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CHARACTERIZATION FOR THE SELECTIVE DETECTION OF SULPHUR COMPOUNDS BY FLAME PHOTOMETRY

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SUMMARY

The molecular emission of the S_2 species from sulphur compounds has been studied by using a flame photometric detector (FPD). From the measurements of the FPD response, we have proposed a mechanism for the emission of S_2 in reactions of sulphur atoms.

The mechanism was confirmed by experimental results measured with the FPD and spectrophotometers. It was found that the S_2 molecular emission arises mostly from a three-body recombination reaction and that the rate of this recombination is too slow for equilibrium to be attained sufficiently rapidly.

The response to sulphur-containing compounds of the FPD in gas chromatography represents an extremely complex function of the concentration of sulphur compounds.

INTRODUCTION

Flames that contain sulphur compounds as additives emit bands of S_2 , SO, SH and CS and a continuum, and the various emissions are highly dependent on the nature of the flames. Of these emissions, S_2 has proved to be the most useful for spectrochemical analysis.

The principle discovered by Drägerwerk and Dräger¹ for the detection of sulphur and phosphorus compounds was first applied to produce a detector for gas chromatography in 1966 by Brody and Chaney². Since that time, this detector has been used extensively in the determination of residues of sulphur- and phosphorus-containing pesticides, natural gases, volatiles in smoke, etc.³⁻¹². In this flame photometric detector (FPD), a quadratic analytical curve was usually given for sulphur; the emission intensity varies as the square of the sulphur concentration⁴. Such curves were also observed by Dagnall *et al.*³ and Mizany⁷.

Sugden *et al.*¹³ studied the reactions of sulphur in hydrogen flames, and showed the manner in which the non-equilibrium concentration of H and OH affects the emission intensity of the sulphur species. The theory was tested by measuring the dependence of the SO, SH and S_2 emission intensities on the distance from the reaction zone and on the concentration of total sulphur. On the other hand, Fair and Thrush¹⁴ discussed the dependence of the S_2 emission intensity on the concen-

tration of hydrogen sulphide using an electrodeless radiofrequency discharge tube. They tried to interpret the relationship between the S_2 emission intensity and the concentration of hydrogen sulphide at various reaction times. Nevertheless, the proposed mechanisms of emission of S_2 species cannot adequately explain the experimental results.

We have observed the characteristics of the FPD in the sulphur mode¹⁵⁻¹⁷. In previous papers, a mechanism of S_2 emission in reactions of sulphur atoms was developed by measuring the intensity of S_2 emission with an FPD. In this paper, the mechanism was confirmed from the relationship between the intensity of the molecular emission of S_2 and the condition of the flames.

EXPERIMENTAL

Apparatus

The FPD used in this study to determine the intensity of the S_2 emission was identical with that described earlier¹⁶. The intensity of the molecular emission due to the S_2 species from a sulphur compound was measured at various flow-rates of air and hydrogen and over a wide range of concentrations of the sulphur compound.

Reagent

Di-*n*-butyl sulphide of guaranteed grade was dissolved in acetone so as to give a concentration of $4.403 \cdot 10^{-3}$ g/ml. This solution was further diluted to give appropriate concentrations required in the experiments.

RESULTS AND DISCUSSION

Intensity of S_2 emission

The intensity of the S_2 emission varies with the flow-rate of hydrogen, and the influence of this flow-rate on the intensity (i_E) of the molecular emission of S_2 is shown in Fig. 1. The intensity decreases with increasing flow-rate of hydrogen.

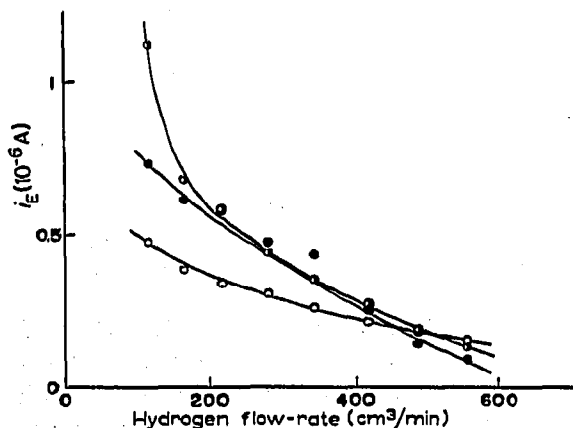


Fig. 1. Emission intensity of S_2 band for the following flame conditions: air flow-rate: ●, 107 ml/min; ◐, 140 ml/min; ○, 171 ml/min; flow-rate of di-*n*-butyl sulphide (f_s), $2.48 \cdot 10^{-8}$ mole/min.

