

CHROM. 9899

GAS CHROMATOGRAPHIC DETERMINATION OF STYRENE AS ITS DIBROMIDE

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(Received December 3rd, 1976)

SUMMARY

The selective and sensitive gas chromatographic determination of trace amounts of styrene was studied. Styrene was converted into styrene dibromide by reaction with bromine, and the latter was detected with an electron-capture detector. The minimum detectable amount of the dibromide was about 0.01 ng and the sensitivity to the dibromide was about 500 times higher than the sensitivity of a flame-ionization detector to the styrene monomer. Dodecene-1 and *o*- and *m*-cresol gave the greatest interference, but the cresols could easily be removed by reaction with a small amount of a dilute aqueous alkaline solution. The application to a practical specimen, namely urban air, is described.

INTRODUCTION

Styrene in air at parts per million levels has been determined by ultraviolet, infrared nitration and gas chromatographic methods¹⁻⁵. However, the styrene at the odour-threshold level (parts per billion*) is not detected with these methods. As the concentration of styrene in environmental air is too low to be measured by gas chromatography using a flame-ionization detector (FID), pre-concentration techniques are necessary. Spinner⁶ reported a procedure for the rapid and easy analysis of paper-board odours based on gas chromatography with a porous polymer pre-column to adsorb the volatile organics, which contains styrene. However, the lack of specificity with respect to styrene presents many problems. The presence of trace amounts of styrene in the Paris atmosphere and gasoline⁷ and in the exhaust gas from simple hydrocarbon fuels⁸ has also been investigated by gas chromatography-mass spectrometry. However, this technique requires complex and expensive instrumentation.

The purpose of this work was to achieve the selective and sensitive gas chromatographic determination of styrene. The styrene is converted into styrene dibromide by reaction with bromine and the dibromide is detected using an electron-capture detector (ECD). The method was applied to the analysis of trace amounts of styrene in urban air.

* Throughout this article the American billion (10⁹) is meant.

EXPERIMENTAL

Reagents

Styrene, minimum assay 95%, stabilized with 0.003–0.004% of *tert.*-butylcatechol (chemical grade), and bromine, assay 99.0–100.5%, of guaranteed reagent grade, were obtained from Wako (Osaka, Japan). *n*-Hexane, guaranteed grade, was obtained from Tokyo Kasei Kogyo (Tokyo, Japan). All other compounds were obtained from Takachiho Trading (Tokyo, Japan), PolyScience (Niles, Ill., U.S.A.), Tokyo Kasei Kogyo, Wako, Katayama Chemical (Osaka, Japan) and Merck (Darmstadt, G.F.R.).

Preparation of styrene dibromide

Large-scale derivative-formation reaction. Styrene dibromide was prepared by the direct reaction of styrene with bromine in chloroform. The precipitate (crystals) formed were isolated by filtration, washed with water until the yellowish colour of bromine disappeared and with cold ethanol and dried over silica gel in a vacuum desiccator. The dibromide (melting point 73°) was then sufficiently pure for gas chromatography, as shown in Fig. 1.

Submicrogram derivative-formation reaction. A 2–400- μ l volume of 1% bromine water was added to styrene (10 μ g) in solution in *n*-hexane (25 ml). After the bromination reaction, the excess of bromine was removed by bubbling a stream of nitrogen through the solution at 60 ml/min for about 5 min, and 1 μ l of the product was analyzed with an ECD.

Gas chromatography

Two gas chromatographs were used, a Shimadzu Model GC5AP₅F equipped with an FID and a Shimadzu Model GC5AIE equipped with an ECD. The gas chromatographic column consisted of a 1 m \times 3 mm I.D. glass tube, packed with 3% OV-17 on Chromosorb W, 60–80 mesh, acid-washed and silanized (Wako).

The chromatographic conditions for the FID were: carrier gas (nitrogen) flow-rate, 55 ml/min; air and hydrogen flow-rates, 1.0 l/min and 50 ml/min, respectively; column temperature, 140°; injection port and detector temperature, 180°.

