Journal of Chromatography, 77 (1973) 309–316

CHROM. 6537

CHARACTERISTICS OF S_2 EMISSION INTENSITY WITH A FLAME PHOTOMETRIC DETECTOR

TOSHIAKI SUGIYAMA, YOSHIHITO SUZUKI AND TSUGIO TAKEUCHI
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Nagoya (Japan)

(Received November 23rd, 1972)

SUMMARY

The molecular emission from sulphur compounds was studied by using a flame photometric detector and determining its intensity as a function of the composition of an air–hydrogen flame and of the concentration of the sulphur compounds.

The relationship between the intensity of emission and the amount of sulphur in the compound is given by

$$i_E = i_0\,(M)^n$$

where i_E is the intensity of the emission, M the amount of sulphur and i_0 and n are constants for a given experimental flame condition. The value of n varies between 1.69 and 2.00, depending on the flame conditions.

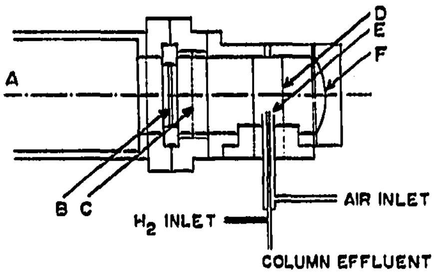
The variations in the values of i_0 and n are discussed by considering reaction kinetics. The recombination reaction of sulphur atoms in a flame, which is the rate-determining step, is affected by the experimental conditions. Therefore, the relationship between the intensity of the emission and the amount of sulphur-containing compounds varies considerably with the flow-rate of air and hydrogen in the burner.

INTRODUCTION

Flame photometry has been applied in gas chromatography in order to attain selective detection of the eluted gas components, by using the flame photometric detector (FPD)[1–6]. The use of the FPD for the selective detection of phosphorus and sulphur compounds was first introduced in 1966 by BRODY AND CHANEY[3]. Since that time, this detector has been used extensively for the determination of residues of phosphorus- and sulphur-containing pesticides[4,5].

The molecular emission due to the S_2 species from sulphur compounds is measured at 394 nm by a photomultiplier tube through an interference filter that transmits only in the region of 394 nm. The relationship between the response of the FPD and the amount of sulphur has been reported[3,6]. However, no systematic study has been published on the characteristics of this detector.

The present work is an attempt to clarify the characteristics and mechanism of the molecular emission from sulphur compounds in terms of the effect of some operating variables on the response of the FPD. By considering reaction kinetics, we can explain the relationship between the response of the FPD and the flame conditions.



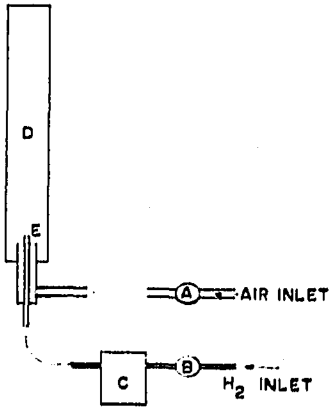


Fig. 1. Flame photometric detector. A, Photomultiplier tube; B, optical filter; C, lens; D, quartz tube; E, burner; F, mirror.

Fig. 2. Shielded burner. A and B, Flow meters; C, saturation cell; D, quartz tube (14 mm I.D.); E, stainless-steel burner tip.

EXPERIMENTAL

Apparatus

An FPD was equipped with an R268 photomultiplier tube operating at 720 V applied potential and a filter with maximum transmittance (32%) at 394 nm with a half-band width of 3.5 nm. This detector was supplied with air and hydrogen through flow meters, which were calibrated by using a soap-bubble flow meter. The detector was connected to a Yanagimoto G8 gas chromatograph (Fig. 1).

The intensity of the molecular emission due to the S_2 species from the sulphur compounds was measured by the FPD at varying flow-rates of air and hydrogen and over a wide range of concentrations of the sulphur compounds. The gas chromatograph was operated under the following conditions: column, glass tube (3 mm I.D. × 1.5 m) packed with 10% of PEG 20M on Celite 545 (80–100 mesh); column temperature, 143°; and carrier gas, nitrogen at 22 ml/min and 0.56 atm.

A shielded burner, shown in Fig. 2, was used to obtain the spectra. Hydrogen containing the vapour of the sulphur compound and air were supplied separately to the burner. The spectra of the flames in the burner were determined with a Shimadzu SV50AL spectrophotometer.

