

Gas Chromatography of Selenium Dioxide Using 2- and 4-Stilbazole as Derivatising Reagents

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Summary: Thermogravimetry (TG) and Differential Thermal Analysis (DTA) of 2-(2'-pyridyl)selenonaphthene (2-PSeN) and 2-(4-pyridyl)selenonaphthene (4-PSeN) prepared by the reactions of selenium dioxide and 2- and 4-stilbazole were recorded. Both of the seleno-derivatives are fairly volatile and loss in weight is almost quantitative upto 300°C. The selenonaphthenes are easily eluted on stainless steel OV101, 3% on chromosorb column at 200°C. The effects of heating time and temperature on the formation of seleno-derivatives are reported.

Introduction

Selenium is a nutrient for animals [1], but its excess causes toxicosis, thus requiring to determination at trace levels. Selenium can be determined spectrophotometrically [2] and fluorimetrically [3,4], but the Gas Chromatographic determination of selenium as piazsenol using halogen and nitro substituted 1,2-diaminobenzene have proven of value for the determination of selenium in different substances [5,7].

Buchler *et al* [8] observed that 2-stilbazole and 4-stilbazole react with selenium dioxide to form 2-(2'-pyridyl)selenonaphthene (I) (2-PSeN) and 2-(4-pyridyl)selenonaphthene (II) (4-PSeN) about 20% yield. In the present work, the volatility and thermal stability of selenonaphthene have been evaluated for their possible use for gas chromatographic determination of selenium dioxide.

Experimental

2-stilbazole and 4-stilbazole, 2-(2'-pyridyl)selenonaphthene (2-PSeN) and 2-(4-pyridyl)selenonaphthene were prepared as reported by Chiany and Hortung [9], and Buchler *et al* [8].

DTA and TG of 2-PSeN and 4-PSeN were recorded on a Shimadzu TG-30 Thermal Analysis using a heating rate of 15°C/min and nitrogen flow rate of 50 cm³/min.

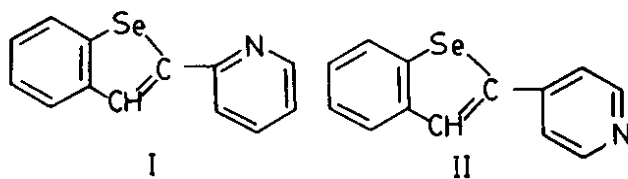


Fig. 1: Structural diagrams of selenonaphthene.

A Hitachi 163 Gas Chromatograph equipped with flame ionization detector and stainless steel column (2mx3mm) packed with OV101, 3% on Chromosorb WHP 80-100 was used throughout the study.

Quantitative Studies

Varying amounts of selenium dioxide (25-500mg) was mixed and heated at 140-50°C with 2-stilbazole (1g) and at 180°C with 4-stilbazole (1g) for 40 min. The mixture was dissolved, filtered and volume adjusted to 25 ml with methanol. 2µl of the solution was injected in the gas chromatograph at column temperature 200°C, injection port 220°C and Nitrogen flow rate 26 to 30 cm³/min.

Results and Discussion

TG of 2-(2'-pyridyl)selenonaphthene (4mg) indicated loss in weight started by 140°C and loss of 98% by 310 with maximum rate of loss at 260°C. DTA

shows a melting endotherm at 140°C and loss of 98% by 310 with maximum rate of loss at 260°C DTA shows a melting endotherm at 140°C, followed by a vaporisation endotherm at 290°C. Similarly TG and DTA with 3.8mg of 2-(4-pyridyl) selenonphthene showed loss in weight started by 180°C and complete loss by 285°C with maximum rate of loss at 230°C. DTA shows a melting endotherm at 155°C, followed by a vaporisation endotherm at 235°C (Fig. 2 & 3).

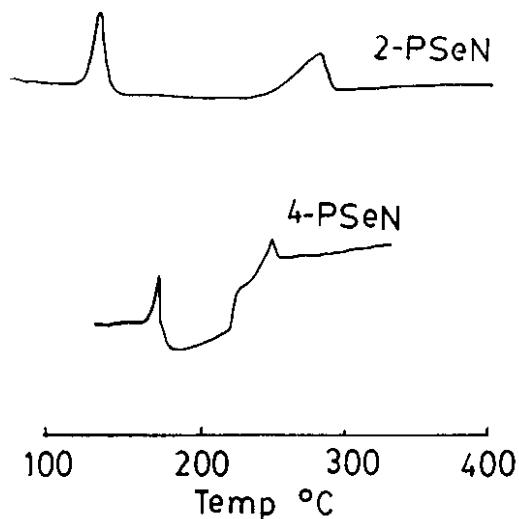


Fig. 2: DTA curve of 2-PSeN and 4-PSeN.

