

(+10%) by isopiestic osmometry<sup>14</sup> on 0.56 and 0.71 *M* solutions.

If differences in kinetic and zero point energies between **1** and **2** are considered to be small, the differences in enthalpies in Table I ( $\Delta H_{\text{isom}}$ ) can be taken to reflect differences in chemical binding energies, energies of specific complexation by the solvent and/or more general solvent effects. Differences in heats of solution of the solvents in ethanol have been eliminated by the procedure used to obtain the heats of hydrolysis (*vide supra*). The 8.3 kcal/mol lower enthalpy of **1** with respect to **2** in di-*n*-butyl ether is consistent with intramolecular association of lithium and oxygen<sup>2,3</sup> although for the present case it clearly must be an effect in a dimeric species and a contribution by an inductive effect is possible.<sup>15</sup> It is also consistent with such an effect that this difference is reduced to  $2.8 \pm 0.9$  kcal/mol in tetramethylethylenediamine a solvent which effectively coordinates with lithium, although the comparison may be tenuous since the state of aggregation of the aryllithiums in TMEDA is not known. The magnitude of differences in specific complexation of isomeric aryllithiums by a common solvent cannot be estimated as yet but it should be noted that total heats of complexation of 2–6 kcal/mol are observed by Quirk for the interaction of different bases with alkyllithiums.<sup>16</sup>

Further speculation about differences in enthalpies will be deferred until more thermodynamic data about isomeric organometallics is available. The present approach should prove exceptionally useful in the acquisition of such information.<sup>17</sup>

(14) The apparatus was constructed by T. L. Brown and colleagues. A MKS Baratron Type 90 is used for the direct measurement of the differential pressure. See J. W. Roddy and C. F. Colman, *J. Inorg. Nucl. Chem.*, **32**, 3891 (1970), for a similar apparatus.

(15) That the contribution of any inductive effect to the enthalpies may be small, is indicated by the lack of a significant difference in the heats of hydrolysis of *m*- and *p*-lithioanisoles.<sup>12</sup>

(16) R. P. Quirk, private communication, Aug 1974.

(17) We are grateful to the National Science Foundation for support of this work, to Professor T. L. Brown for access to the Baratron and to Professor R. P. Quirk for prepublication information.

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### A Striking Deuterium Effect in Phosphorus Chemiluminescence. Identification of the Emitting Species

Sir:

Under conditions similar to naturally occurring phosphorus chemiluminescence,<sup>1</sup> a substitution of deuterium oxide for water in the reaction of phosphorus, molecular oxygen, and water was undertaken in our laboratory, and a marked frequency shift and changes in the intensity distribution were observed in the chemiluminescence spectrum. Comparative analysis of the spectra identifies the major emitters in the visible region as  $(\text{PO})_2^*$  excimer and HPO. In the ultraviolet we confirm the finding of Rumpf<sup>2</sup> that the major emitting species is PO, and, in the assignment of PO  $\gamma$  (a) and weak PO  $\beta$  bands (b), we also concur with Walsh.<sup>3</sup>

(1) See E. N. Harvey, "A History of Luminescence," The American Philosophical Society, Philadelphia, Pa., 1957.

(2) K. Rumpf, *Z. Phys. Chem., Abt. B*, **38**, 469 (1938).

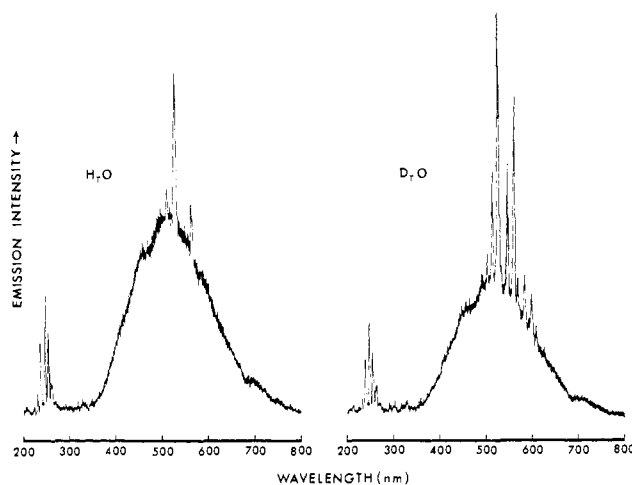
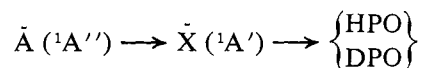


Figure 1. Chemiluminescence spectra of phosphorus. Left-hand side chemiluminescence due to the reaction of phosphorus,  $\text{H}_2\text{O}$ , and  $\text{O}_2$ . Right-hand side chemiluminescence due to the reaction of phosphorus,  $\text{D}_2\text{O}$ , and  $\text{O}_2$ .