Reagents

Di-*n*-butyl sulphide and benzo[*b*]thiophene of guaranteed grade were used without further purification. Benzo[*b*]thiophene was dissolved in acetone to a concentration of 4.397×10^{-4} g/ml for the gas chromatographic experiments. This solution was further diluted to the concentrations required for the individual experiments.

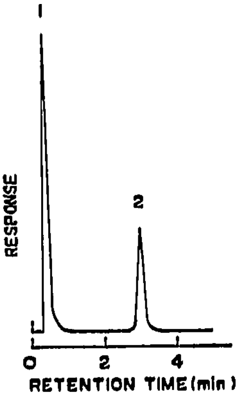


Fig. 3. Gas chromatogram: $2.30 \cdot 10^{-8}$ g of sulphur in 2 μl of acetone solution. 1, Acetone; 2, benzo[*b*]thiophene.

TABLE I

RESPONSE OF BENZO[*b*]THIOPHENE (PEAK HEIGHTS IN mm)

Air flow-rate (ml/min)	*M (ng as sulphur)*	*Hydrogen flow-rate (ml/min)*			
		116	*168*	*225*	*289*
128	207	1598	462	224	153.4
		1598	456	223	153.8
	69.0	276	71.2	33.9	19.8
		278	70.0	32.7	20.8
	23.0	42.7	10.1	4.3	1.9
		41.6	10.2	3.9	1.9
	7.67	6.5	—	—	—
		6.0	—	—	—
152	207	3814	1594	899	573
		3830	1594	885	589
	69.0	730	315	148.8	90.8
		727	316	152.8	91.2
	23.0	87.8	36.8	21.1	10.8
		88.0	39.8	20.3	11.9
	7.67	12.5	5.5	2.6	—
		13.2	4.7	—	—
174	207	5306	3450	1984	1334
		5370	3450	2010	1350
	69.0	896	558	352	234
		875	559	352	238
	23.0	102.4	79.6	46.8	33.6
		100.8	76.0	47.4	30.4
	7.67	14.2	10.5	5.4	4.0
		14.5	10.6	5.2	4.0
195	207	5917	8333	5318	3485
		5702	8378	5312	3427
	69.0	945	1184	746	501
		927	1184	743	513
	23.0	114.4	131.6	78.6	47.8
		115.0	129.2	74.8	48.4
	7.67	15.8	21.8	12.8	9.1
		17.0	19.5	12.5	8.0

RESULTS AND DISCUSSION

Fig. 3 shows a typical gas chromatogram obtained at flow-rates of 174 ml/min of air and 225 ml/min of hydrogen.

Intensity of emission

The intensity of the molecular emission, represented by peak heights, is given in Table I for various flame conditions and concentrations of the sulphur compound. The concentration of the sulphur compound in a carrier gas at the maximum of a peak is approximately proportional to the amount of sulphur compound injected, for a small sample size. The response to the sulphur compound of the FPD is, however, not linearly proportional to the concentration of the sulphur compound, but the relationship between the intensity of the emission and the concentration can be found from the following equation:

$$i_E = i_0 \, (M/M_0)^n \tag{1}$$

where i_E is the observed intensity of the molecular emission due to the S_2 species, M is the weight of sulphur injected and $M_0 = 2.30 \cdot 10^{-8}$ g of sulphur. The values of i_0 and n are both constant under given experimental conditions. Fig. 4 illustrates the relationship between the flow-rates of air and hydrogen and the value of the constant i_0 (a) and that of the constant n (b).

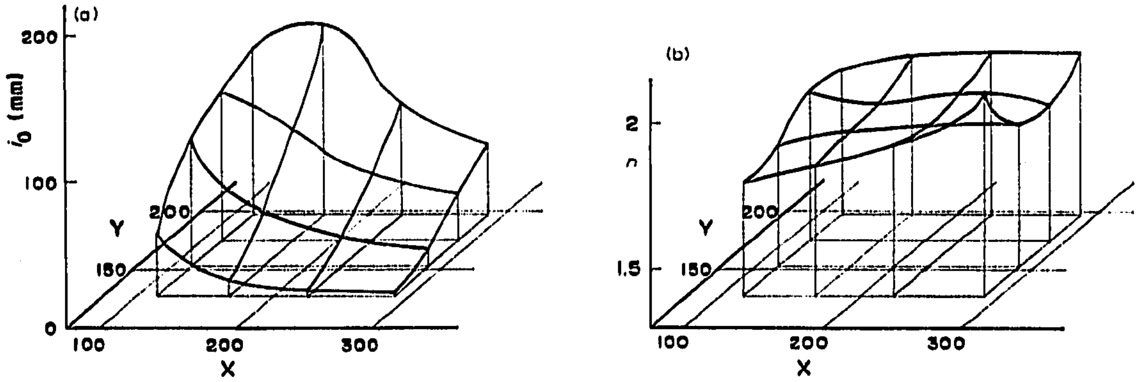


Fig. 4. Relationships between constant i_0 (a) and exponent n (b) and flow-rates of air and hydrogen. X-axis: hydrogen flow-rate (ml/min); Y-axis: air flow-rate (ml/min).