A ⁶³Ni (10 mCi) ECD was used at 250° with a pulsed voltage (48 V, pulse width 8 μ sec) and a carrier (nitrogen) flow-rate of 55 ml/min. The temperatures of the column and injection port were as for the FID.

Response factor (F_i) of styrene dibromide in ECD

For the determination of the response factor^{9–12} of styrene dibromide, a sample solution was prepared by dissolving the dibromide ($3.8 \cdot 10^{-8}$ mole) and *p*-dibromobenzene ($4.2 \cdot 10^{-8}$ mole) as an internal standard in 25 ml of *n*-hexane. The F_i value was calculated from the equation

$$F_i = A_s/W_s \times W_i/A_i$$

where A_s and W_s are the peak height (logarithm) and weight, respectively, of the internal standard and A_i and W_i are the peak height (logarithm) and weight, respectively, of styrene dibromide.

RESULTS AND DISCUSSION

Preparation of standard graph

In the preparation of the standard graph for styrene dibromide, a sample solution was prepared by dissolving 1–10 μg of the dibromide in 25 ml of *n*-hexane. The response (peak height) of the ECD to styrene dibromide was a rectilinear relationship in the range 0.02–0.8 ng. The minimum detectable amount of the dibromide was about 0.01 ng, and the derivative therefore has sufficient electron-capturing properties. The sensitivity to the dibromide was about 500 times higher than the sensitivity of the FID to the styrene monomer.

Fig. 1 shows typical gas chromatograms of styrene dibromide obtained by using the FID and ECD. The gas chromatographic properties of the dibromide were excellent in each instance.

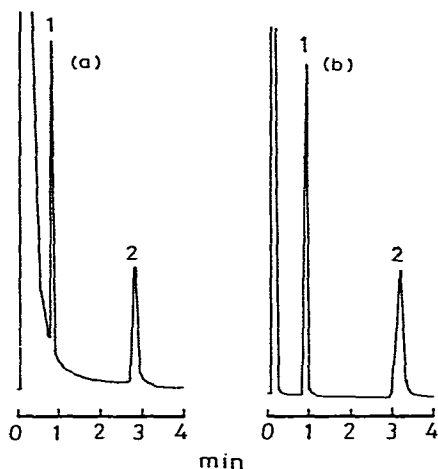


Fig. 1. Gas chromatograms of styrene dibromide. (a) FID. 1 = Internal standard (0.4 μg); 2 = styrene dibromide (0.4 μg). (b) ECD. 1 = Internal standard (0.4 ng); 2 = styrene dibromide (0.4 ng).

Response factor (F_i) of styrene dibromide

The reproducibility and the uniformity of the response for styrene dibromide were evaluated with respect to the F_i value. The F_i value and its standard deviation (0.88 ± 0.00) showed good reproducibility and uniformity.

Evaluation of reaction conditions

The yield of styrene dibromide produced was evaluated with respect to the molar ratio of bromine to styrene and the reaction time and reaction temperature.

As shown in Figs. 2–4, a completely quantitative reaction took place with a molar ratio of bromine to styrene of 20:1, a reaction temperature of 40° and a reaction time of 5 min.

Interference studies

Bromine has a high reactivity towards many organic compounds, *e.g.*, alkenes, alicyclics, amides, amines, aromatic hydrocarbons, carboxylic acids, ketones and

