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Chemiluminescent Reactions of CS_2, COS, and H_2S with Atomic Oxygen*

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In a study designed to elucidate the chemiluminescent reactions associated with the oxidation of CS_2, COS, and H_2S, we recently compared the spectra produced in the reactions of the above compounds and atomic oxygen with that of the SO_2 afterglow.

A conventional fast-flow system was used for the present study. Atomic oxygen was produced by a microwave discharge through a 100:1 mixture of argon and O_2. CS_2, COS, or H_2S were admixed in a 2-cm i.d. Pyrex tube equipped with a quartz window for the observation of uv spectra. The SO_2 afterglow was produced in the same system by the discharge of a mixture of SO_2 and argon. Spectra were recorded with a Perkin–Elmer (Model 99) monochromator equipped with a 600 lines/mm grating and an EMI 9558Q photomultiplier tube.

The spectra resulting from the three chemiluminescent reactions and that of the SO_2 afterglow were normalized to the same peak intensity. [See (a) Fig. 1.] They appear to be continuous in all cases with similar profiles. This strongly indicates that the process responsible for the observed chemiluminesce is the same in all three investigated reactions as that in the SO_2 afterglow.

It has been suggested by earlier investigators[1–3] that the SO_2 afterglow continuum is mainly due to

$$O+SO \rightarrow SO_2+h\nu. \qquad (1)$$

Herman *et al.*[3] observed that the short-wavelength cutoff of the SO_2-afterglow continuum at 2400 Å coincides with the onset of the dissociation continuum in the SO_2 absorption spectra. They, therefore, concluded that Reaction (1) is mainly responsible for the emission of the SO_2 afterglow. The conclusion was further supported by Halstead and Thrush[4] who reported that the intensity of the SO_2 afterglow is directly proportional to the product of the concentrations of atomic oxygen and SO radicals.

The spectral response of the recording system employed was calibrated with a standard light source (GE quartz iodine tungsten filament lamp, Model 6.6A/T4Q/1CL-200W). The absolute irradiance of the lamp was obtained from Stair *et al.*[5] The corrected