The dependence of the emission intensity of S_2 on the concentration of the sulphur compound was measured for two flame conditions. The intensity is not linearly proportional to the concentration of di-*n*-butyl sulphide. The relationship between the intensity of the S_2 emission and the concentration of the sulphide, f_S , can be written as:

$$i_E = i_0(f_S)^n \quad (1)$$

Both i_0 and n are constant over a narrow concentration range under experimental conditions used. Fig. 2 shows the plot of $\log(i_E)$ against $\log(f_S)$. The relationship between the S_2 emission intensity and the concentration of the sulphide is quadratic only at the lowest concentration; a plot of $\log(i_E)$ against $\log(f_S)$ is taken as linear over a narrow range and so the slope of the line can be represented by n . However, an almost first-order dependence of the emission intensity on the concentration of the sulphide is observed at concentrations higher than $5 \cdot 10^{-8}$ moles/min at a flow-rate of hydrogen of 165 ml/min and higher than $2 \cdot 10^{-7}$ moles/min at a flow-rate of hydrogen of 417 ml/min. The slope of the curve, n , at a flow-rate of hydrogen of 417 ml/min is steeper than that at 165 ml/min at the same concentration of di-*n*-butyl sulphide.

Fig. 3, which is taken from Fig. 10 in ref. 13, calculated and redrawn, shows the time dependence of the emission intensity expressed as the S_2 band emission intensity (3950 Å) versus distance from the reaction zone.

Figs. 1 and 5 in ref. 14 suggest the dependence of the S_2 emission on the concentration of sulphur atoms in an electrodeless radiofrequency discharge tube at

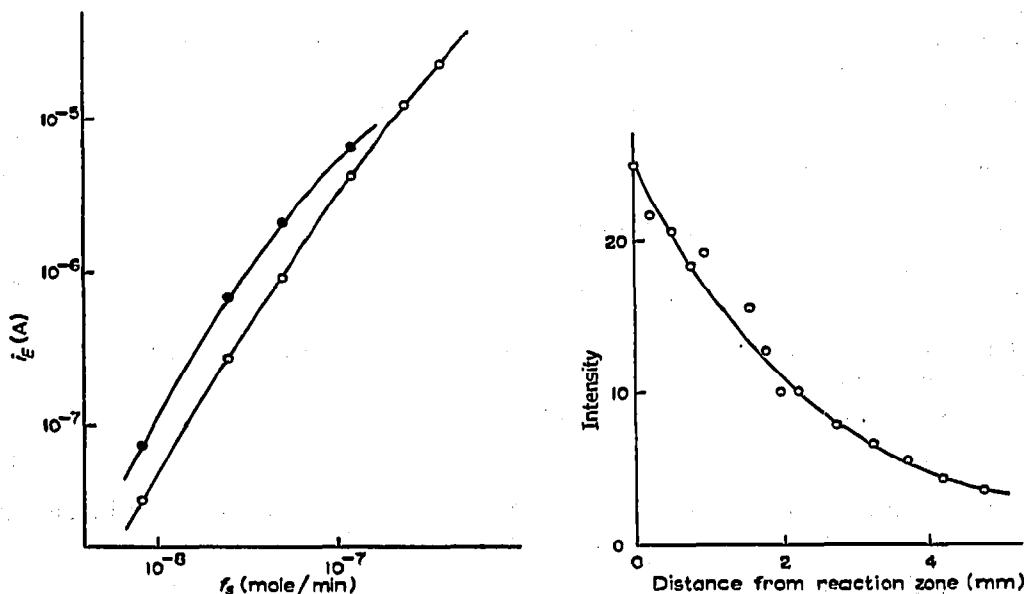


Fig. 2. Analytical curves for di-*n*-butyl sulphide, $\log(i_E)$ vs. $\log(f_S)$, at flow-rates of air of 140 ml/min and hydrogen of 165 ml/min (●) and 417 ml/min (○). f_S is determined from the equations in ref. 15.

