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Temperature Dependence of Chemiluminescent Reactions. III. The Sulfur Dioxide Afterglow

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TABLE II. The gross atomic, net atomic, and overlap populations, and their subdivisions into the σ and π contributions.

		Full LCAO-SCF calculations			CNDO calculation
		I	II	III	
		Gross population			
O	σ	6.9443	6.9596	7.0182	6.9249
	π	1.4872	1.4944	1.5610	1.6108
	total	8.4315	8.4540	8.5792	8.5357
N	σ	6.1116	6.0808	5.9635	6.1503
	π	1.0255	1.0112	0.8779	0.7783
	total	7.1371	7.0919	6.8414	6.9286
		Net population			
O	σ	6.8008	6.8314	7.1078	6.7716
	π	1.3979	1.4018	1.4643	1.5237
	total	8.1987	8.2332	8.5721	8.2953
N	σ	5.7645	5.7554	5.9561	5.8070
	π	0.8323	0.8093	0.6260	0.5927
	total	6.5968	6.5647	6.5821	6.3997
		Overlap population			
(O–N)	σ	0.3470	0.3253	0.0075	0.3433
	π	0.1942	0.2019	0.2519	0.1856
	total	0.5402	0.5272	0.2594	0.5289
(O–O)	σ	−0.0601	−0.0690	−0.1868	−0.0368
	π	−0.0145	−0.0167	−0.0584	−0.0113
	total	−0.0746	−0.0857	−0.2452	−0.0481

well all the principal features of the electron distribution of the nitrite ion, and gives the gross populations which are also very close to those of the calculation III. The CNDO method and the calculation III give the effective charge on the nitrogen atom to be 0.0714 and 0.1518, respectively. These values are in reasonable agreement with the Pauling's prediction that the effective charge on the nitrogen atom should vanish according from the consideration of the chemical resonance structure of the nitrite ion.[10]

It may be concluded from the results of this Note that the integrals disregarded in the CNDO method do not actually make appreciable contributions to the electron distribution of the molecules with the closed-shell structure, and that the semiempirical parameters have been chosen so as to reproduce the orbital energies of the polyatomic molecules very well. This sort of approximate molecular-orbital theory has recently been extended in some respects,[11,12] and provides a very promising tool for investigating molecular properties of large systems beyond the present range of the full calculations.

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Temperature Dependence of Chemiluminescent Reactions. III. The Sulfur Dioxide Afterglow[*]

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Previous reports from this laboratory[1] have described the construction of the glow-discharge shock-tube facility and its application to the determination of the temperature dependence of the NO–O, CO–O, N_2, and NO chemiluminescent afterglows. In this Note we report results obtained by applying the glow-discharge shock-tube technique to the SO_2 afterglow. We also present a new measurement of the absolute total intensity of this chemiluminescent reaction.

The SO_2 afterglow was established in the glow tube by two independent techniques: (a) passing SO_2 through a microwave discharge and injecting it into a N_2 stream, or (b) passing O_2 through the discharge and adding OCS downstream. In the second procedure,

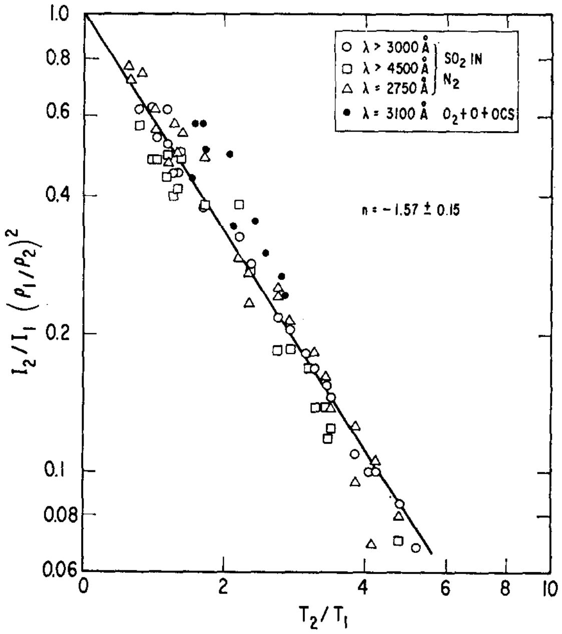

FIG. 1. Temperature dependence of the SO_2 afterglow. [The slope of the plot of log (I_2/I_1) (ρ_1/ρ_2) vs log (T_2/T_1) is the exponent n when the rate constant for the reaction $O+SO\rightarrow SO_2+h\nu$ is written $k=AT^n$.]

