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

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

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

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.

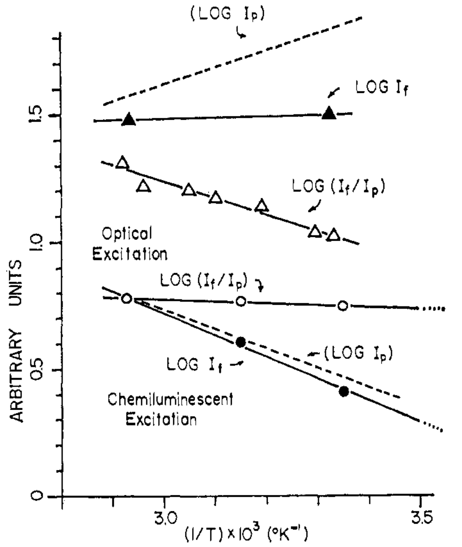

Figure 1. Arrhenius plots of emission intensities of $\mathrm{SO_2}$ vapor excited optically and by chemiluminescent reaction. Phosphorescence data (- - - -) determined by difference.

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

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 $\sim$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.

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[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.

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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

Table I. Isotropic → Nematic Shifts at the Transition Temperature[a]

Liquid crystal	TMS	CH_4	CF_4	SF_6
I	0.11 ± 0.02	0.18 ± 0.02	0.16 ± 0.01	0.08 ± 0.01
II	0.11 ± 0.01	0.18 ± 0.01		
III	0.13 ± 0.01	0.22 ± 0.01	0.26 ± 0.02	0.18 ± 0.02

[a] All downfield, in ppm. Results for CH_4 and CF_4 were obtained using Table II. Errors quoted are standard deviations obtained from at least six measurements.

solvents have frequently been studied, but differences in "solvent effects" in the two phases have proved a serious difficulty to interpretation, particularly in proton work.[1,2] The solvent shielding comprises long-range (volume susceptibility) and local (σ_{local}) contributions; the former is eliminated by using an internal reference, but, because the average local environments of solute and reference molecules are different, difficulties may arise from changes in $\Delta\sigma_{\text{local}}$ in the isotropic → nematic transition. As an illustration of these difficulties we report shifts for CH_4, TMS, CF_4, and SF_6 (none of which should be oriented) for different temperatures and liquid crystals.

The liquid-crystal solvents used were (I) a mixture of 40% *p*-valeryloxy-*p*′-ethoxyazobenzene ($C_2H_5OC_6H_4N_2C_6H_4OCOC_4H_9$) and 60% *p*-caproyloxy-*p*′-ethoxyazobenzene ($C_2H_5OC_6H_4N_2C_6H_4OCOC_5H_{11}$), (II) *p,p*′-di-*n*-hexyloxyazoxybenzene ($C_6H_{13}OC_6H_4N_2OC_6H_4OC_6H_{13}$), and (III) *p*-*n*-octyloxybenzoic acid ($C_8H_{17}OC_6H_4COOH$). Samples were prepared as before.[3] HA spectra were run on a Varian HA-100 spectrometer; $CHCl_3$ and SF_6 provided lock signals. A V-4343 unit was used for temperature control (to ±1°).

Table II. Temperature Dependence of Relative Chemical Shifts and Their Values Extrapolated to Isotropic → Nematic Transition Temperatures

System	Transition temp. °C[a]	Temp dependence of shifts,[b] ppm/°C: Isotropic (spinning)	Temp dependence of shifts,[b] ppm/°C: Nematic (nonspinning)	Extrapolated shifts,[b] ppm: Isotropic (spinning)	Extrapolated shifts,[b] ppm: Nematic (nonspinning)
CF_4–SF_6 in I	125	0.0088 ± 0.0001	0.0080 ± 0.0001	120.730 ± 0.002	120.651 ± 0.002
CF_4–SF_6 in III	146	0.0082 ± 0.0002	0.0099 ± 0.0002	120.919 ± 0.003	120.837 ± 0.004
TMS–CH_4 in I	99	-0.00013 ± 0.00002	-0.00025 ± 0.00009	0.179 ± 0.001	0.250 ± 0.003
TMS–CH_4 in II	98	-0.00007 ± 0.00001	-0.00081 ± 0.00010	0.177 ± 0.001	0.245 ± 0.002
TMS–CH_4 in III	133	-0.00016 ± 0.00002	-0.00051 ± 0.00008	0.172 ± 0.001	0.261 ± 0.002

[a] Temperatures are V-4343 dial readings accurate to ±4°. [b] Errors quoted are least-squares standard deviations.