Fig. 3. S_2 band emission intensity at 3950 Å. Flame conditions: $N_2:H_2:O_2 = 4:4.7:1$. (This figure has been adapted from Fig. 10 by Sugden *et al.*¹³.)

reaction times of 0 and 0.208 sec, respectively. At zero reaction time, the intensity of emission obeys the relationship $I=I_0[\text{H}_2\text{S}]^2$, where $[\text{H}_2\text{S}]$ is the concentration of hydrogen sulphide added. However, at a fixed reaction time (0.208 sec), the S_2 emission intensity does not increase appreciably when the pressure of the hydrogen sulphide is raised.

Mechanism of emission

The processes involved in the molecular emission of S_2 from sulphur-containing compounds are advanced as follows¹⁶



The emission in reaction *vii* contributes little to the over-all S_2 molecular emission.

The concentration of sulphur atoms is given by

$$[\text{S}] = K_2 K_3 \frac{[\text{H}_2\text{S}][\text{H}]^2}{[\text{H}_2]^2} = K[\text{H}_2\text{S}] \quad (2)$$

The rate of formation of the S_2 species is given by

$$\frac{d[\text{S}_2]}{dt} = k_4[\text{S}]^2[\text{M}] \quad (3)$$

Then, the concentration of S_2 for a reaction time of t sec is

$$[\text{S}_2](t) = \frac{aK}{2} \left(1 - \frac{1}{2aKk_4[\text{M}]t+1} \right) \quad (4)$$

where a is the initial concentration of the sulphur compound and $[\text{M}]$ the concentration of the third body.

The emission intensity in a whole flame is

$$I_{\text{S}_2} = [\text{S}_2](t_0) \quad (5)$$

where t_0 is the reaction time at the top of the flame. On the other hand, the intensity of emission in part of the flame at a reaction time of t sec is given by

$$I_{\text{S}_2}(t) = \frac{d[\text{S}_2](t)}{dt} \quad (6)$$

Hence,

$$I_{\text{S}_2}(t) = \frac{a^2 K^2 k_4 [\text{M}]}{(2aKk_4[\text{M}]t+1)^2} \quad (7)$$

The theoretical intensity of S_2 emission in the whole of a flame has been shown in Fig. 6 in ref. 16 to be a function of the initial concentration of a sulphur compound. It agrees very closely with Fig. 2 in this paper. At flow-rates of hydrogen of 165 ml/min and air of 140 ml/min, the value of k_4 calculated from the dependence of the emission on the concentration of sulphur atoms is $10^{17} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1}$, on the assumption that K and M are 1 and N_2 , respectively. This value can be compared with rate constants for the combination of other atoms in a flame, e.g., $H+H+M$, $H+OH+M$, $N+N+M$, etc.¹⁸.

Sugden *et al.*¹³ showed that the molecular emission intensity of the sulphur species varies with the concentration of hydrogen atoms only. Comparing the emission intensity of S_2 with that of SO measured by them, the decrease in the intensity of S_2 species with the distance from reaction zone should be identical with SO according to their theory, but they are, in fact, entirely different. In the flame with an $N_2:H_2:O_2$ ratio of 4:4.7:1 (Figs. 7 and 10 in ref. 13), a 0.98th order dependence of the S_2 emission intensity on the concentration of hydrogen atoms is found, provided that the intensity of SO emission is proportional to the fourth power of the concentration of hydrogen atoms. These emissions, therefore, do not seem to follow the mechanism of Sugden *et al.*

The measurements and mechanism described by Fair and Thrush¹⁴ have provided good expressions for the dependence of the S_2 emission intensity on the concentration of sulphur atoms. However, the experimental results cannot be completely represented by their mechanism.