Keeping in view the reasonable thermal stability and volatility of the selenium derivatives, suitable stationary phase OV101, 3% on chromosorb WHP 80-100 mesh size was selected a column temperature of 200°C, injection port temperature 220°C and nitrogen flow rate of 30 cm³/min proved to be sufficient to obtain symmetrical peaks with base line separation between derivatizing reagent and selenonaphthene, with retention times of 5-10 min and 5-25 min. for 4-PSeN and 2-PSeN respectively.

In order to confirm if the response of the detector was linear with the amount of selenonaphthene injected, known amounts of the pure 2-PSeN in methanol were injected and average peak height of at least two injections was measured, and linear calibration curves were obtained in the range 0.5-5.5µg of PSeN with detection limit, of 0.1µg of metal deriva-tive.

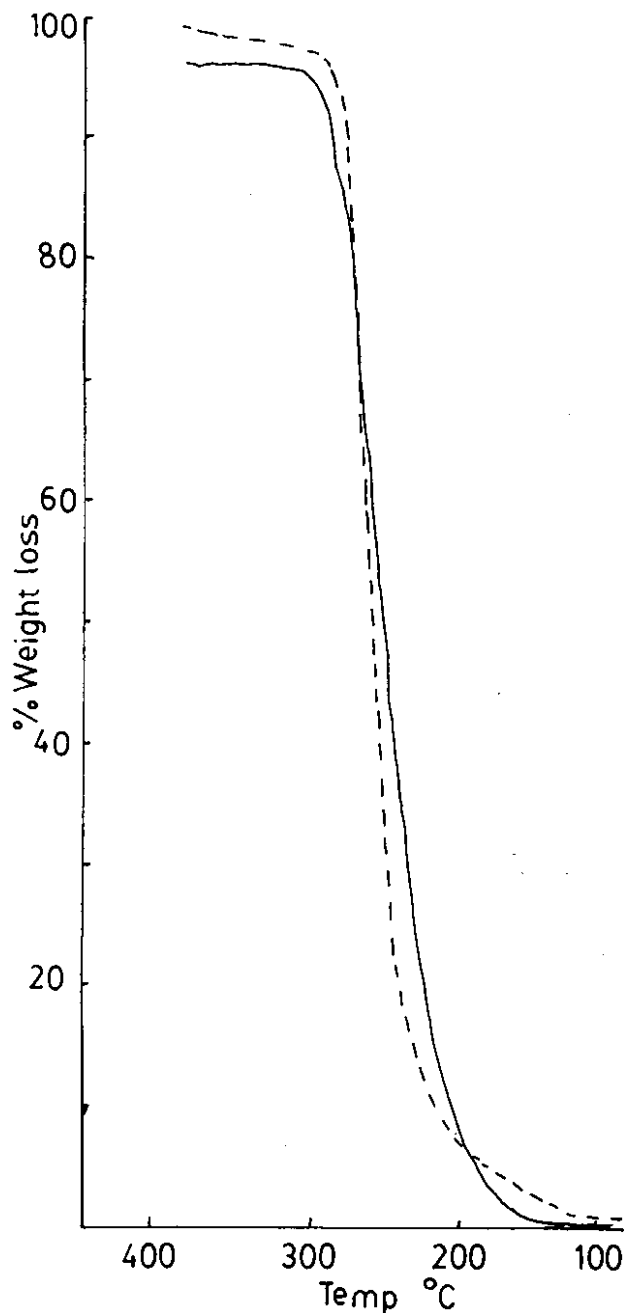


Fig. 3: TG curves _____ 2-PSeN and - - - - - 4PSeN.