Near the isotropic → nematic phase change, it was possible, by careful temperature adjustment, to obtain simultaneously signals from the molecules dissolved in isotropic and nematic layers; under these conditions HR measurements were made on TMS and SF_6. Downfield isotropic → nematic shifts of about 0.1 ppm were found (Table I). The relative shifts between CH_4 and TMS, and between CF_4 and SF_6, show a discontinuity at the phase change, indicating that the shifts are different for each species (Figure 1). This discontinuity has been reported before.[2]

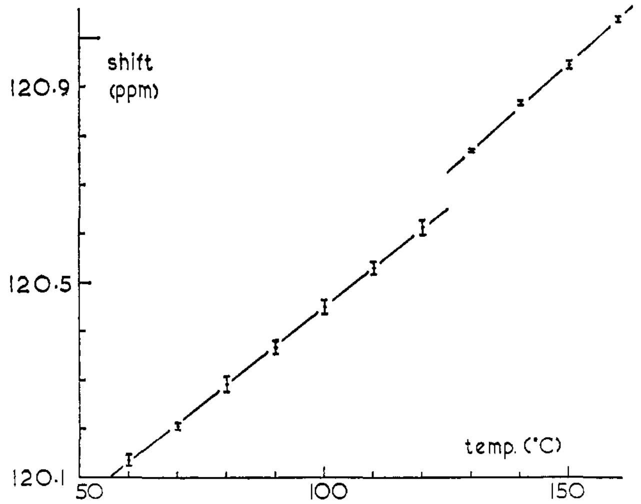

Figure 1. High-field chemical shifts of CF_4 relative to SF_6 in I. The isotropic → nematic phase change is at 125°. Error limits are twice standard deviations.

The temperature dependence of the relative shift is small for CH_4–TMS, but appreciable for CF_4–SF_6, in both phases. The isotropic spectra were obtained while spinning the sample tubes, the nematic without spinning. Slow spinning in the nematic temperature range did not completely destroy the orientation[4] but lessened the discontinuity at the phase change, indicating that $\Delta\sigma_{\text{local}}$ is related to the degree of orientation of the liquid crystal. Results, extrapolated to transition temperatures by least squares, are in Table II.

The isotropic → nematic shifts (Table I) can be written as

$$\Delta\sigma = \sigma_{\text{nematic}} - \sigma_{\text{isotropic}} = \frac{4\pi}{9}(\chi_{\parallel} - \chi_{\perp}) + \Delta\sigma_{\text{local}}$$

where $\chi_{\parallel} - \chi_{\perp}$ is the volume susceptibility anisotropy of the nematic solvent. Changes in χ due to volume changes have been neglected.[1] It has been found[2] that in II $\chi_{\parallel} - \chi_{\perp}$ is about 0.2 ppm and $\Delta\sigma_{\text{local}}$ about −0.4 ppm, the resulting isotropic → nematic shift being about −0.2 ppm. Our result agrees with this.

TMS apparently orients slightly in a nematic solvent;[5] however, the consequent isotropic → nematic shift is negligible. No splittings in the spectra of the other molecules studied have been observed. As $\chi_{\parallel} - \chi_{\perp}$ is the same for all solutes, $\Delta\sigma_{\text{local}}$ differs by about 0.1

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(1) A. D. Buckingham and E. E. Burnell, *J. Am. Chem. Soc.*, **89**, 3341 (1967).

(2) R. A. Bernheim and T. R. Krugh, *ibid.*, **89**, 6784 (1967).

(3) A. D. Buckingham, E. E. Burnell, C. A. de Lange, and A. J. Rest, *Mol. Phys.*, **14**, 105 (1968).

(4) We have found that slow spinning (1–10 Hz, depending on the system) narrows the lines, especially the outer lines in highly oriented molecules. This is probably due to improved temperature homogeneity. The mean solute orientation depends on spinning rate.

(5) L. C. Snyder and S. Meiboom, *J. Chem. Phys.*, **44**, 4057 (1966).

ppm for these highly symmetric species. Presumably changes in $\Delta\sigma_{\text{local}}$ between one of these molecules and a solute of lower symmetry are at least of this order of magnitude. Also, shift changes may depend on concentration. If the actual isotropic → nematic shift is not large compared to $\Delta\sigma_{\text{local}}$, the measurement of $(\sigma_{\|} - \sigma_{\perp})_H$ for the solute is unreliable. Even nonequivalent protons in the same molecule might experience differences in $\Delta\sigma_{\text{local}}$. Fluorine isotropic → nematic shifts may be an order of magnitude greater than $\Delta\sigma_{\text{local}}$, but care is still needed in determining $(\sigma_{\|} - \sigma_{\perp})_F$ because of temperature dependence of the shift (Figure 1). The actual shifts should be extrapolated to the phase-change temperature, but even then there is the effect of $\Delta\sigma_{\text{local}}$ to be considered.

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Partial Photoresolution. Preliminary Studies on Some Oxalato Complexes of Chromium(III)

Sir:

We are investigating the use of circularly polarized light as a means of partially resolving a racemic mixture. We have irradiated racemic aqueous solutions of trioxalatochromate, *cis*-dioxalatodiaquochromate, and di-μ-hydroxy-tetraoxalatodichromate with right-handed circularly polarized (RHCP) light at 546 nm and observed an induction of optical activity. Unlike related earlier experiments[1-3] in which the optical activity induced in a chemical system always disappeared upon continued photolysis, the above-named systems attained an equilibrium optical activity as shown in Figures 1-3. The photolytic induction of optical activity occurs because the enantiomers of the racemic mixtures possess circular dichroisms ($\epsilon_L - \epsilon_R$) which are equal but opposite in sign; hence the rates of absorption of one kind of circularly polarized light are unequal. If there is a photochemical reaction at the wavelength of appreciable CD then the reaction will proceed asymmetrically, inducing optical activity into the system. Moreover, if the only photochemical reaction undergone by an isomer is inversion to its enantiomer, the effect of the circularly polarized light on the racemic mixture will be a partial resolution, a process which can be called photoresolution. The maximum extent of photoresolution is governed by the dissymmetry factor, CD/ϵ, and amounts to a few per cent for the systems we have studied. This fraction is large enough to study kinetics and determine ORD–CD curves.

