

methanol in the temperature region near the condensation point. Preliminary measured  $\Delta H$  values for each member in the series of reaction (1) at 100 Torr are as follows: ( $n, n - 1$  in parenthesis): (2,1) 4.6 kcal/mole; (3,2) 2.0 kcal/mole; (4,3) 1.1 kcal/mole, and (5,4) 0.4 kcal/mole. These values must remain tentative until the contribution from additional clustering in the beam expansion and other contributions to cluster intensity can be explored.

Cluster formation with carbon dioxide as sample gas appears to be dominated by growth in the molecular beam expansion jet. At very short nozzle-skimmer (NS) distances (of the order of 2 nozzle diameters), essentially no  $\text{CO}_2$  dimer intensity is observed. Under relatively severe expansion conditions (320 Torr  $\text{CO}_2$  pressure,  $-40^\circ\text{C}$  nozzle temperature, NS distance = 23 nozzle diameters) cluster ions corresponding to  $(\text{CO}_2)_n^+$  with  $1 \leq n \leq 20$  are observed, with the upper limit defined by our maximum mass spectrometer scan range. The photoionization efficiency curve of  $\text{CO}_2$  dimer,  $m/e$  88, taken under molecular beam conditions such that only the dimer is produced shows that the onset of ionization is shifted 0.37 eV lower than the onset of the molecular ion with substantial broadening of the autoionization structure in the spectrum. Only three broad autoionizing peaks in the 700 - 800 Å region of the  $m/e$  88 photoionization efficiency curve were observed, and these peaks could be fit to a Rydberg series with a limit of 18.04 eV, slightly lower than the 18.07 eV energy of the  $B^2\Sigma_u^+$  state in  $\text{CO}_2^+$ . These features may provide insight into the structure of the dimer. Finally, the photoionization efficiency curves of  $m/e$  88 taken at higher photon energies than 14 eV and under molecular beam conditions which produce significant amounts of higher polymers shows strong evidence of higher cluster ion fragmentation enhancing the  $m/e$  38 intensity.

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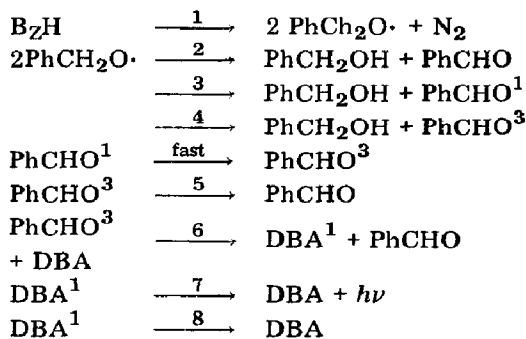
## Chemiluminescence from Alkyl Hyponitrite Decomposition

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Chemiluminescence was observed from solutions of dibenzyl hyponitrite and 2-pentyl hyponitrite at  $25 - 70^\circ\text{C}$ . At  $53.5 \pm 0.3^\circ\text{C}$  in benzene, the rate constant for decay of chemiluminescence from dibenzyl hyponitrite below about 0.03 M was  $(7.9 \pm 0.4) \times 10^{-4} \text{ s}^{-1}$ , alone and in the presence of 0.00027, 0.0027, or 0.026 M 9,10-dibromoanthracene (DBA) as a luminescence enhancer. At higher concentrations of benzyl hyponitrite the decay occurred at an accelerated rate, which is presumably associated with an induced decomposition. [1] In carbon tetrachloride and with 0.026 M 9,10-dibromoanthracene, the initial light intensity from 0.010 M dibenzyl hyponitrite was about 2.5 fold greater than in benzene, although the same rate constant for decay was observed ( $7.9 \times 10^{-4} \text{ s}^{-1}$  at  $53.3^\circ\text{C}$ ).

The following kinetic scheme and equations were assumed:

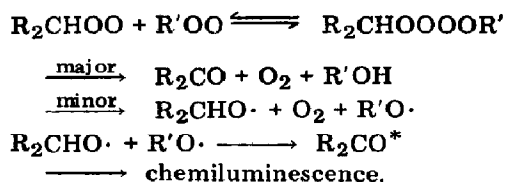


$$I = \frac{dh\nu}{dt} = \frac{k_1 k_6 k_7 [\text{DBA}]}{(k_6 + k_7)(k_3 + k_4)} \times \frac{[\text{B}_2\text{H}]}{(k_2 + k_3 + k_4)(k_5 + k_6 (\text{DBA}))}$$

A plot of  $I$  vs.  $[\text{B}_2\text{H}]$  in the presence of 0.027 M DBA could be represented by a straight line that intersected the origin and data points up to 0.03 M in  $\text{B}_2\text{H}$ .