In order to develop a method for the gas chromatographic determination of selenium based on the formation of 2-PSeN or 4- PSeN from the reaction of 2-stilbazole or 4-stilbazole with selenium dioxide, 0.2g selenium dioxide was heated with 0.5g of 2-stilbazole and 4-stilbazole for 40 min. In the

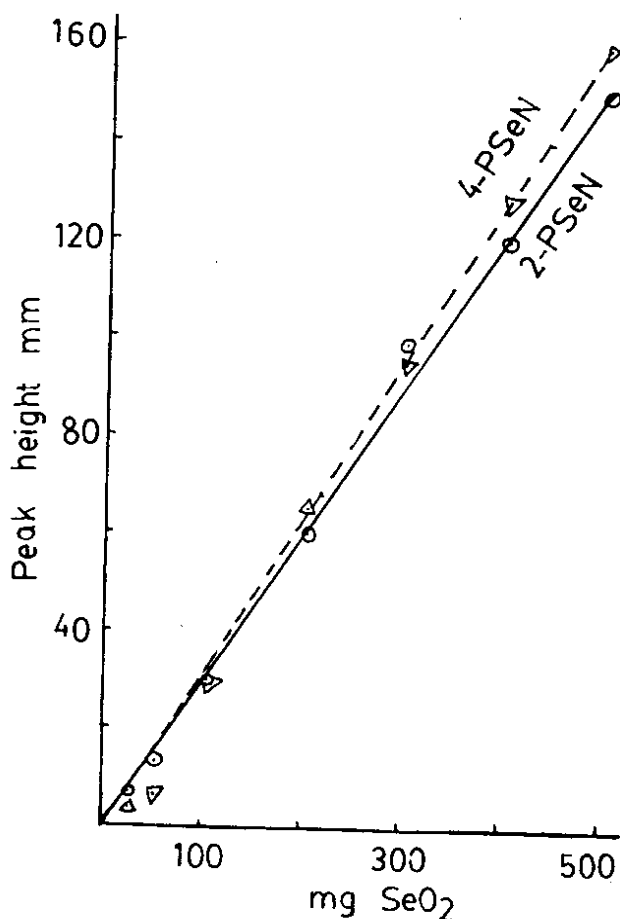


Fig. 4: Linear Calibration plot of SeO_2 for the formation of 2-PSeN and 4-PSeN.

temperature range of 125-250°C intervals, it was observed the maximum formation of 2-PSeN was within the range of 140-150°C, and 4-PSeN required 175-190°C. The effect of heating time does not seem to be critical and seleno-derivative remained constant between 30-60 min and heating time of 40 min. proved to be optimum. However, only about 20% of selenium can be converted to selenonaphthene and remaining selenium is reduced and precipitated out as Selenium (o).

In order to ascertain if the amount of selenonaphthene formation and GC elution is linear with the selenium dioxide added, different amounts of solid selenium dioxide were heated together with 2 or 4-stilbazoles and their methanolic solutions were injected to gas chromatograph at optimized conditions. Linear calibration curves in the range of 25-500

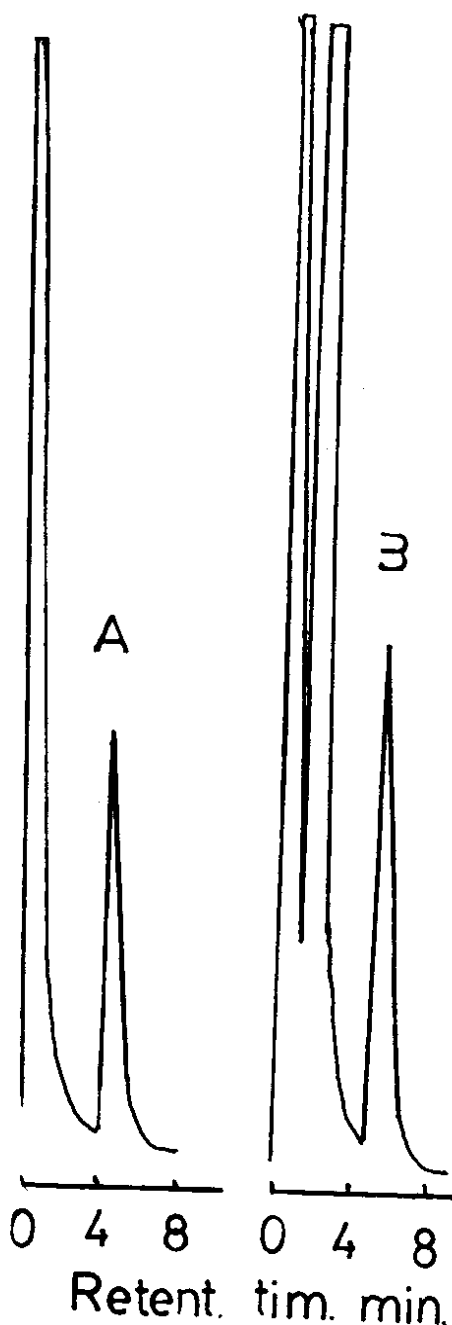


Fig. 5: Chromatographic response of (A) 5ug of 2-PSeN (B) 200mg SeO_2 after derivatization to 2-PSeN dissolved in 25ml methanol and 2 μ l injected.