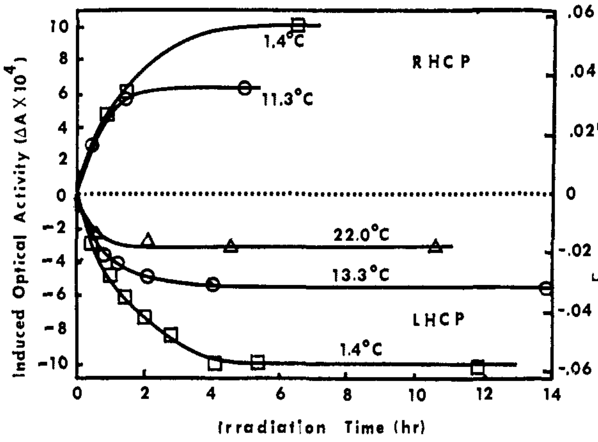

Figure 1. Photoresolution of trioxalatochromate(III), 2.6 × 10^{-2} *M*, in RHCP and LHCP light at 546 nm.

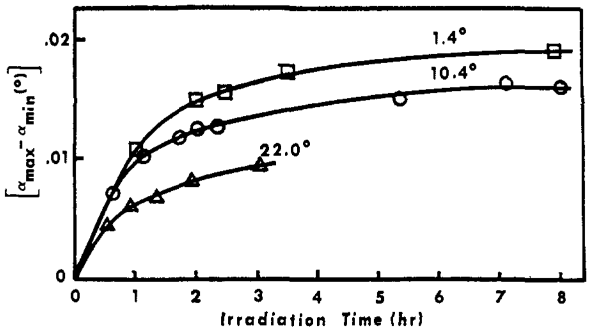

Figure 2. Optical activity induced in di-μ-hydroxy-tetraoxalatodichromate(III), 6 × 10^{-3} *M*, in RHCP light at 546 nm.

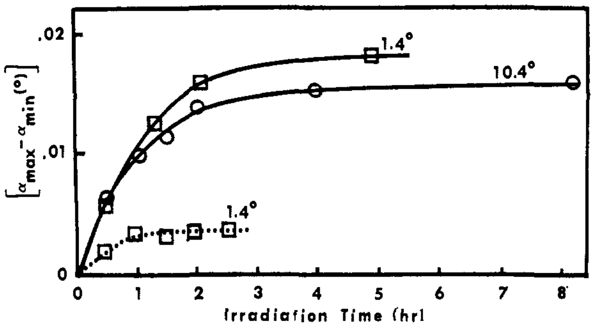

Figure 3. Optical activity induced in (———) *cis*-dioxalatodiaquochromate(III), 2.7 × 10^{-2} *M*, and (- - - -) *trans*-dioxalatodiaquochromate(III), 2.5 × 10^{-2} *M*, in RHCP at 546 nm.

For our systems, named above, there do not seem to be any irreversible photoreactions, and an equilibrium state is attained such as that shown for trioxalatochromate in Figure 1. For this system it is known that thermal racemization occurs along with the photointerconversion of enantiomers,[4] and the equilibrium state is determined by this competition. The data of Figure 1 are well represented by the integrated rate expression

$$\Delta A = [k_p a/(k_p b + k_T)][1 - \exp(-k_p b - k_T)t] = \Delta A_{\text{eq}}[1 - \exp(-ak_p t/\Delta A_{\text{eq}})]$$

where $\Delta A = A_L - A_R$, the measured difference in absorbance of solution in LHCP and RHCP light; "eq" denotes equilibrium value; $a = 0.5$ (concentration of solution) × (CD of + isomer); $b = \epsilon/[(\text{cell length})\cdot(\text{CD of + isomer})]$; k_T is the thermal racemization rate constant, and k_p is a photoresolution rate constant (a function of light intensity and quantum yield). Using this equation and the value for k_T as obtained by Spees and Adamson[4] we obtain the CD of either isomer at the irradiating wavelength. Our data yield a CD of

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(1) W. Kuhn and E. Braun, *Naturwissenschaften*, **17**, 227 (1929).

(2) R. Tsuchida, A. Nakamura, and M. Kobayashi, *J. Chem. Soc. Japan*, **56**, 1335 (1935).

(3) R. L. Davis and R. Heggie, *J. Am. Chem. Soc.*, **57**, 377 (1935).

(4) S. T. Spees and A. W. Adamson, *Inorg. Chem.*, **1**, 531 (1962).