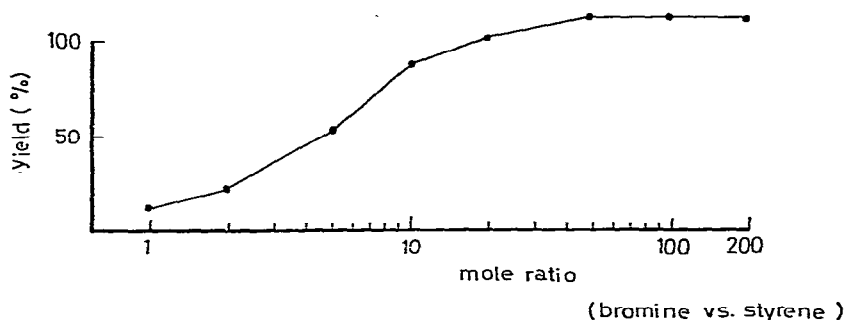


Fig. 2. Effect of molar ratio of bromine to styrene on yield of styrene dibromide. A volume of 2–400 μl of 1% bromine solution was added to styrene (10 μg) in *n*-hexane (25 ml). The reaction was carried out at 40° for 30 min.

phenols^{13–14}, which can lead to problems in the analysis of styrene by this bromination method. Therefore, 138 representative compounds (22 alkanes, 33 alkenes, 2 alicyclic hydrocarbons, 15 aromatic hydrocarbons, 29 alcohols, 14 aldehydes, 12 ketones, phenol and 10 phenols) were tested under the following conditions. The reaction of these compounds (about 10 μl or 10 mg of each compound was taken, this amount being about 25 times that of bromine) with bromine (using 80 μl of 1% bromine water) was carried out in 25 ml of *n*-hexane at 40° for 10 min. After the reaction was complete, 1 μl of the *n*-hexane solution was analysed with an ECD. Many compounds gave peaks with the same elution position as styrene dibromide. The results obtained are listed in Table I.

When the bromination of styrene (10 mg) was carried out under the above conditions, 100 μg of styrene dibromide were produced. Therefore, if 1 μl of the *n*-hexane solution was analysed, 4 ng of styrene dibromide was contained in the solution.

Dodecene-1 and *o*- and *m*-cresols gave the greatest interferences, but the cresols could easily be removed by reaction with small amount of a dilute aqueous alkaline solution without loss of styrene.

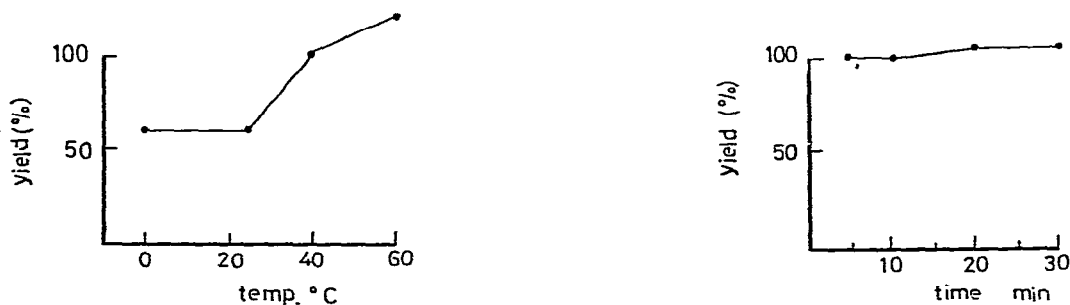


Fig. 3. Effect of reaction temperature on yield of styrene dibromide. A 200- μl volume of 1% bromine solution was added to styrene (10 μg) in *n*-hexane (25 ml); reaction time, 30 min.

Fig. 4. Effect of reaction time on yield of styrene dibromide. An 80- μl volume of 1% bromine solution was added to styrene (10 μg) in *n*-hexane (25 ml); reaction at a 40°.

