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INTERFERENCES OF S_2 MOLECULAR EMISSION IN A FLAME PHOTO-METRIC DETECTOR

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SUMMARY

   The presence of gaseous non-sulphur-containing organic compounds in a carrier gas causes a decrease in the response of flame photometric detectors. The way in which such organic compounds interfered with the response of sulphur-containing compounds in the flame photometric detector was determined. The interference by organic compounds increases exponentially with increase in concentration of the substances. The interference by an organic compound is, however, independent of the concentration of sulphur-containing compounds in the presence of a certain concentration of the organic compound, and it was found that the decrease in the response of a flame photometric detector can be explained by inactivation of the excited S_2 species by its combination or collision with an organic compound and/or its degradation products.

INTRODUCTION

   Flame spectrophotometry has been used extensively for the analysis of sulphur-containing compounds[1–12], which give rise to the S_2 band in a hydrogen-rich flame. The emission is highly dependent on the nature of the flame. The effect of other gaseous substances on the molecular emission of the S_2 species has been reported by Crider[1], Rupprecht and Phillips[5] and Perry and Carter[9], who found that the presence of other gaseous organic compounds in the carrier gas used to carry sulphur compounds into a flame photometric detector (FPD) led to a decrease in response, compared with that observed in their absence. Sulphur emission is obscured by the presence of hydrocarbons (methane, ethane, propane, butane and 2-methylpentane), alcohols (isobutanol and 3-pentanol) and carbon dioxide.
   The object of this work was to explore the characteristics of the interference of organic compounds on the S_2 molecular emission. The interference was studied with an FPD and a spectrophotometer at various concentrations of organic compounds. The dependence of quenching on the concentration of organic compounds and the nature of the interference are discussed.

EXPERIMENTAL

Apparatus

The device with which the emission of S_2 at 394 nm was measured was identical with that described in the previous paper[13]. Organic compounds were passed in a stream of hydrogen through a buffer tank of 500 cm³ volume in order to study the interference that they caused.

The spectra of flames in a burner shielded with a 9.5 mm quartz tube were obtained with a Shimadzu SV50AL spectrophotometer. Air and hydrogen were supplied to this burner, the hydrogen containing the vapour of the sulphur compound (di-*n*-butyl sulphide) and organic compounds being introduced into the air stream.

The concentrations of the compounds added to the hydrogen stream were determined with a Shimadzu GC-1C gas chromatograph equipped with a flame ionization detector. The chromatographic column consisted of a 3 mm I.D. × 1 m copper tube packed with 10% of PEG 20M on 80–100 mesh Celite 545.

Reagents

Di-*n*-butyl sulphide and benzo-[*b*]-thiophene of guaranteed grade were used. Benzo-[*b*]-thiophene was dissolved in acetone to a concentration of $2.678 \cdot 10^{-3}$ g/ml for gas chromatographic experiments, and this solution was further diluted as required. The other chemicals used were of reagent grade.

RESULTS AND DISCUSSION

Spectrum of the S_2 band

Fig. 1 shows the spectra of the molecular emission of S_2 from di-*n*-butyl sulphide in the presence of various concentrations of an organic compound (acetone) in the air stream. The presence of the acetone decreased the intensity of the emission, and this decrease is independent of wavelength and almost uniform over the whole wavelength range.

Interference by organic compounds

The interference with the molecular emission of S_2 was measured with an FPD
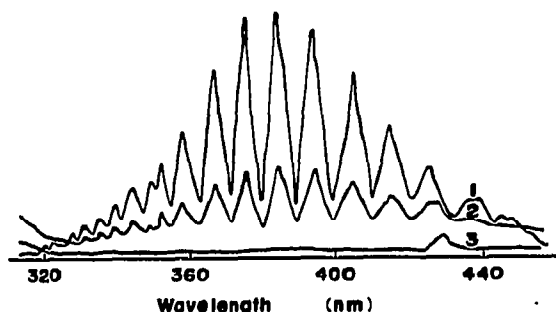

Fig. 1. Emission spectrum of S_2 species obtained by introducing $6 \cdot 10^{-7}$ mole/min of di-*n*-butyl sulphide into the hydrogen stream and acetone into the air stream and measuring under the following conditions: response, 1; slit width, 0.4 mm; air flow-rate, 171 ml/min; H_2 flow-rate, 343 ml/min; acetone flow-rate: (1), 0 mole/min; (2), $1.2 \cdot 10^{-4}$ mole/min; (3), $2.3 \cdot 10^{-4}$ mole/min.

in the presence of volatile organic compounds in the hydrogen stream. The intensity ratio, Φ, of the S_2 emission is defined as follows:

$$\Phi = \frac{\text{Response of FPD (compound present)}}{\text{Response of FPD (compound absent)}} \qquad (1)$$