Based on our experiments, our tentative assignments are: (a) 228.8–272.1 nm PO  $\gamma$  system ( $\text{A } ^2\Sigma \rightarrow \text{X } ^2\Pi$ ), (b) 325.0–337.0 nm PO  $\beta$  system ( $\text{B } ^2\Sigma \rightarrow \text{X } ^2\Pi$ ), (c) 335.0–800 (possibly to 1250) nm; diffuse band system, excimer emission

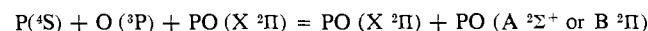


(d) 450.0–650.0 nm; discrete band system<sup>4–6</sup>



The phosphorus (Baker) source was a 50-ml glass flask immersed in a water bath (57°). Nitrogen (Airco) saturated with  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  (Columbia, 99.5%) at room temperature was passed through a flask into a 3-mm glass tube. Chemiluminescence occurred at the end of the tube, with air being used as the source of molecular oxygen. A 0.3-m McPherson Model 218 monochromator with an EMI 9558 QB photomultiplier, an Eldorado Model 201 universal photometer, and a Sargent Model TR recorder were used to obtain the spectra.

In Figure 1 the continuum which produces most of the visible green color starts at around 335.0 nm and extends to 800 nm. (In a different experiment performed only with  $\text{H}_2\text{O}$  and using a RCA 7102 photomultiplier and a Warner Swasey scanning monochromator coupled to a Nicolet 1074 signal averager, the continuum extends to 1250.0 nm). We are tentatively suggesting that this emission originates from  $(\text{PO})_2^*$  excimer,<sup>7</sup> based on the following considerations. (1) The Walsh<sup>3</sup> excitation mechanism proposed to explain the PO  $\beta$  and  $\gamma$  band emission is



(3) A. D. Walsh in "The Threshold of Space," M. Zelikoff, Ed., Pergamon Press, London, 1957, p 165.

(4) M. Lam Thanh and M. Peyron, *J. Chim. Phys. Physicochim. Biol.*, **60**, 1289 (1963).

(5) M. Lam Thanh and M. Peyron, *J. Chim. Phys. Physicochim. Biol.*, **63**, 266 (1966).

(6) See G. Herzberg, "Molecular Spectra and Molecular Structure, III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand, New York, N. Y., 1966.

(7) For a general discussion on excimer see J. B. Birks, "Photo-physics," Wiley-Interscience, New York, N. Y., 1970.

This mechanism would perforce generate an electronically excited PO\* in the close proximity of a ground state PO, an ideal situation for excimer formation. (2) The overall spectral characteristics—a discreet band juxtaposed to a broad diffuse band on the longer wavelength side—are strongly indicative of excimer formation. Since an excimer has a bound excited electronic state and a dissociative ground state, the excimer emission is diffuse and red shifted from the monomer emission. (3) In the chemiluminescent reaction we observe an isotope effect on the kinetics of the luminescence reactions, in which emission from PO  $\gamma$  falls to 84% of its original value, and the intensity of the continuum decreases to 70%. The kinetic dependence is currently under investigation.

The discrete visible bands show the most marked deuterium effect. The few weak bands seen with H<sub>2</sub>O are increased in intensity by a factor of 5 in D<sub>2</sub>O and a number of new bands are seen. Unlike the PO bands which do not exhibit frequency shift, the most intense band at 525.5 nm (19,030 cm<sup>-1</sup>) is shifted to 523.5 nm (19,100 cm<sup>-1</sup>) and other bands are similarly shifted to the blue (see Table I). The characteristic frequency

Table I

	HPO ( $\nu_1'\nu_2'\nu_3'$ ) → ( $\nu_1''\nu_2''\nu_3''$ )	DPO ( $\nu_1'\nu_2'\nu_3'$ ) → ( $\nu_1''\nu_2''\nu_3''$ )
Lam Thanh and Peyron <sup>4,5</sup>	(000) → (010) 17,860 cm <sup>-1</sup> (559.91 nm)	(000) → (010) 17,931 cm <sup>-1</sup> (557.69 nm)
This work	17,850 cm <sup>-1</sup> (560.2 nm)	17,930 cm <sup>-1</sup> (557.8 nm)
Most intense transition Lam Thanh and Peyron <sup>4,5</sup>	(000) → (000) 19,047 cm <sup>-1</sup> (525.01 nm)	(000) → (000) 19,116 cm <sup>-1</sup> (523.12 nm)
This work	19,030 cm <sup>-1</sup> (525.5 nm)	19,100 cm <sup>-1</sup> (523.5 nm)

shift due to isotopic substitution indicates the species has H covalently bound (d). In an electric discharge investigation of the Ludlam<sup>8</sup> bands associated with the burning of phosphorus in hydrogen, Lam Thanh and Peyron<sup>4</sup> attributed similar bands to HPO and DPO (d). The increase in the emission intensity of DPO compared to HPO can be understood in terms of decrease in the Franck-Condon factors in substituting D<sub>2</sub>O for H<sub>2</sub>O and the consequent decrease in the radiationless transitions.<sup>9</sup> An interpretation of this phenomenon would possibly be similar to the case of pre-dissociative HNO.<sup>10</sup>

Currently we are investigating kinetic aspects of the excimer emission and are attempting to clarify the assignments associated with some weak lines in the ultraviolet. Since the essential features of the emitting species have now been established, it should be possible to understand the detailed nature of the oldest known chemiluminescence system.