TABLE I

INTERFERENCE EFFECTS OF 138 COMPOUNDS ON THE BROMINATION REACTION OF STYRENE

| No. | Type | Compound | Error (%)* |
|-----|--------------------------------------|---|------------|
| 1 | Aliphatic and alicyclic hydrocarbons | Ethylene | — |
| 2 | | Acetylene | — |
| 3 | | Propylene | — |
| 4 | | Butene-1 | — |
| 5 | | Isobutene | — |
| 6 | | <i>cis</i> -Butene-2 | — |
| 7 | | <i>trans</i> -Butene-2 | — |
| 8 | | 1,3-Butadiene | + 5.0 |
| 9 | | Hexene-1 | + 1.8 |
| 10 | | Hexene-2 | + 1.3 |
| 11 | | 2-Methylpentene-1 | — |
| 12 | | 4-Methylpentene-1 | — |
| 13 | | 4-Methylpentene-2 | — |
| 14 | | 2-Ethylbutene-1 | — |
| 15 | | Heptene-1 | — |
| 16 | | Heptene-2 | + 2.3 |
| 17 | | Heptene-3 | — |
| 18 | | Octene-1 | + 0.8 |
| 19 | | Octene-2 | — |
| 20 | | 2-Ethylhexene-1 | — |
| 21 | | 2,4,4-Trimethylpentene-1 | + 4.5 |
| 22 | | 2,4,4-Trimethylpentene-2 | — |
| 23 | | Nonene-1 | + 18.8 |
| 24 | | Nonene-4 (<i>cis</i> - and <i>trans</i> -) | + 0.5 |
| 25 | | 3,5,5-Trimethylhexene-1 | — |
| 26 | | Decene-1 | + 1.3 |
| 27 | | Undecene-1 | + 3.5 |
| 28 | | Dodecene-1 | + 100 |
| 29 | | Tridecene-1 | — |
| 30 | | Tetradecene-1 | + 1.3 |
| 31 | | Hexadecene-1 | — |
| 32 | | Octadecene-1 | — |
| 33 | | Eicosene-1 | + 0.5 |
| 34 | | 2-Methylpentane | — |
| 35 | | 3-Methylpentane | — |
| 36 | | 2,2-Dimethylbutane | — |
| 37 | | <i>n</i> -Heptane | — |
| 38 | | 3-Methylhexane | — |
| 39 | | 2,3-Dimethylpentane | — |
| 40 | | 2,4-Dimethylpentane | — |
| 41 | | <i>n</i> -Octane | — |
| 42 | | 3-Methylheptane | — |
| 43 | | 2,4- and 2,5-dimethylhexane | — |
| 44 | | 2,2,4-Trimethylpentane | — |
| 45 | | 2,3,4-Trimethylpentane | — |
| 46 | | 2,2,5-Trimethyl pentane | — |
| 47 | | <i>n</i> -Nonane | — |
| 48 | | <i>n</i> -Decane | — |
| 49 | | <i>n</i> -Undecane | — |

(Continued on p. 100)

TABLE I (continued)