Our proposed mechanism will now be applied to above spectrophotometric experimental results. Firstly, the theoretical dependence of the S_2 emission intensity on the reaction time is shown in Fig. 4, derived from eqn. 7. The dependences in both Fig. 3 and in Fig. 4 are similar. Furthermore, the S_2 emission intensity at zero reaction time ($t=0$) is shown to be proportional to the square of the concentration of sulphur atoms by eqn. 7. Fig. 5 shows the concentration dependence of $I_{S_2}(t)$ at a reaction time of t sec. These express satisfactorily the dependence of the molecular

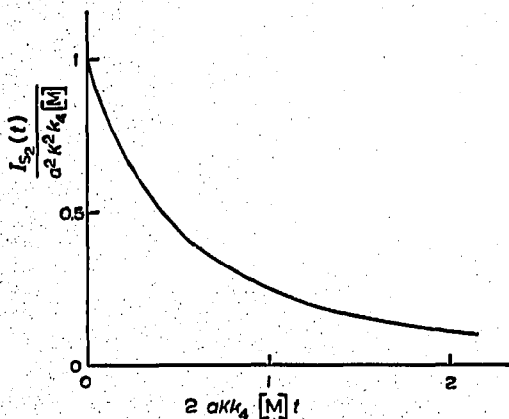


Fig. 4. Theoretical relationship between emission intensity and reaction time.

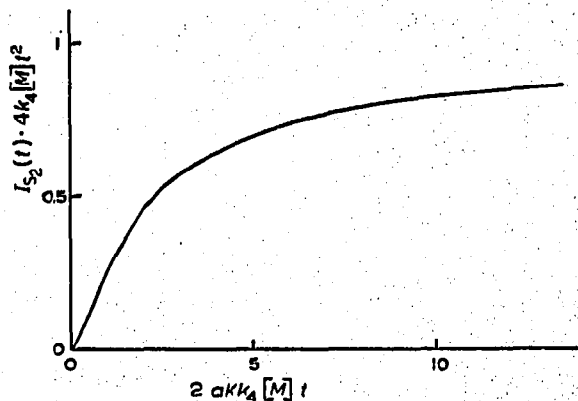


Fig. 5. Theoretical relationship between the S_2 emission intensity at a reaction time t and the initial concentration of sulphur atoms.

emission intensity of the S_2 species from sulphur compounds on the concentration of sulphur atoms as measured by Fair and Thrush (Figs. 1 and 5 in ref. 14).

Luminescent radiation by hydrogen atoms

The radicals present in a flame recombine if they can transfer their surplus energy to a third body in a triple collision. Such a recombination is possible in a collision with an atom in a hydrogen-rich flame:



where X^* represents an excited emitting species. The excited species can lose its surplus energy in the form of a light quantum:



The emission of the S_2 species can be compared with that of an atom of a metal such as sodium. The formation of a sodium atom is a much smoother reaction than that of S_2 , because the latter involves a three-body recombination (reaction *iv*). Therefore, the conversion of a sulphur compound into S_2 will be vanishingly small compared with the conversion of a sodium salt into atoms. These emission species must be excited by the three-body collision with hydrogen atoms (reaction *viii*) in order to emit light. The emission of S_2 after reaction *viii*, therefore, becomes much less in intensity than that of Na. However, the S_2 emission process involves emission of light in reaction *v*, which is not attended by reaction *viii* (i.e., reaction *vi*). Although the emission of sodium atoms follows according to reaction *ix*¹⁹, the emission of S_2 in reaction *vii* is consequently presumed to contribute little toward the over-all S_2 molecular emission.

CONCLUSION

The concentration and time dependences of S_2 chemiluminescence provide good evidence that it is associated with the recombination of two sulphur atoms. It is considered that the bulk of the S_2 molecular emission arises from the three-body recombination reaction. The rate of the recombination is too slow for equilibrium to be attained sufficiently rapidly and so it is the rate-determining step in the emitting process. It is therefore apparent how and why the response of the FPD to sulphur-containing compounds provides an extremely complex function of the concentration of sulphur compounds.

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