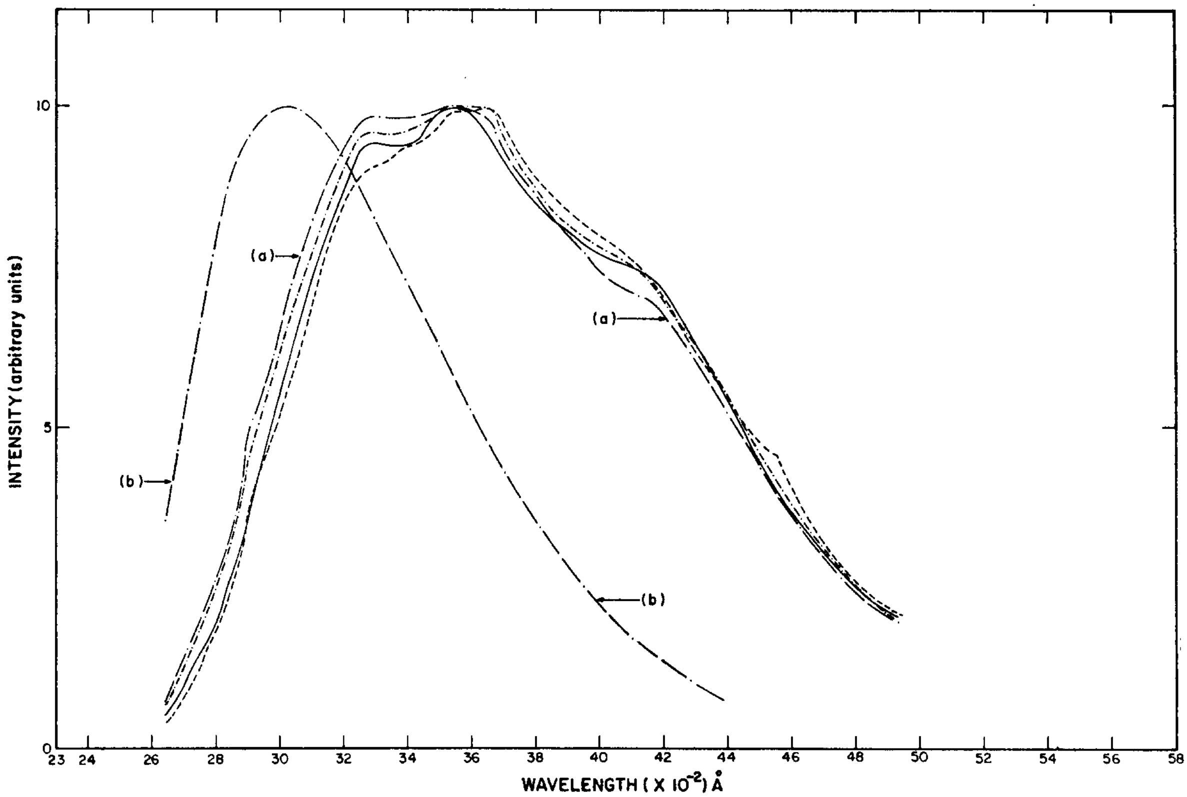

FIG. 1. The observed (uncorrected) spectra of the chemiluminous reactions of CS_2, COS, and H_2S with atomic oxygen, and that of SO_2 afterglow (Curves a). The corrected spectrum of SO_2 afterglow is shown by (Curve b). For (a) ——, O+COS chemiluminescence; – – –, O+CS_2 chemiluminescence; –·–·–·–, O+H_2S chemiluminescence; ·— —·, SO_2 afterglow (uncorrected). For (b) ·———·, SO_2 afterglow (corrected).

profile of the SO_2-afterglow spectrum observed by this technique is designated by (b) in the figure. A similar plot of the three chemiluminescent reactions also results in the same profile as that of our SO_2 afterglow. According to our observations, the wavelength of peak intensity in the spectrum lies at about 3000 Å. Herman *et al.* found it to be at about 2800 Å. Considering the different experimental techniques employed, the disagreement between the two observations is not that severe.

Accepting[6,7] Reaction (1) as the origin of the SO_2-afterglow continuum, it appears from the similarity of the spectra observed by us that Reaction (1) may also be responsible for the chemiluminescence produced during the reaction of atomic oxygen with CS_2, COS, and H_2S. Harteck and collaborators[8–10] have made this assumption for some time.

The conclusion can be further supported by the identification of the products in the initial stage of the reactions. One of these reactions, i.e., between atomic oxygen and COS, has been quantitatively studied by Sullivan and Warneck.[11] The first two major steps in the mechanism are

$$\mathrm{O+COS\rightarrow CO+SO} \qquad (2)$$

$$\mathrm{SO+SO\rightarrow SO_2+S.} \qquad (3)$$

During the initial stage of the reaction, they identified appreciable concentrations of SO radicals and atomic oxygen with a mass spectrometer. Furthermore, Liuti *et al.*[10] have qualitatively shown that the first major step in the reaction of H_2S and atomic oxygen is

$$\mathrm{H_2S+O\rightarrow H_2+SO.} \qquad (4)$$

The combination of Reactions (4) and (3) leads to a similar mechanism of production of chemiluminescence in the H_2S reaction as that during the reaction of COS with atomic oxygen. A similar mechanism is also then indicated for the reaction of CS_2 with atomic oxygen.

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Statistical-Mechanical Model for the $\alpha\rightleftharpoons\beta$ Transformation in Keratins

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Although there has been a large amount of experimental and theoretical work done[1–5] on the $\alpha\rightleftharpoons\beta$ transformation in keratins, no fully satisfactory model for this transformation has yet been presented. In attempting to understand the transformation, it seems worthwhile to generalize the work done by others on the problem of the thermal denaturation[6–10] of α proteins to the case of a polymer chain under external tension. The x-ray work of Krimm and Tobolsky[11] indicates that the $\alpha\rightleftharpoons\beta$ transformation takes place in at least two stages: (1) individual chain extension, and (2) relaxation to form sheetlike β structures. Hence, in the present work it is assumed that there is an equilibrium number of α and "β" residues in the chain and in comparison to the work of Hill,[4] no interchain bonds are assumed.

We assume that a given state of the keratin polypeptide chain which consists of amide groups connected by α-carbon atoms[12] can be completely described by a statement as to the state of the oxygen atoms alone, i.e., by a statement as to whether or not each is bonded to the hydrogen of the third preceding segment.[6] For simplicity we adopt the simplified α helix employed by Davidson,[13] in which binding occurs to the hydrogen of the preceding segment. For every hydrogen-bonded residue we ascribe a length l_α and for every nonbonded residue we ascribe length l_β. Consider a partially helical polymer chain consisting of n_α short (α) residues of length l_α and n_β long (β) residues of length l_β, ($l_\beta\cong 2l_\alpha$) under an external tension τ in the helical axis direction. Let L represent the length of the chain and N the total number of residues:

$$L(N,\tau,T)=n_\alpha(N,\tau,T)l_\alpha+n_\beta(N,\tau,T)l_\beta, \qquad (1)$$

$$N=n_\alpha+n_\beta. \qquad (2)$$

Equations (1) and (2) give the tension–length isotherms in terms of the equilibrium values of n_α and n_β.

In order to determine the equilibrium values of n_α and n_β, it is necessary to introduce a model for the polypeptide chain. Consider the formalism of Zimm and Bragg[6] with $\mu=1$. In this model, all β residues are assigned a relative probability of 1. An α residue following an α residue is assigned a relative probability of $s(T)$ equal to the ratio of the partition functions $j_\alpha(T)$ and $j_\beta(T)$ for the α and β residues, respectively. The probability of an α residue following a β residue is denoted by $\sigma s(T)$, where σ represents a *nucleation*