Our observations are consistent with, but do not demand the hypothesis that the very weak chemiluminescence associated with auto-

oxidation processes [2, 3] arises from a relatively efficient production of excited states from alkoxy radical disproportionations. Such alkoxy radicals can arise in low concentrations from non-Russell termination pathways of dialkyl tetroxides:



- 1 S. K. Ho and J. B. DeSousa, *J. Chem. Soc.*, 1788 (1961).
- 2 R. F. Vasil'ev, *Progress in Reaction Kinetics*, 4 (1967) 305 and references therein.
- 3 G. Lundeen and R. L. Livingston, *Photochem. Photobiol.*, 4 (1965) 1085.

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#### Major Emitting Species in Phosphorus Chemiluminescence

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The phosphorescence of phosphorus oxidation is the oldest and the best known chemiluminescing reaction, but a definitive spectroscopic study of this classic system has been lacking. In this talk we report the results of an investigation of the oxidation of P<sub>4</sub> vapor under atmospheric conditions, with added H<sub>2</sub>O or D<sub>2</sub>O vapor. The visible and ultraviolet spectrum of the reaction consists of discrete band structure in the 228.8 - 272.1 nm region and a broad continuum onseting at 335 nm and extending to 800 nm and longer, upon which are superimposed a number of weak bands from 450 - 650 nm. Discrete band emissions at 228.8 - 272.1 nm belong to the PO  $\gamma$ -system transitions, PO(A<sup>2</sup> $\Sigma^+$ )  $\rightarrow$  PO(X<sup>2</sup> $\Pi$ ). Spectral changes arising from the substitution of D<sub>2</sub>O vapor for H<sub>2</sub>O vapor in the reaction led to the assignment of the weak bands at 450 - 650 nm to HPO (or DPO),  $\tilde{A}(^1A')$   $\rightarrow$   $\tilde{X}(^1A)$ . The main band emission in the visible region, the broad continuum which cannot be identified with any simple electronic transition, exhibits the kinetic and spectral characteristics of an excimer.

In this case the excimer is (PO\*...PO) and the equilibrium reaction for its formation is (PO\*...PO)  $\rightleftharpoons$  PO(<sup>4</sup> $\Pi$ ) + PO(B<sup>2</sup> $\Pi$ )  $\rightleftharpoons$  PO(B<sup>2</sup> $\Sigma^+$ ) + PO(X<sup>2</sup> $\Pi$ ). The existence of the (PO)<sub>2</sub> excimer has been confirmed by affecting the dynamic of this equilibrium through dilution with nitrogen gas and through thermal dissociation of the excimer, resulting in the appearance of the formerly quenched (0,0) transition of the PO  $\beta$ -emission in the spectrum. Our investigation has eliminated the possibility that the visible continuum arises from either PO<sub>2</sub> or HOPO. Enough information has been extracted from temperature dependent studies to construct the approximate shapes of the potential energy surfaces of the ground ( $\Delta\bar{\nu}_g = 35 \pm 200 \text{ cm}^{-1}$ ) and the first excited states ( $\Delta\bar{\nu}_{ex} = 846 \pm 200 \text{ cm}^{-1}$ ) of the (PO)<sub>2</sub>\* excimer.

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#### The Quantum Yield of Fluorescence of Quinine Bisulphate, Azulene and 9,10-Diphenylanthracene

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The quantum yield of fluorescence of quinine bisulphate (in 1N H<sub>2</sub>SO<sub>4</sub>) has been determined by an absolute method involving the rise in temperature of a solution due to light energy absorbed but not emitted as luminescence. Quinine bisulphate (in 1 N H<sub>2</sub>SO<sub>4</sub>) and potassium chromate (in 0.05 M KOH) were compared. A measured quantity of electrical energy ( $E_q$  and  $E_k$ , respectively) was put into the systems so that the heating (and cooling) curves were made to coincide. A 366 nm interference filter (100 Å band pass and blocking to infinity) was utilized in connection with a 500 W high-pressure mercury arc. Temperature changes were monitored with a potted glass-bead thermistor in conjunction with a Jones impedance bridge, operating in the A.C. mode, and a lock-in amplifier at 4000 Hz (100  $\mu$ V sensitivity and 300 ms time constant). At 25.00 °C the temperature coefficient was 760  $\Omega \text{ deg}^{-1}$  while solution temperature fluctuations were about 0.10  $\Omega$ , and total changes over a 500 s experiment were about 100  $\Omega$ .