Effect of air in the flame

Complete molecular emission spectra of the S_2 species are shown in Fig. 5. The flow-rate of hydrogen was maintained constant at 60 ml/min, while the flowrate of air was varied between 100 and 200 ml/min. The intensity of the molecular emission decreased with increase in the ratio of the flow-rates of air to hydrogen in flames containing an excess of oxygen, and the following factors seem to affect the emission intensity:

(1) the temperature of the flame is too high to allow the formation of the S_2 species[6,7];

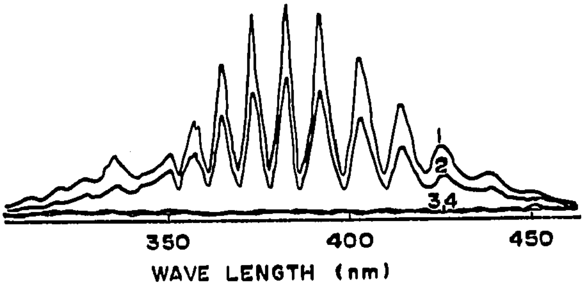


Fig. 5. Flame emission spectra of di-*n*-butyl sulphide. Hydrogen flow-rate, 60 ml/min. Air flow-rate: (1) 100 ml/min; (2) 135 ml/min; (3) 170 ml/min; (4) 200 ml/min.

(2) oxygen in the flame prevents the formation of the S_2 species from the sulphur atom by the competitive reactions:

$$S + \tfrac{1}{2}\, O_2 \rightarrow SO \qquad (2)$$

$$2\, S \rightarrow S_2 \qquad (3)$$

It can be seen from Fig. 5 that the decrease in the emission intensity is more affected by the latter factor than the former. Therefore, no characteristic response can be observed in the range of high air–hydrogen flow ratios (Table I).

Effect of hydrogen in the flame

In the range of low air–hydrogen flow ratios, a characteristic response of the FPD can be observed, as shown in Table I. The intensity of the emission decreased with increase in the hydrogen flow-rate at a constant flow-rate of air. The temperature of the air–hydrogen flame will decrease as the flow-rate of hydrogen increases. The intensity of the molecular emission is approximately proportional to the temperature of the flame[1].

Mechanism of emission

In a very hydrogen-rich flame, H_2S will be a dominant constituent of the products from organic sulphur-containing compounds[8].

$$\text{Sulfur compound} \xrightarrow{k_1} H_2S \qquad (4)$$

The formation of sulphur atoms is rapid[9]:

$$H_2S + H \overset{K_2}{\rightleftharpoons} HS + H_2 \qquad (5)$$

$$HS + H \overset{K_3}{\rightleftharpoons} S + H_2 \qquad (6)$$

The simplest mechanism involves a rate-determining step that is a three-body recombination:

$$S + S + M \xrightarrow{k_4} S_2{}^* + M \qquad (7)$$

(where M is the third body) and which is followed by

$$S_2{}^* \longrightarrow S_2 + h\nu \qquad (8)$$

The S_2 species reacts as follows:

$$S_2 + H + H \longrightarrow S_2^* + H_2 \qquad (9)$$

$$S_2^* \longrightarrow S_2 + h\nu \qquad (10)$$

The concentration of H_2S corresponds with that of the sulphur compound, provided that H_2S is produced predominantly and stoichiometrically in reaction 4.

It can be assumed that

(1) the reactants distribute uniformly in a cross section of a flame;

(2) sulphur atoms are rapidly formed in a reaction zone;

(3) reaction 7 is a rate-determining step.

