microanalysis. The reaction behavior of **3** toward alkyl halides and acetylenes is quite akin to those of some Co(II) complexes.[11,12,14-16] While the reactions of olefins with divalent cobalt complexes had not given unambiguous results, the generation of a metal-carbon bond has been effected in the case of divalent rhodium porphyrin as noted above. Further studies on the properties of OEPRh(III)-H and $[\mathrm{OEPRh^{II}}]_2$ are in progress.

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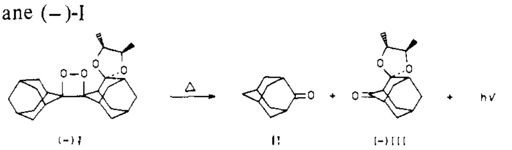
The Detection of Optical Activity in Chemiluminescence

Sir:

We have reported,[1] that the optically active dioxetane (−)-I shows chemiluminescence as a result of the reaction shown:

Scheme I. Thermal Decomposition of the Optically Active 1,2-Dioxetane (−)-I



In this equation *hν* represents emission from the ketones II and (−)-III. Since one of the emitting species is chiral, one expects the luminescence of this system to be circularly polarized. We have now succeeded in measuring this circular polarization of luminescence (CPL).

The light induced CPL[2] and chemically induced CPL are obviously closely related, the latter differing—inter alia—in the manner in which the excited state is obtained. When optically active dioxetane (−)-I[1] (4 mg in 1 mL of dodecane) was injected into a specially constructed cell[3a] maintained at a temperature close to 197 °C, light was emitted for about 10 min.

In a series of measurements reproducible data were obtained; some of these are depicted in Figures 1 and 2. Figure 1 shows the chemiluminescence as a function of wavelength.[3b] It appears that the spectrum is characteristic of ketone fluorescence.[2f] Apparently under these experimental conditions phosphorescent processes are effectively quenched. In Figure 2 two curves are shown. Curve A measures the total intensity of the chemiluminescence as a function of time. After injection of the solution at $t = 0$ the intensity grows until thermal equilibrium is reached; afterwards curve A represents the decay curve of the chemiluminescence at temperature T. As expected for the unimolecular decomposition of 1,2-dioxetanes this curve obeys first-order kinetics. The second curve (B) represents the circular anisotropy ΔI of the chemiluminescence as a function of time,[3c] measured in an apparatus described earlier.[4] The nonzero value of ΔI in the chemiluminescence is prima facie evidence for chirality in the emitting species and represents to our knowledge the first measurement of this kind. A useful parameter to describe optical activity in emission is the dissymmetry factor which equals the ratio of $\Delta I = I_L - I_R$ to the average intensity $I = \frac{1}{2}(I_L + I_R)$, i.e., $g_{\text{chemlum}} = \Delta I/I$. From several experiments we find $g_{\text{chemlum}} = +(3 \pm 1) \times 10^{-3}$. Lacking the experimental g_{lum} value for the light-induced CPL of pure (−)-III,[5] an estimated value for the chemically induced CPL may be derived as follows. Previous work[2f] indicates that in a series of ketones g_{lum} is roughly a factor 5 smaller than g_{abs}, the dissymmetry factor in the n → π* absorption band.[6] We now make two assumptions: the factor 1/5 also applies to the $g_{\text{lum}}/g_{\text{abs}}$ ratio of ketone (−)-III; and the ratio of excited states of the emitting species II/(−)-III is about 1/1. Based on these assumptions g_{chemlum} is expected to be $\frac{1}{10}g_{\text{abs}} = +4 \times 10^{-3}$. This is in qualitative agreement with the observed value $+(3 \pm 1) \times 10^{-3}$.

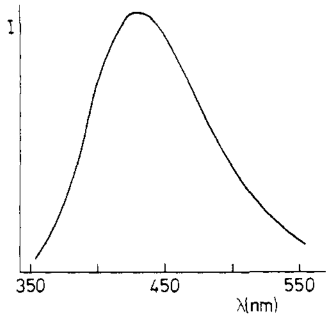


Figure 1. Luminescence spectrum from the thermal decomposition of (−)-I.

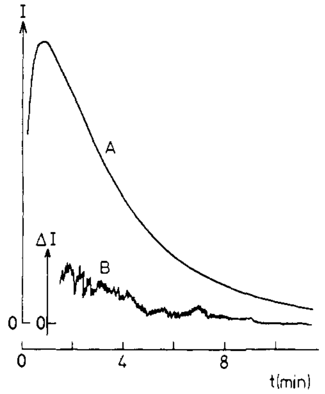


Figure 2. A, Decay curve of chemiluminescence of (−)-I. Intensity in arbitrary units. B, Circular anisotropy, ΔI, of the chemiluminescence as a function of time, ΔI in arbitrary units. Both curves measured over entire band width.

This successful measurement represents only a first step in the investigation of circular polarization of chemiluminescence of this and related systems. It is evident that an area of excited state geometry[2g] and mechanism is now open to study using this new tool. Novel may also be the implication of our observation on model system I to similar phenomena in nature. No mention of the possibility that bioluminescence might be circularly polarized appears in the literature. The existence of a new dimension in animal communication cannot be excluded.[8,9]

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(3) (a) In order to perform the chemiluminescence experiments at temperature *T* a cell was constructed to meet three main requirements: (i) sample should reach temperature *T* rapidly, (ii) *T* must be constant during the measurement, (iii) large optical aperture. Essentially the cell consists of a massive copper block, electrically heated, containing a small cylindrical hole covered with a suprasil plate. After the cell is brought slowly to temperature *T*, the sample is injected. (b) Detection system: monochromator (Spex Minimate), bandwidth 5 nm; photomultiplier (EMI 6256B). (c) Average of the measurements. Time constant 30 s. To exclude artifacts, it was verified that ΔI is zero in the chemiluminescence of the optically inactive adamantylideneadamantane-1,2-dioxetane: J. H. Wieringa, J. Strating, H. Wynberg and W. Adams, *Tetrahedron Lett.*, 169 (1972).

