

CHROM. 9389

Note

Selective and sensitive gas chromatographic determination of benzaldehyde

YASUYUKI HOSHIKA

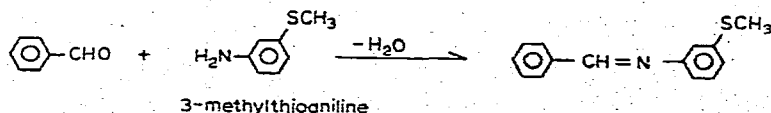
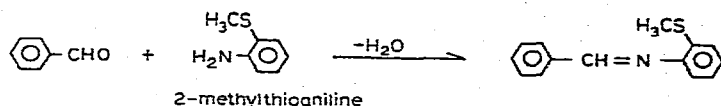
Aichi Environmental Research Center, 7-6, Tsuji-machi, Kita-ku, Nagoya-shi, Aichi (Japan)

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Aromatic and aliphatic aldehydes are formed as a result of incomplete combustion in internal combustion engines, incinerators and other sources. Of the aromatic aldehydes, benzaldehyde is of considerable interest in that it inhibits the formation of photochemical smog^{1,2}.

The gas chromatographic analysis of benzaldehyde in internal combustion engines has been carried out by gas chromatography-mass spectrometry (GC-MS)³ and by derivatization^{4,5}. The former technique is costly, requires complex instrumentation and is not convenient for on-site environmental pollution analysis. On the other hand, the formation of derivatives of aromatic aldehydes in GC analysis, *i.e.*, 2,4-dinitrophenylhydrazones^{4,5}, oximes^{6,7} and thiosemicarbazones⁸, requires a high temperature, at which thermal decomposition and isomerization may take place. A method using a glass capillary column at a relatively low column temperature, such as 100°, has been reported for the analysis of benzaldehyde and *o*-, *m*- and *p*-tolu-aldehydes in car exhaust gas⁹. These four aromatic aldehydes were treated with *n*-butylamine to form the corresponding Schiff bases, and were then detected by use of a flame ionization detector (FID). The minimum detectable quantity of the derivatives was *ca.* 0.01 µg. The sample volume injected was 1 µl of an ethanol solution.

This paper describes an improved derivative-formation reaction for benzaldehyde, involving treatment with 3-methylthioaniline to form the corresponding sulphur-containing Schiff base. The derivative is detected by means of a flame photometric detector (FPD) which is selective for sulphur compounds and permits the use of large sample volumes. The reaction is illustrated in the following scheme:



EXPERIMENTAL

Reagents

Benzaldehyde (95% minimum) and ethanol (99.5%) were obtained from Wako, Osaka, Japan. 2-Methylthioaniline (97%, b.p. 234°) and 3-methylthioaniline (97%; b.p. 163–165°, 16 mmHg) were obtained from Aldrich, Milwaukee, Wisc., U.S.A. *n*-Heptadecane was used as an internal standard (PolyScience, Niles, Ill., U.S.A.).

Gas chromatography

The gas chromatograph was a Shimadzu Model GC5AP₅FFp equipped with a FID and a FPD; it was also equipped with a digital integrator (Shimadzu Model ITG-2A) for the determination of the reaction percentage of the Schiff-base formation. The glass analytical columns were packed with 5% SE-30 on Chromosorb W (AW, DMCS, 60–80 mesh, 3 m × 3 mm I.D.) or with 3% OV-17 on Chromosorb W (AW, DMCS; 60–80 mesh, 1 m × 3 mm I.D.).

The GC conditions for the FID were as follows: column, 5% SE-30; column temperature, held for 1 min at 110° and then raised at 10°/min to 270°; injection port and detector temperatures, 270°; flow-rates, 50 ml/min (nitrogen or hydrogen), 1.0 l/min (air). For the FPD the conditions were: column, 3% OV-17; column temperature, 200° (isothermal); injection port and detector temperatures, 230°; flow-rates, 50 ml/min (nitrogen or hydrogen), 40 ml/min (air).

Preparation of Schiff bases

Benzaldehyde ($1 \cdot 10^{-3}$ mole) was treated directly with 2- or 3-methylthio-

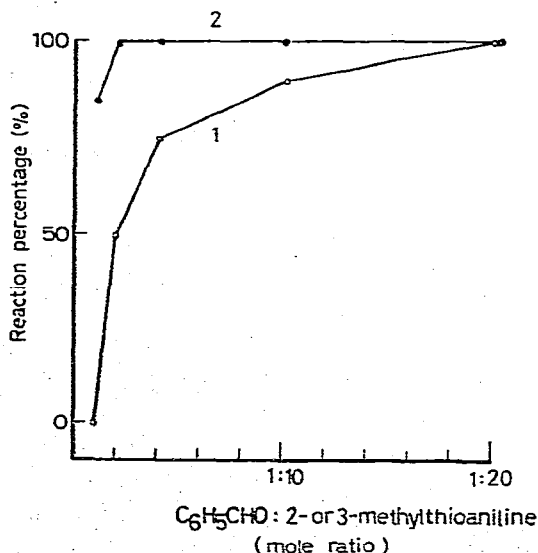


Fig. 1. Effect of mole ratio on the reaction percentage of benzaldehyde with (1) 2-methylthioaniline and (2) 3-methylthioaniline. Reaction conditions: temperature, 25°; time, 4 h; sample volume injected, 1 μ l.

aniline ($1-20 \cdot 10^{-3}$ mole). The product was dissolved in 25 ml of ethanol (containing *n*-heptadecane as an internal standard, $2 \cdot 10^{-4}$ mole) at room temperature.