Benzo-[b]-thiophene was used as the sulphur-containing compound. The interference with the molecular emission caused by the organic compounds depends on the concentration of the compounds. The nature of the interference caused by ethanol and acetone for two different concentrations of benzo-[b]-thiophene is shown in Fig. 2. The decrease in the emission for the two concentrations of benzo[b]-thiophene with increase in the concentration of the organic compounds is similar for both compounds, i.e., the interference with the emission is almost independent of the concentration of the sulphur-containing compound.
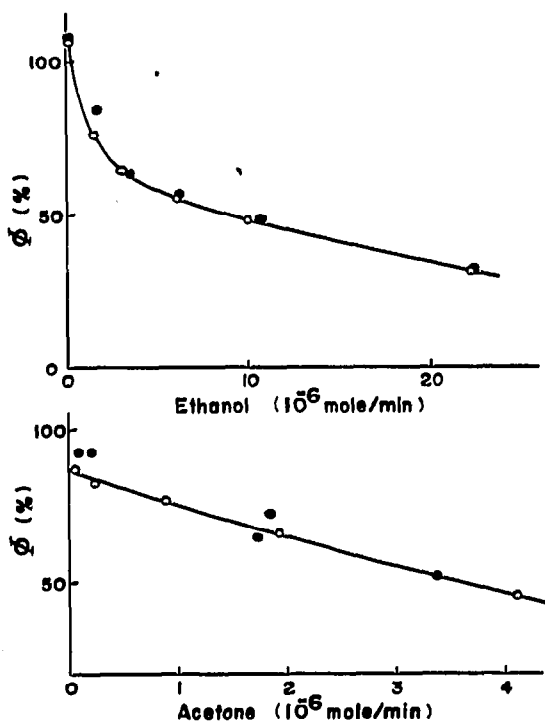

Fig. 2. S_2 emission quenching: relationship between Φ and flow-rates of interfering substances (ethanol and acetone) in the FPD. Air–hydrogen flame: air flow-rate, 171 ml/min; H_2 flow-rate, 343 ml/min. Flow-rate of benzo-[b]-thiophene at the maximum point of peak: $\bigcirc$, $2.28 \cdot 10^{-9}$ mole/min; $\bullet$, $7.02 \cdot 10^{-9}$ mole/min.

Fig. 3 shows the interferences caused by four organic compounds, and can be seen to be similar in each instance. An exponential decrease in the emission intensity is caused by an arithmetic increase in the concentration of the organic compounds.
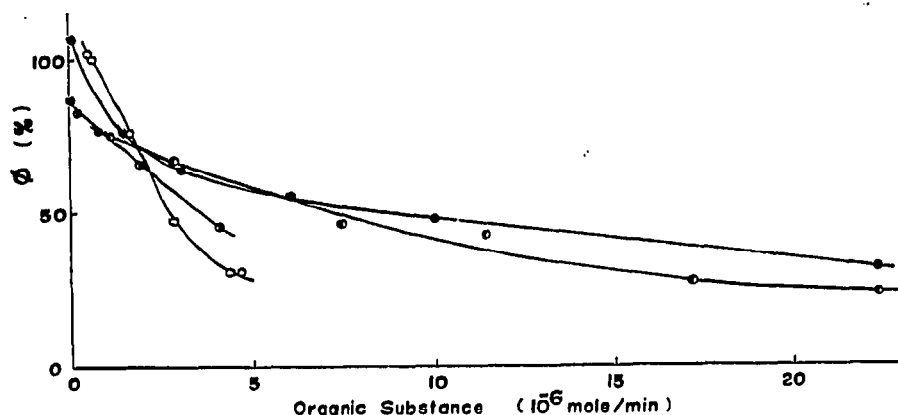
Fig. 3. S_2 emission quenching. Flame conditions; air flow-rate, 171 ml/min; H_2 flow-rate, 343 ml/min. Interfering substances: ○, cyclohexane (flow-rate of benzo-[b]-thiophene, $f_s = 2.59 \times 10^{-9}$ mole/min); ◌, acetone ($f_s = 2.28 \cdot 10^{-9}$ mole/min); ◐, methanol, ($f_s = 5.18 \cdot 10^{-9}$ mole/min); ●, ethanol, ($f_s = 2.28 \cdot 10^{-9}$ mole/min).

Interference with the S_2 molecular emission

The processes involved in the molecular emission of S_2 from sulphur-containing compounds are as follows[13]

$$\text{Sulphur compound} \rightarrow H_2S \tag{i}$$

$$H_2S + H \overset{K_2}{\rightleftharpoons} HS + H_2 \tag{ii}$$

$$HS + H \overset{K_3}{\rightleftharpoons} S + H_2 \tag{iii}$$

$$2\,S + M \overset{k_4}{\rightarrow} S_2^* + M \tag{iv}$$

$$S_2^* \rightarrow S_2 + h\nu \tag{v}$$

$$S_2 + H + H \rightarrow S_2^* + H_2 \tag{vi}$$

$$S_2^* \rightarrow S_2 + h\nu \tag{vii}$$

The emission in reaction vii contributes little to the overall S_2 molecular emission.

The following effects are probably responsible for the interference caused by organic compounds.

(1) An organic compound or its degradation products may absorb light due to the molecular emission of S_2. From Fig. 1, the interference caused in the molecular emission is found not to be due to the absorption of light by an organic compound, since the decrease in emission was uniform over the whole wavelength range.

