Cu^{++} (at 0°) (see ref. 3b, for the mechanism in water solutions); see also H. Seliger in ref. 3.

or protonated fully⁵—(emitting at 424 m μ), and an excited aminophthalate ion not bonded in this way (emitting at 485 m μ). As water is added to a dimethyl sulfoxide system, the chemiluminescence peak at 424 m μ develops at a slower rate than the fluorescence peak at 424 m μ (Fig. 1). This effect is not understood at present; it may be the result of emission of the aminophthalate ion from slightly different solvent cages in the two excitation pathways (*vide infra*), possibly as the result of the involvement of nitrogen in only the chemiluminescence pathway.¹ Similar fluorescence data have been obtained for three other phthalic hydrazides. Related experiments eliminate from consideration as possible light emitters in the reaction compounds such as aminophthalic anhydride, luminol, and sodium aminobenzoate.

The main steps in the chemiluminescence of luminol are then the reaction of the dinegative ion of luminol with oxygen to yield, ultimately, an excited singlet state of the aminophthalate ion, and the emission of a photon by this species. This view of the chemiluminescence is supported by the fact that a parallelism



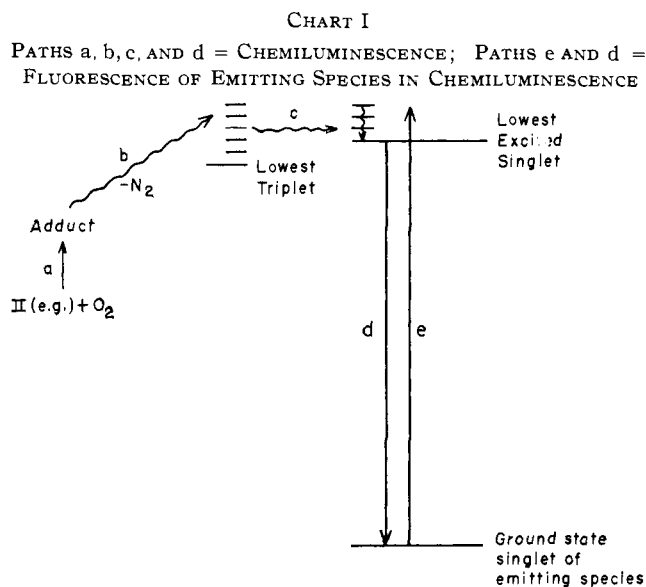
exists between the efficiencies of fluorescence of a number of aromatic acid anions and the chemiluminescent efficiencies of the corresponding hydrazides. Thus, the *o*- and *m*-aminobenzhydrazides (IV) are chemiluminescent (in dry dimethyl sulfoxide with potassium *t*-butoxide and oxygen) and the *o*- and *m*-aminobenzoates are fluorescent; the corresponding *para* derivatives, however, are neither chemiluminescent nor fluorescent in the visible region. Similar trends are noted in the hydroxybenzhydrazide series. In general, electron-supplying substituents increase the efficiency of emission in both chemiluminescence and fluorescence.⁶ Both compounds V and VI, to illustrate the point, are more efficient in chemiluminescence than luminol (by 13 and 30%, respectively, in dimethyl sulfoxide). Only these two compounds and a third reported by Gundermann and Drawert⁷ have been found to date to be more efficient than luminol in light production.



The quantum yield for the chemiluminescence of luminol in dimethyl sulfoxide is about 5%; this is the highest quantum yield yet measured for a chemiluminescent reaction.⁸ Since the fluorescence yield of the aminophthalate ion is about 5–10%,⁸ it is apparent that 50% or more of the luminol molecules yield aminophthalate ions in the excited state.

The precise mechanism of formation of excited state species from ground state molecules in solution at room temperature (eq. 2) is unknown. The only clue is that molecular oxygen is a reactant or product in

most, if not in all, chemiluminescent reactions.^{3b,9} Since oxygen is in a triplet ground state, adducts of oxygen may exist as triplet state complexes or diradicals.¹⁰ Loss of nitrogen from the adduct (or the gain of energy by some other process in the general case) could lead to a vibrationally excited triplet state of the potential emitter. Intersystem crossing to an isoenergetic level of the excited singlet state and emission of a photon would then complete the process (Chart I).^{11,12}



The light emitted in the chemiluminescence of luminol (*ca.* 350 to 600 m μ) has an energy equivalence of *ca.* 50 to 80 kcal. per mole. Generalizing from our results and examples in the literature, it seems probable that most exergonic reactions¹³ yielding fluorescent products and involving oxygen will be chemiluminescent.

Acknowledgment.—We thank the National Institutes of Health for its support of this work (Grant No. 10849), and Dr. Charles P. Kulier for valued assistance.

(9) See review articles listed previously.¹ For exceptions in bioluminescence, see J. W. Hastings and Q. H. Gibson, *J. Biol. Chem.*, **238**, 2537 (1963).

(10) D. Kearns and S. Ehrenson [*J. Am. Chem. Soc.*, **84**, 739 (1962)] have proposed that Yang's diradical [N. C. Yang and A. J. Castro, *ibid.*, **82**, 6208 (1960)] has a triplet ground state.

(11) The reverse process is well established [D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949)] often proceeding with high efficiency [H. L. J. Bäckström and K. Sandros, *ibid.*, **23**, 2197 (1955); W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961)]. Triplet states are efficiently quenched by oxygen [H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958)]; a delayed fluorescence type of luminescence from the ground vibrational level of the triplet state [C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, **67**, 1894 (1961)] seems unlikely, then, in chemiluminescence. See also ref. 2b and E. Chandross, *Tetrahedron Letters*, 761 (1963). The direct formation of an excited singlet state is, of course, possible; the virtual necessity of oxygen is not then apparent, however.

(12) Sodium aminophthalate is strongly phosphorescent at low temperatures.

(13) H. Eyring, "The Luminescence of Biological Systems," F. H. Johnson, Ed., American Association for the Advancement of Science, Washington, D. C., 1955, p. 244.

(14) National Science Foundation Cooperative Graduate Fellow, 1960–1963.

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MAURICE M. BURSEY¹⁴

RECEIVED NOVEMBER 1, 1963

Synthesis of a Methylene-cyclopropane

Sir:

The number of aromatic cyclopropenium compounds isolated in stable form over the past 6 years has steadily increased since Breslow's initial preparation of the

(5) Th. Förster, "Photochemistry in the Liquid and Solid States," L. J. Heidt, et al., Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 10.

(6) H. D. K. Drew and F. H. Pearson, *J. Chem. Soc.*, 586 (1937); A. Spruit-van der Berg, *Rec. trav. chim.*, **69**, 1536 (1950).

(7) K. D. Gundermann and M. Drawert, *Chem. Ber.*, **95**, 2018 (1962).

(8) Unpublished work by Professor H. H. Seliger and Dr. J. Lee, Department of Biology, The Johns Hopkins University.