Column 2mx3mm packed with OV101, 3% on chromosorb WHP 80-100, injection post 220°C, Nitrogen flow rate (A) 30cm³/min (B) 26cm³/min. Chart speed 2.5mm/min.

mg of selenium dioxide were obtained with both of the derivatizing reagents (Fig. 5). The limit of detection of Selenium dioxide was 6mg when final volume of the methanolic solution was adjusted to 25 ml after

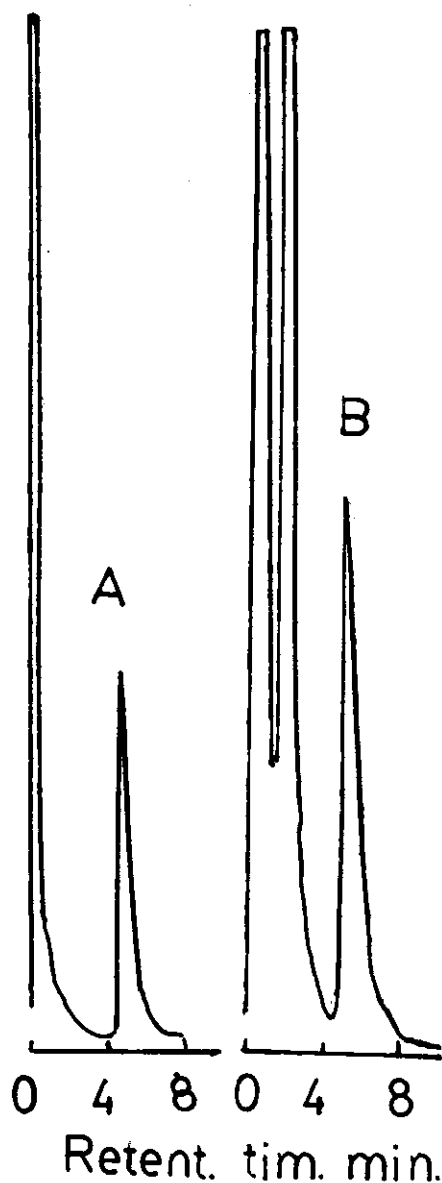


Fig. 6: Chromatographic response of (A) 3 μ g of 4-2PSeN (B) 200mg of SeO₂ after derivatization to 4-PSeN dissolved in 25ml methanol and 2 μ l injected.

Column 2m \times 3mm packed with OV101, 3%, on chromosorb WHP 80-100 injection port 220. Nitrogen flow rate (A) 30cm³/min (B) 26cm³/min. chart speed 2.5mm/min. (Detector range 10² Attenuation 16).

derivatization and 2 μ l methanolic solution was injected.

Finally when 1.0g of 2- and 4-stilbazole was mixed and heated together with 0.2g of Al₂O₃, Bi₂O₃, PbO, Sb₂O₃, SnO₂, HgO, Hg₂O, ZnO, CdO, Fe₂O₃,

MnO₂, V₂O₅, Cr₂O₃, GaO₂, As₂O₃, in the temperature range of 140-200°C for 40 min. none of the metal ions formed a volatile metal derivative which eluted from the gas chromatographic column under the conditions optimized for selenonaphthenes. However, when a mixture of equal amount of SeO₂ and the metal oxides was heated together with 2 or 4-stilbazole and their methanolic solution was injected to GC, a decrease in peak height of the selenonaphthene was observed, probably due to diluting effect of the solid metal oxide on the formation of 2-PSeN and 4-PSeN.

Conclusion

2-PSeN and 4-PSeN show excellent thermal stability and volatility with favourable gas chromatographic properties and detection limits at μ g levels per injection using an FID. The derivatizing reagents are highly promising for the gas chromatographic determination of selenium dioxide but suffer from the defect that only a part of the SeO₂ could be converted to selenonaphthene.

Reference

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