(2) The presence of an organic substance may cause an increase in the flame temperature, which may become too high to allow the formation of the S_2 species. In this study, a hydrogen-rich flame was used so that only an increase in flame temperature could be caused by contamination with organic compounds. On the contrary, the addition of such compounds will cause a decrease in temperature owing to an increase in heat capacity.

(3) Hydrogen atoms in a flame may combine with scavengers (Sc), and the following reaction will reduce hydrogen atoms:

$$H + Sc \xrightarrow{k_8} H\text{-}Sc \qquad \text{(viii)}$$

so that the concentration of sulphur atoms may become small.

In this case, the scavengers are organic compounds or their degradation products (radicals and ions).

The concentration of hydrogen atoms is given by

$$[H] = [H]_0 \exp(-k_8[Sc]t) \qquad (2)$$

where t is the reaction time and $[H]_0$ is the concentration of hydrogen atoms in the absence of scavengers. The concentration of sulphur atoms is given by

$$[S] = K_2 K_3 \frac{[H_2S]\,[H]_0{}^2}{[H_2]^2} \exp(-2k_8[Sc]t) \qquad (3)$$

The decrease in the concentration of sulphur atoms is dependent on [Sc]. Provided that nothing except the concentration of hydrogen atoms changes in the presence of scavengers, then the extent of the decrease in the number of sulphur atoms is independent of the concentration of the sulphur compound. The ratio of the decrease in the number of S_2 species at the various concentrations of sulphur compounds was therefore shown to be constant in the presence of a certain concentration of an organic compound. The intensity of the S_2 emission is given by

$$I_{S_2} = I_0[S]^n \qquad (4)$$

where I_0 and n are both constant. The value of Φ is given by

$$\Phi = \frac{I_{S_2}}{I_{S_2,0}}$$
$$= \exp(-2nk_8[Sc]t) \qquad (5)$$

When ethanol is used as the scavenger (Fig. 2), the value of k_8 calculated from eqn. 5 is 10^7 cm³ mole⁻¹sec⁻¹. This value is much lower than rate constants for the recombination reactions (10^{14} cm³mole⁻¹sec⁻¹), e.g., $H + C_2H_6$, $H + C_3H_8$, $H + C_4H_{10}$, etc.[14].

(4) Sulphur atoms formed in reaction iii may combine with scavengers. The competitive reactions will prevent the formation of the S_2 species:

$$2S + M \xrightarrow{k_4} S_2^* + M \qquad \text{(iv)}$$

$$S + Sc \xrightarrow{k_9} S\text{-}Sc \qquad \text{(ix)}$$

It is assumed that the concentrations of organic compounds and their degradation products are much less than that of the third body (M). A qualitative consideration of these reactions must account for the effect of scavengers. The reaction of S to produce S_2 is second-order and the reaction of S and Sc to produce S–Sc is pseudo-first-order, so that making the concentration of sulphur atoms low will tend

to decrease more rapidly the chance of the occurrence of the reaction to form S_2 than that to form S–Sc. Therefore, the conversion of the sulphur atoms into the S_2 species decreases with the decrease in the concentration of sulphur atoms in these competitive reactions. In this mechanism, the value of Φ is shown to decrease with the decrease in the concentration of sulphur-containing compounds. However, the value measured is independent of the concentration of the sulphur-containing compound.

(5) The S_2 species in the excited states may be inactivated by collision with scavengers. The intensity of the molecular emission will decrease as the number of excited S_2 species (S_2^*) decreases by reaction x:

$$S_2^* + Sc \xrightarrow{k_{10}} S_2 + Sc \qquad\qquad (x)$$

The concentration of excited S_2 species that actually emit light is given by

$$[S_2^*] = [S_2^*]_0 \exp(-k_{10}[Sc]t) \qquad\qquad (6)$$

where $[Sc] \gg [S_2^*]$, t is the mean lifetime of the excited S_2 species and $[S_2^*]_0$ is the concentration of the excited S_2 species in the absence of scavengers. The decrease in the ratio of the concentration of the excited S_2 followed by chemiluminescence is independent of the magnitude of $[S_2^*]_0$ for a certain concentration of scavengers. The value of Φ is given by

$$\Phi = \exp(-k_{10}[Sc]t) \qquad\qquad (7)$$

$[S_2^*]$ decreases exponentially with $[Sc]$.

When ethanol is used as the scavenger (Fig. 2), the value of k_{10} calculated from eqn. 7 is 10^{14} $cm^3mole^{-1}sec^{-1}$ where t is 10^{-7} sec (ref. 15). This value can be compared with the rate constants for re-combination in a flame[14].

CONCLUSION

The magnitude of the interference caused by organic compounds on the molecular emission due to the S_2 species increases exponentially with the concentration of volatile organic compounds. The value of Φ is independent of the concentration of sulphur-containing compounds in the presence of a certain concentration of the organic compound. The decrease in the intensity of the S_2 molecular emission is based on the inactivation of the excited S_2 species by combination or collision with an organic compound and/or its degradation products.

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