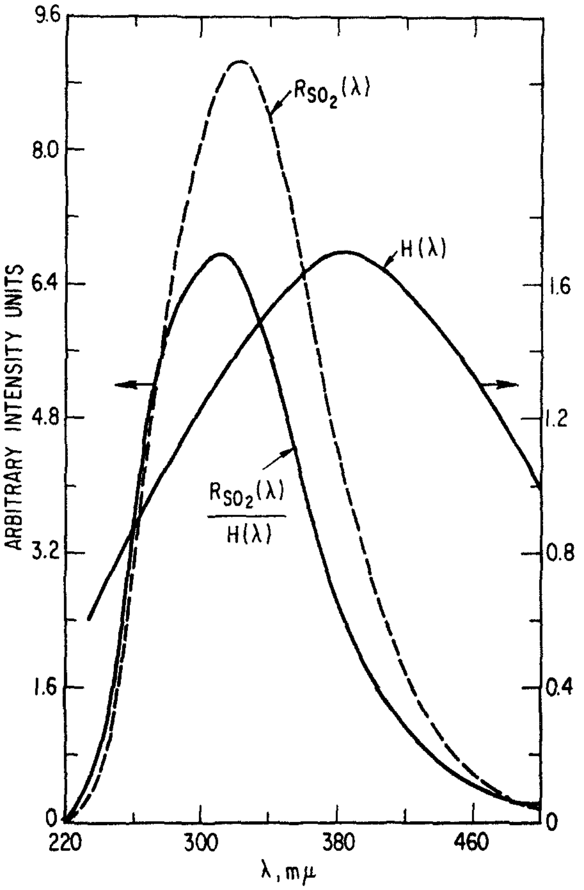

FIG. 2. Intensity of the SO_2 afterglow as a function of wavelength. [$R_{SO_2}(\lambda)$ is the uncorrected intensity; $H(\lambda)$ is the instrument sensitivity relative to a value at 500 mμ; $R_{SO_2}(\lambda)/H(\lambda)$ is the corrected intensity.]

OCS reacts with O atoms formed in the discharge to produce CO and SO. The SO radicals then react with excess O atoms to produce the violet SO_2 emission. In procedure (a), the emission was monitored by three separate photomultipliers. One, used in conjunction with a Bausch & Lomb monochromator, was set at 2750 Å, with a half-width of about 15 Å. A second and third photomultiplier monitored all radiation above 3000 and 4500 Å, respectively. In procedure (b), intensity was monitored at 3200 Å, the maximum emission.

In Ref. 1 it was shown that for a chemiluminescent reaction of the form $A+B(+M)\xrightarrow{k}AB(+M)+h\nu$, the ratio of emission intensities before (subscript 1) and after (subscript 2) the shock is given by the product of the ratio of rate constants times the ratio of densities raised to the appropriate power:

$$I_2/I_1=[k(T_2)/k(T_1)](\rho_2/\rho_1)^{s+2}$$

where $s=0$ or 1 depending on whether the reaction is second or third order. In Fig. 1, we plot $\log(I_2/I_1)(\rho_1/\rho_2)^2$ vs $\log(T_2/T_1)$. The data for all three spectral regimes, regardless of the mode of production of the SO_2, fall on the same straight line of slope -1.6 when s is taken to be 0. Thus, the data reinforce the conclusion[2] that the over-all reaction rate is independent of total pressure and, furthermore, indicate that I varies as $T^{-1.6}$. Our data cover the temperature range of 300°–1500°K, with pressures behind the shock of about 2–5 torr.

In an independent series of room-temperature measurements, the absolute total emission intensity of the SO_2 afterglow (2200–5000 Å) was determined. This we obtained by measuring the emission as a function of wavelength, correcting for the spectral response of the monochromator–photomultiplier system, and calibrating absolutely by observing the NO_2 afterglow in the same apparatus (Fig. 2). By use of Fontijn, Meyer, and Schiff's[3] absolute quantum yield of the NO_2 chemiluminescence, a room-temperature rate constant for the SO_2 afterglow of $1.9\times10^5 M^{-1}\cdot\text{sec}^{-1}$ is obtained. This value compares favorably to the value of $1.5\times10^5 M^{-1}\cdot\text{sec}^{-1}$ reported by Clyne, Halstead, and Thrush,[2] but is lower than other reported values.[4,5]

Combining the room-temperature absolute measurement with the temperature dependence measured in the shock tube, we obtain the emission intensity $I=1.9\times10^5(300/T)^{1.6}[\text{O}][\text{SO}]M\ \text{sec}^{-1}$.

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Relative Orientation of Molecules Involved in Triplet–Triplet Energy Transfer

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The exchange interaction necessary for the nonradiative triplet–triplet transfer of energy is a short-range interaction sensitive to the overlap of the electronic wavefunctions of the participating molecules.[1–3] Hence, there can be an optimum transfer geometry for the sensitizer–acceptor pair.[4–7]

The aim of this work is to examine this orientation dependence in triplet–triplet transfer using a new technique. It involves the excitation of the sensitizer molecules with polarized light and the measurement of the polarization of the triplet–triplet absorption in the acceptor molecules. Thus, a knowledge of the transition