| No. | Type | Compound | Error (%) ^a |
|-----|-----------------------|-------------------------|------------------------|
| 50 | | <i>n</i> -Dodecane | — |
| 51 | | <i>n</i> -Tridecane | — |
| 52 | | <i>n</i> -Tetradecane | — |
| 53 | | <i>n</i> -Pentadecane | — |
| 54 | | <i>n</i> -Hexadecane | — |
| 55 | | <i>n</i> -Heptadecane | — |
| 56 | | Cyclohexane | — |
| 57 | | Methylcyclohexane | — |
| 58 | Aromatic hydrocarbons | Benzene | — |
| 59 | | Toluene | — |
| 60 | | <i>o</i> -Xylene | — |
| 61 | | <i>m</i> -Xylene | — |
| 62 | | <i>p</i> -Xylene | — |
| 63 | | Ethylbenzene | — |
| 64 | | Cumene | — |
| 65 | | Mesitylene | — |
| 66 | | <i>p</i> -Cumene | — |
| 67 | | <i>n</i> -Propylbenzene | — |
| 68 | | <i>n</i> -Butylbenzene | — |
| 69 | | <i>n</i> -Hexylbenzene | — |
| 70 | | <i>n</i> -Octylbenzene | — |
| 71 | | <i>n</i> -Decylbenzene | — |
| 72 | | α -Methylstyrene | — |
| 73 | | Allyl benzene | — |
| 74 | Alcohols | Methanol | — |
| 75 | | Ethanol | — |
| 76 | | 1-Propanol | — |
| 77 | | 2-Propanol | — |
| 78 | | 1-Butanol | — |
| 79 | | 2-Butanol | + 0.5 |
| 80 | | 2-Methyl-1-propanol | — |
| 81 | | 2-Methyl-2-propanol | — |
| 82 | | 1-Pentanol | + 0.5 |
| 83 | | 2-Pentanol | + 0.5 |
| 84 | | 3-Pentanol | — |
| 85 | | 2-Methyl-1-butanol | — |
| 86 | | 3-Methyl-1-butanol | — |
| 87 | | 2-Methyl-2-butanol | — |
| 88 | | 1-Hexanol | — |
| 89 | | 2-Hexanol | + 1.3 |
| 90 | | 3-Hexanol | — |
| 91 | | 2-Methyl-1-pentanol | — |
| 92 | | 4-Methyl-2-pentanol | — |
| 93 | | 2-Methyl-3-pentanol | — |
| 94 | | 3-Methyl-3-pentanol | — |
| 95 | | 2-Ethyl-1-butanol | — |
| 96 | | 3,3-Dimethyl-2-butanol | — |
| 97 | | 1-Heptanol | — |
| 98 | | 2-Heptanol | + 1.3 |
| 99 | | 2,2-Dimethyl-2-butanol | + 0.8 |
| 100 | | 1-Octanol | — |
| 101 | | 2-Octanol | + 0.5 |

TABLE I (continued)

| No. | Type | Compound | Error (%) [*] |
|-----|-----------------------------------|-------------------------|------------------------|
| 102 | Aldehydes | Formaldehyde | — |
| 103 | | Acetaldehyde | — |
| 104 | | Propionaldehyde | — |
| 105 | | <i>n</i> -Butyraldehyde | — |
| 106 | | Isobutyraldehyde | — |
| 107 | | <i>n</i> -Valeraldehyde | — |
| 108 | | Isovaleraldehyde | — |
| 109 | | Capronaldehyde | + 0.5 |
| 110 | | Acrolein | — |
| 111 | | Crotonaldehyde | — |
| 112 | | Benzaldehyde | — |
| 113 | | <i>o</i> -Tolualdehyde | — |
| 114 | | <i>m</i> -Tolualdehyde | + 0.8 |
| 115 | | <i>p</i> -Tolualdehyde | + 1.3 |
| 116 | | Ketones | Acetone |
| 117 | Ethyl methyl ketone | | + 1.3 |
| 118 | Isopropyl methyl ketone | | + 1.3 |
| 119 | <i>n</i> -Butyl methyl ketone | | — |
| 120 | Isobutyl methyl ketone | | — |
| 121 | <i>sec.</i> -Butyl methyl ketone | | + 1.3 |
| 122 | <i>tert.</i> -Butyl methyl ketone | | + 1.3 |
| 123 | Diethyl ketone | | + 1.3 |
| 124 | Cyclohexanone | | + 0.5 |
| 125 | Diacetyl | | + 0.8 |
| 126 | Acetylacetone | | — |
| 127 | Acetophenone | | + 0.8 |
| 128 | Phenols | Phenol | + 3.0 |
| 129 | | <i>o</i> -Cresol | +150.0 |
| 130 | | <i>m</i> -Cresol | + 45.0 |
| 131 | | <i>p</i> -Cresol | — |
| 132 | | <i>o</i> -Ethylphenol | + 3.3 |
| 133 | | <i>p</i> -Ethylphenol | — |
| 134 | | 2,3-Xylenol | + 20.0 |
| 135 | | 2,5-Xylenol | + 4.0 |
| 136 | | 2,6-Xylenol | + 2.0 |
| 137 | | 3,4-Xylenol | + 7.5 |
| 138 | | 3,5-Xylenol | + 20.0 |

* — represents no peak in the chromatograms and/or a peak which did not overlap with the peak of styrene dibromide.