The concentration of sulphur atoms is given by:

$$[S] = K_2K_3 \frac{[H_2S]\,[H]^2}{[H_2]^2} \qquad (11)$$

$$= K\,[H_2S] \qquad (12)$$

The rate of the formation of the S_2 species is given by reaction 7, and then the concentration of S_2 is

$$[S_2] = \frac{aK}{2}\left(1 - \frac{1}{2aKk_4[M]t + 1}\right) \qquad (13)$$

for a reaction time of t sec, where a is the initial concentration of the sulphur compound and [M] the concentration of the third body. The total number of the S_2 species is given by

$$N_{S_2} = \frac{Av}{4k_4[M]}\,\{x - \ln(x + 1)\} \qquad (14)$$

where A is the cross section of a flame, v the velocity of S_2 rising in a flame and $x = 2aKk_4[M]t$.

The intensity of the emission in reaction 8 is

$$I_{S_2} = [S_2] \qquad (15)$$

On the other hand, the intensity in reaction 10 is

$$I_{S_2} \propto N_{S_2} \qquad (16)$$

The calculated intensity can be compared with the molecular emission intensity observed.

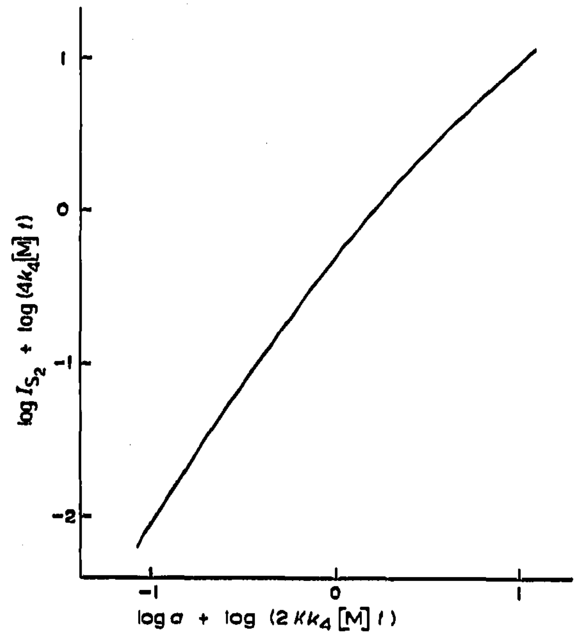
Provided that the emission in reaction 10 contributes little to the over-all molecular emission of S_2, the theoretical relationship between a and I_{S_2} is shown in Fig. 6. The exponent n can be calculated by the following equation:

$$n = \frac{d(\log I_{S_2})}{d(\log a)} = 1 + \frac{1}{2aKk_4[M]t + 1} \qquad (17)$$

Fig. 7 shows the variation of n. The value of n decreases with increase in the concentration, a, from 2 to 1.

Figs. 6 and 7 indicate the following criteria:

(1) When the air–hydrogen flow ratio is constant, an increase in the total flow-rate leads to a lower intensity of the molecular emission because the concentration of the sulphur compound decreases.



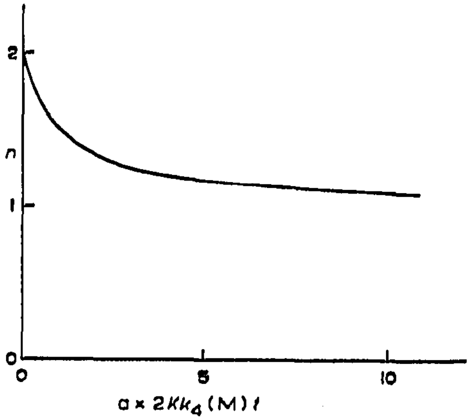


Fig. 6. Theoretical relationship between log I_{S_2} and log a.

Fig. 7. Theoretical relationship between exponent n and initial concentration of sulphur atoms, a.

(2) The value of n varies with the flame conditions and is inversely proportional to the intensity of the molecular emission.

(3) Because of the decrease in the concentration of the sulphur compound, the intensity of S_2 emission decreases and the value of n becomes larger with increasing hydrogen flow-rate.

These criteria can satisfy the effect of some operating variables on the intensity measured by the FPD. Consequently, the mechanism of the molecular emission due to the S_2 species from the sulphur compound can be interpreted as follows. Reactions 4–7 occur in an air–hydrogen flame and reaction 7 is the rate-determining step. However, reaction 9 occurs to only a small extent. Eqn. 15, the relationship between the intensity of the S_2 molecular emission and the amount of sulphur compound, therefore provides fairly complex functions of flow-rates of air and hydrogen, and of concentration of sulphur-containing compounds. Finally, the response of the FPD is shown by this mechanism to be proportional to about the second power of the amount of sulphur compounds, for small sample size[10].

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