Temperature Effect on Sulfur Dioxide Vapor Luminescence

Sir:

Halstead and Thrush[1] have recently interpreted the temperature effects on the chemiluminescent emission intensities in terms of activation energies for the corresponding three-body reaction.

$$\mathrm{SO} + \mathrm{O_3} + \mathrm{M} = {}^1\tilde{\mathrm{X}}\ \mathrm{SO_2} + \mathrm{O_2} + \mathrm{M};\quad k_1 = 1.5 \times 10^{12} \exp(-2100/RT) \quad (1)$$

$$= {}^1\tilde{\mathrm{A}}\ \mathrm{SO_2} + \mathrm{O_2} + \mathrm{M};\quad k_2 = 10^{11} \exp(-4200/RT) \quad (2)$$

$$= {}^3\tilde{\mathrm{a}}\ \mathrm{SO_2} + \mathrm{O_2} + \mathrm{M};\quad k_3 = 3 \times 10^{10} \exp(-3900\ RT) \quad (3)$$

and

$${}^1\tilde{\mathrm{A}}\ \mathrm{SO_2} = {}^1\tilde{\mathrm{X}}\ \mathrm{SO_2} + h\nu_\mathrm{f} \quad I_\mathrm{f} \quad (\mathrm{a})$$

$${}^3\tilde{\mathrm{a}}\ \mathrm{SO_2} = {}^1\tilde{\mathrm{X}}\ \mathrm{SO_2} + h\nu_\mathrm{p} \quad I_\mathrm{p} \quad (\mathrm{b})$$

The present account deals with the temperature dependence of the optically excited emissions a and b, by absorption into selected regions of ${}^1\tilde{\mathrm{A}}$ only. The result is an "inverse" temperature effect on I_p; that is, ${}^3\tilde{\mathrm{a}}$ $\mathrm{SO_2}$ appears to be "temperature quenched."

Arrhenius plots (Figure 1) of the data from both laboratories, separated by arbitrary ordinate units, suggest that the actual activation energy for (3) must be nearly 8000 cal and that the former workers measured a composite value.

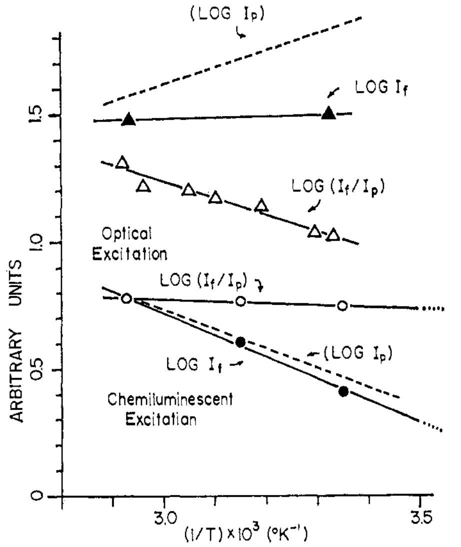

Figure 1. Arrhenius plots of emission intensities of $\mathrm{SO_2}$ vapor excited optically and by chemiluminescent reaction. Phosphorescence data (- - - -) determined by difference.

$$E_\text{over-all}(3900) = E_\text{reaction}(8000) + E_\text{phosphoresence}(-4100)$$

The experimental measurements differ slightly in the two cases. I_f and I_p are taken as proportional to filtered radiation falling on a photomultiplier in the former work, while resolution was accomplished by a 0.75-m spectrometer in the present study.[2] Corrections for a contribution of I_f to I_p were made in both instances.

Excitation by photon absorption was accomplished with a monochromatic beam at right angles to the optical axis of the spectrometer. Six exciting wavelengths, at 200-μ pressure (at 27°), showed no great difference in this temperature effect. Temperatures were measured by a simple $\mathrm{H_g}$ thermometer placed in a heated asbestos jacket surrounding the brass absorption cell container. The cell windows were not heated so that absolute reliability of the measured temperatures could not be assured as being the temperature experienced by the average gas molecule.

Even a very slight ($\sim 5\%$) decrease in I_f was noted between the temperature extrema (27–70°). This was attributed to increased molecular velocities effectively increasing the number of collisions experienced by ${}^1\tilde{\mathrm{A}}$ $\mathrm{SO_2}$. Since nearly every collision quenches this state,[1,3] the above result is anticipated.

The more abrupt decrease in I_p with temperature can be rationalized in three ways, among others. (i) At higher temperatures the collisional partitioning of ${}^1\tilde{\mathrm{A}}$ $\mathrm{SO_2}$ to give ${}^1\tilde{\mathrm{X}}$ $\mathrm{SO_2}$ or ${}^3\tilde{\mathrm{a}}$ $\mathrm{SO_2}$ favors the former. (Collisions are the principal if not the only way to form ${}^3\tilde{\mathrm{a}}$ $\mathrm{SO_2}$.) (ii) A temperature-dependent destruction of ${}^3\tilde{\mathrm{a}}$ $\mathrm{SO_2}$ occurs, but not *via* a chemical reaction, with an activation energy of ~ 4100 cal. (iii) Vibrational relaxation of the ${}^3\tilde{\mathrm{a}}$ $\mathrm{SO_2}$ to the lowest levels, the parent levels for I_p, occurs more slowly when the collision partner (${}^1\tilde{\mathrm{X}}$ $\mathrm{SO_2}$ in the present case) is at a higher vibrational temperature. Then alternative nonradiative losses of ${}^3\tilde{\mathrm{a}}$ $\mathrm{SO_2}$ may become more important.

Because of the relatively small change in vibrational-state occupation numbers of ${}^1\tilde{\mathrm{X}}$ $\mathrm{SO_2}$ over the present temperature range, reason ii would likely be favored. Quite apart from the explanation, it appears that the "true" (if other intermediate steps are not important) activation energy for reaction 3 is about twice that of (2). It is worth noting that if this reaction proceeds *via* an intermediate complex, which would be a triplet, then according to Laidler's discussion[4] of the spin correlation rules, this complex could be decomposed to give (a) a singlet + a triplet, (b) two doublets, or (c) two triplets. On this basis either reaction 2 or 3 would be equally valid, and some other explanation must be sought for the larger activation energy of (3).

Acknowledgments. The financial support of the Robert A. Welch Foundation and the helpful guidance of Professor W. Albert Noyes, Jr., are gratefully acknowledged.

---

[1] C. J. Halstead and B. A. Thrush, *Proc. Roy. Soc.* (London), **A295**, 380 (1966).

[2] See original reference for details. The present technique will be published shortly.

[3] H. D. Mettee, submitted for publication. Other references, listed in ref 1, find near unit efficiency in quenching ${}^1\tilde{\mathrm{A}}$ $\mathrm{SO_2}$ also.

[4] K. J. Laidler, "The Chemical Kinetics of Excited States," Clarendon Press, Oxford, 1955, pp 21–22.

H. D. Mettee
Department of Chemistry, University of Texas at Austin
Austin, Texas 78712

Received March 18, 1968

The Determination of Nuclear Magnetic Shielding Anisotropies of Solutes in Liquid-Crystal Solvents

Sir:

Shifts in nmr spectra due to molecular orientation have been used to measure shielding anisotropies. The isotropic → nematic shifts for solutes in liquid-crystal