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(5) The quantities of (−)-III isolated after decomposition of the 1,2-dioxetane (−)-I were too small to allow an accurate measurement of light induced CPL at this time. These data will be reported in a subsequent publication. We have previously completely identified (−)-III.[1]

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Direct Measurement of the Lifetimes of the $^3B_1$ State of Sulfur Dioxide in Air at Atmospheric Pressure

Sir:

To date, the lifetime and rates of quenching of SO_2 phosphorescence by various gases have been measured at pressures lower than 20 Torr.[1-5] It has generally been assumed that a linear, Stern–Volmer, extrapolation of the low pressure data would yield reasonable values for the quenching of the triplet SO_2 species under atmospheric conditions. We report here direct measurements of the lifetimes of SO_2 phosphorescence in air which show that the lifetime of the $^3B_1$ state is longer than expected from extrapolation of low pressure data to atmospheric conditions.

The lifetimes were measured using a single photon counting instrument. The details of the apparatus are described elsewhere.[6] Excitation was into the excited singlet state of SO_2 at 3159 Å. The phosphorescence emission was isolated from scattered exciting light and cell emission by an interference filter. Emission spectra obtained over the pressure range of lifetime measurements were found to be identical with those previously attributed[2] to the $^3B_1$ state of SO_2.

Low intensity prohibited the measurement of accurate lifetimes in air for SO_2 pressures below 20 Torr. This necessitated obtaining data as a function of SO_2 pressure to permit an extrapolation to the low pressures of SO_2 which are of atmospheric interest. One set of experiments involved a constant 760 ± 10 Torr of dried laboratory air, a second set involved 745 ± 10 Torr of dried air with 15 Torr of water vapor added, and a third set involved 600 ± 10 Torr of dried laboratory air. In each of the above the SO_2 pressure was varied between 20 and 300 Torr. In a final set of experiments the water vapor pressure was varied from 0 to 20 Torr while the SO_2 pressure was maintained at 130 Torr and the pressure of dried air was maintained at 760 ± 10 Torr. In all cases the laboratory air was dried by passage through a dry ice trap. The pressure and lifetime measurements were made at temperatures of 24 ± 2 °C.

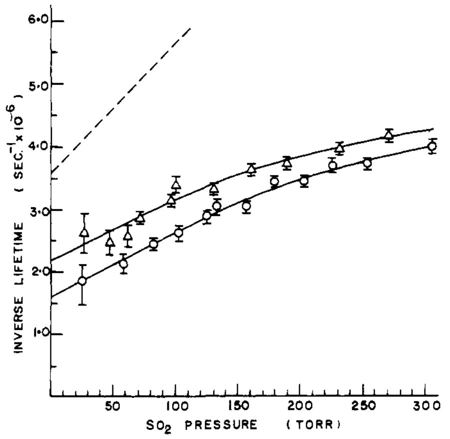

Figure 1. Phosphorescence decay rate of SO_2 in air. Circles are in 760 Torr of dry air; triangles are in 745 Torr dry air plus 15 Torr of water vapor. The dashed line shows values calculated from low pressure rate constants.[5]

The rates of phosphorescence decay are plotted as a function of SO_2 pressure for the first two sets of data in Figure 1. The extrapolated low pressure SO_2 phosphorescent lifetime in 760 Torr of dry air is $(6.3 \pm 0.3) \times 10^{-7}$ s, and the lifetime in 760 Torr of air containing 15 Torr of water vapor is $(4.5 \pm 0.3) \times 10^{-7}$ s. For comparison, the dashed line shows the decay rates calculated for 760 Torr of dry air by extrapolation of the low pressure data of Calvert and co-workers[5] assuming Stern–Volmer behavior. Clearly, the observed lifetime is about twice as long as would be expected from low pressure data.

For the sake of clarity, the last two sets of data are not included in Figure 1. The decay rates in 600 Torr of dry air are uniformly slightly lower than in 760 Torr. The extrapolated lifetime at low SO_2 pressure is $(7.1 \pm 0.3) \times 10^{-7}$ s. This represents an 11% decrease in decay rate for a 21% decrease in the air pressure. Thus the air pressure dependence of the lifetime is about half as great as that predicted from Stern–Volmer behavior. When the water vapor pressure was varied holding the SO_2 and air pressure constant, a water quenching rate of $(6.9 \pm 1.4) \times 10^8$ L mol^{-1} s^{-1} was obtained. This is quite close to the value of $(8.9 \pm 1.2) \times 10^8$ L mol^{-1} s^{-1} obtained by Calvert and co-workers[5] at low pressures.

The lifetime of the $^3B_1$ state of SO_2 in air is longer than expected because quenching of this state by many gases shows strong deviations from Stern–Volmer behavior. In particular, inert gases like N_2 and CO_2 quench by collision induced intersystem crossing to the ground state, and this process is found to saturate at high pressures, with the lifetime becoming independent of quencher gas pressure. Quenching by SO_2 itself partially saturates. The effects of O_2 and H_2O are more complicated; quenching by O_2 at least does not appear to saturate. To our knowledge, this is the first report of pressure saturation of intersystem crossing in gases. Deviations of quantum yields at high pressures have been observed by other workers,[7,8] but were interpreted in other ways. Pressure saturation of intersystem crossing has been predicted theoreti-