Recovery test

The recovery of styrene, using the over-all treatment with a cold trap containing liquid oxygen and bromination, was measured by using a 14-l Tedlar bag with a known concentration of styrene in the gas (nitrogen) in the bag of 13 ppb.

One litre of gas from the bag was trapped with liquid oxygen, then extracted from the trap by 4 ml of *n*-hexane. The extracted solution was subjected to the bromination reaction, in which 200 μ l of 1% bromine water were used. The temperature of bromination reaction was 40° and the reaction time was 20 min. The amount of sample injected into the ECD was 4 μ l. Table II shows the efficiency of recovery

TABLE II
RECOVERY OF STYRENE FROM PREPARED STANDARD GAS

| Run | Styrene added (ppb) | Styrene found (ppb) | Recovery (%) |
|-----|---------------------|---------------------|--------------|
| 1 | 13 | 12 | 92 |
| 2 | 13 | 12 | 92 |
| 3 | 13 | 12 | 92 |
| 4 | 13 | 11 | 85 |
| 5 | 13 | 12 | 92 |
| 6 | 13 | 12 | 92 |

Application to urban air

Fig. 5 shows a typical gas chromatogram obtained subsequent to the bromination of urban air from Nagoya. Styrene dibromide was identified, and the concentration of styrene detected was 0.2 ppb. This value is very low, and the odour of styrene at this level is barely detectable.

The procedures for collection of the sample gas and for preparation of the dibromide were as follows. Condensate collected by the direct cold trapping of the urban air (1 m³) with liquid oxygen was extracted with *n*-hexane (25 ml), the extract was treated with 10 ml of 0.1 *N* sodium hydroxide solution to remove interfering compounds such as cresols, and 200 μ l of 1% bromine water were added to the *n*-hexane layer. After reaction for 10 min at 40°, the excess of bromine was removed by

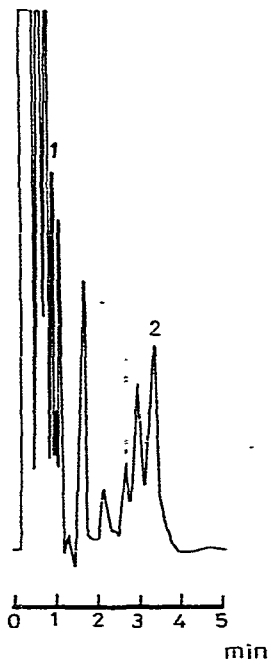


Fig. 5. Typical gas chromatogram from the bromination of the condensate isolated from urban air (1 m³). 1 = Internal standard (0.4 ng); 2 = styrene dibromide as styrene (0.2 ppb).

bubbling nitrogen through the solution at 60 ml/min for 5 min, and 1 μ l of the *n*-hexane solution was then analysed with an ECD.

The gas chromatography of a large volume (500 l) of urban air was also studied, using a Tenax-GC pre-column method¹⁵⁻¹⁷. The gas chromatography was carried out using a glass capillary column under the following conditions: liquid phase, PEG-20M; column size, 30 m \times 0.25 mm I.D.; column temperature, 60°; carrier gas (helium) flow-rate, 0.7 ml/min; detector, FID. Dodecene-1 and nonene-1, which give large interference effects in the determination of styrene by the bromination method, were not detected in the gas chromatograms.

The range of the concentrations of styrene detected in four samples of urban air collected in the period November 21st-25th, 1975, was 0.1-0.4 ppb.

ACKNOWLEDGEMENTS

The author thanks Y. Baba, National Research Institute for Pollution & Resources, Y. Takata, Hitachi Research Laboratory, Hitachi Ltd., and K. Yoshimoto, Aichi Environmental Research Centre, for useful suggestions.

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