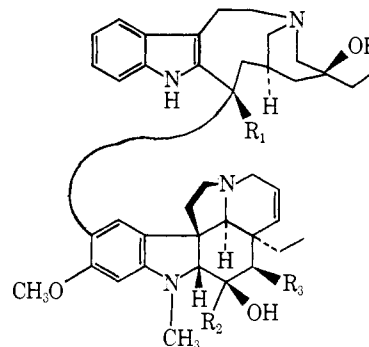
(8) E. B. Ludlam, *J. Chem. Phys.*, **3**, 617 (1935).(9) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); **38**, 1187 (1963).(10) M. J. Y. Clement and D. A. Ramsay, *Can. J. Phys.*, **39**, 205 (1961).

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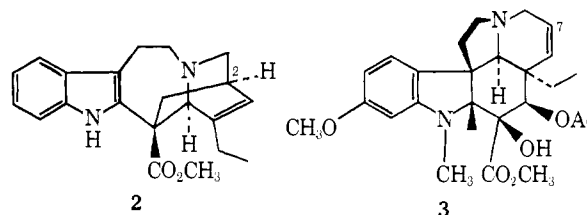
## Biosynthesis of the Dimeric Indole Alkaloids. Vincaleukoblastine<sup>1</sup>

Sir:

Although the biosynthetic pathway(s) for the three main structural variants of the indole alkaloids found in *Vinca rosea* L. (*Catharanthus roseus* G. Don) is rather well understood,<sup>2</sup> the details of the bioorganic chemistry leading to vincaleukoblastine (VLB), **1a**, and other



**1a**, R<sub>1</sub> = COOCH<sub>3</sub>; R<sub>2</sub> = COOCH<sub>3</sub>; R<sub>3</sub> = OAc  
**1b**, R<sub>1</sub> = H; R<sub>2</sub> = CONHNH<sub>2</sub>; R<sub>3</sub> = OH



dimeric alkaloids found in this plant<sup>2</sup> are only presumptive. Because of the obvious structural similarity between catharanthine (**2**), vindoline (**3**), and VLB, the biogenesis of **1a** can be assumed to occur *via* a direct dimerization of **2** and **3**, or closely related alkaloids. Experimental corroboration of such a hypothesis has never been reported in the literature, although suitable experiments have been carried out in other laboratories.<sup>3</sup> We now report experimental results that can be viewed as a substantiation of a dimerization hypothesis, although nothing can be said from consideration of them about the precise bioorganic details of VLB's biosynthesis.

The report of Scott, *et al.*,<sup>4</sup> describing results from feeding experiments with (5RS)-[5-<sup>3</sup>H<sub>2</sub>]- and (5S)-[5-<sup>3</sup>H<sub>1</sub>]mevalonic acid, and the preliminary data of Battersby, *et al.*,<sup>5</sup> derived from feeding experiments with [3,6-<sup>3</sup>H<sub>3</sub>;CH<sub>3</sub>O-<sup>14</sup>C]loganin (**4**), both are in accord with an *apparently* stereospecific tritium retention in the biosynthesis of **2** and **3**.<sup>6</sup> For these reasons, the doubly

(1) Supported in part by a grant from the National Institutes of Health (CA 13616).

(2) R. J. Parry in "The *Catharanthus* Alkaloids: Botany, Chemistry, and Pharmacology," W. I. Taylor and N. R. Farnsworth, Ed., Marcel Dekker, New York, N. Y., in press.

(3) (a) Professor E. Leete, personal communication; (b) Professor A. I. Scott, Dr. J. D. Michael, and Dr. C. L. Yeh, personal communication.

(4) A. I. Scott, P. B. Reichardt, M. B. Slaytor, and J. G. Sweeny, *Recent Advan. Phytochem.* **6**, 138 (1973).

(5) A. R. Battersby, C. R. Hutchinson, N. D. Westcott, and R. A. Larson, manuscript in preparation. Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., 1972, Abstracts ORGN 11.

(6) The stereospecific retention of the 5S tritium of mevalonate and the 6 *pro R* tritium of **4** on their incorporation into **2** and the 6 *pro S* tritium of **4** on its incorporation into **3** *must* be viewed only as the most likely of several alternatives,<sup>4</sup> due to the lack of or as yet incomplete chemical degradation of the resulting radioactive **2** and **3** obtained by these investigators.