The reaction percentages of the Schiff-base formation were calculated from the disappearance of benzaldehyde as monitored using the SE-30 column and the FID.

RESULTS AND DISCUSSION

Reaction of benzaldehyde with 2- or 3-methylthioaniline

Fig. 1 shows the reaction percentages of benzaldehyde with 2- or 3-methylthioaniline to form the corresponding Schiff bases. These reactions were complete in 4 h at room temperature. As shown in Fig. 1, the reaction of 3-methylthioaniline was more rapid than that of 2-methylthioaniline. Fig. 2 shows a graph of the reaction percentage of benzaldehyde with 3-methylthioaniline against reaction time. Fig. 3 shows typical gas chromatograms of the reaction of benzaldehyde with 3-methylthioaniline to form the corresponding Schiff base. A complete quantitative reaction took place in 1 h at room temperature when a 1:3 mole ratio of benzaldehyde to 3-methylthioaniline was used.

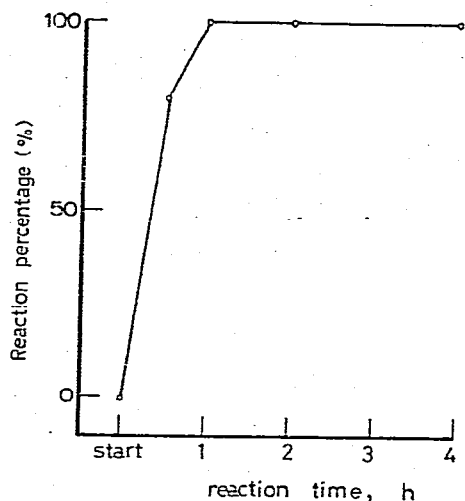


Fig. 2. Effect of reaction time on the reaction percentage of benzaldehyde with 3-methylthioaniline (1:3 mole ratio) at 25°.

Preparation of calibration graph for the FPD response

The FPD response was rectilinear in the range 10-900 ng of the Schiff base derived from benzaldehyde with 3-methylthioaniline. The minimum detectable quantity of the Schiff base was *ca.* 4 ng. The sensitivity of the FPD to the Schiff base was 2.5 times higher than that of the FID. However, the merit of this method is that up to 50 μ l of sample can be used.

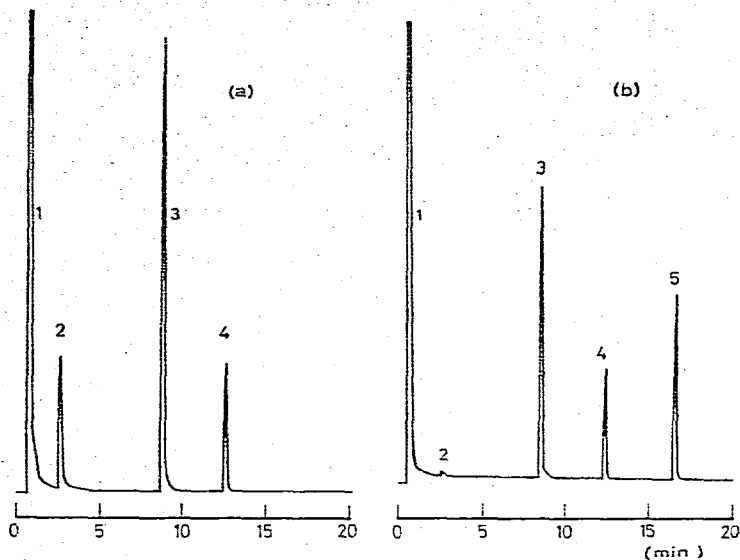


Fig. 3. Typical gas chromatograms of the reaction of benzaldehyde with 3-methylthioaniline. (a) Starting point. Peaks: 1 = ethanol (solvent); 2 = benzaldehyde; 3 = 3-methylthioaniline; 4 = *n*-heptadecane (internal standard). (b) After reaction for 0.5 h. Peaks: 1-4 as in Fig. 2; 5 = sulphur-containing Schiff-base condensate. Conditions: column, 5% SE-30 on Chromosorb W (AW, DMCS; 60-80 mesh, 3 m \times 3 mm I.D.); column temperature, held for 1 min at 110° then raised at a rate of 10°/min to 270°; nitrogen flow-rate, 50 ml/min; detection, FID. For other GC conditions, see Experimental.

ACKNOWLEDGEMENT

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