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Pentafluorobenzyl *p*-Toluenesulfonate as a New Derivatizing Reagent for Gas Chromatographic Determination of Mercaptan

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ABSTRACT

A new derivatizing agent, pentafluorobenzyl *p*-toluenesulfonate, has been synthesized, which is designed to enhance the volatility of analytes and to introduce a detector-oriented tag into the molecules for gas chromatographic determination with electron capture detection. The derivatization of *n*-butyl mercaptan with the reagent was studied. A new gas chromatographic method for its determination has been developed. *n*-Butyl mercaptan can be derivatized to *n*-butyl pentafluorobenzyl thioether by using tetra-*n*-amylammonium chloride as the phase transfer catalyst. The derivative is subsequently determined by gas chromatography with flame ionization detection. The effects of added acid or base, of the concentration of each of the phase transfer catalyst and the reagent, and of reaction time on the pentafluorobenzylation were discussed.

Key Words: Gas chromatography, Derivatization, Determination of mercaptan, Pentafluorobenzylation, New derivatizing agent, Pentafluorobenzyl *p*-toluenesulfonate

Introduction

Mercaptans are commercially important compounds which are used extensively in the manufacture of agricultural chemicals, pharmaceutical products, gas odorants, and specialty chemicals. They are also introduced into the environment in large quantities as unwanted by-products of paper manufacture and petroleum refining. Mercaptans are characterized by their generally disagreeable odor and adversely affect the palatability of water at low concentrations. Mercaptans are usually determined by gas chromatography with flame photometric detection, which is very selective to sulfur-containing compounds but is not so sensitive. Therefore, preconcentration is required in the determination of trace amounts of mercaptans in the environment. A variety of methods including adsorption and absorption techniques¹⁾ have been used to preconcentrate mercaptans at trace levels in the environment. Another means of determination of trace mercaptans is the preparation of other derivatives with a blocked -SH groups.

Gas chromatography is a valuable technique for determining volatile organic and inorganic compounds because of its unmatched separating power. By use of derivatization, furthermore, this technique can be extended to the determination of non-volatile and thermally unstable compounds²⁻⁷⁾. Derivatization has been used not only to increase the volatility of compounds but also to introduce a detector-oriented tag into the molecules. Electron capture detection (ECD) has been studied in conjunction with derivatization, due to its very high sensitivity⁸⁾, and various derivatizing agents have been developed for electron capture gas chromatography.

Pentafluorobenzylation has been used in the derivatization of mercaptans to enhance the sensitivity^{9,10)}. Pentafluorobenzylation is a very useful technique for electron capture gas chromatography, because of the volatility and very high ECD responses of pentafluorobenzyl derivatives. However, only pentafluorobenzyl bromide has been used as the pentafluorobenzylating reagent for the derivatization of various organic⁹⁻¹³⁾ and inorganic¹⁴⁻¹⁸⁾ compounds.

In this work, we have succeeded to synthesize a new agent, pentafluorobenzyl *p*-toluenesulfonate,

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and investigated its applicability to the derivatization of mercaptans for gas chromatography. This paper describes a preliminary study of the determination of *n*-butyl mercaptan at relatively high concentrations using flame ionization detection (FID). In the presence of aqueous sodium hydroxide and the phase transfer catalyst, relatively high concentration of *n*-butyl mercaptan is made to react with pentafluorobenzyl *p*-toluenesulfonate, and the resulting derivative is subsequently determined by gas chromatography with FID. The final objective of this work, of course, is to develop a new gas chromatographic method for the simultaneous determination of trace mercaptans by using ECD.

Experimental

Apparatus.

A Shimadzu GC-3BF gas chromatograph equipped with a dual FID system (Shimadzu, Kyoto, Japan) was used together with a glass coiled tube (2.1 m × 3mm I.D.) packed with 5% PEG-HT on 60-80 mesh Uniport HP. The packing material was obtained from Gasukuro Kogyo (Tokyo, Japan). Nitrogen was used as the carrier gas at a constant flow-rate of 30ml/min. The column and injection port temperatures were maintained isothermally at 155 and 190°C, respectively. A Shimadzu Chromatopac C-R3A data processor was used as the recorder and integrator. A Hitachi RMU-6E mass spectrometer was employed with an ionization source of 200°C, an electron energy of 70 eV, and an acceleration energy of 1.8KV.

Reagents.

Analytical-reagent grade *n*-butyl mercaptan and commercial grade tetra-*n*-amylammonium chloride were obtained from Wako (Osaka, Japan). The new derivatizing agent, pentafluorobenzyl *p*-toluenesulfonate, was prepared from *p*-toluenesulfonyl chloride and pentafluorobenzyl alcohol by modification of the literature method¹⁹⁾ and recrystallized from methanol. It was identified by mass spectrometry and infrared spectrometry (Figure 1). Dichloromethane and deionized water were distilled before use for analysis. All other chemicals were also of analytical-reagent grade.

Procedure.

The recommended procedure for the determination of *n*-butyl mercaptan was as follows. A brown colored test tube with a screw cap (ca. 10ml) was used as the reaction vessel in order to protect the contents from the light. To 1.0ml of a reference standard solution containing *n*-butyl mercaptan in dichloromethane were added 0.90ml of a 0.10M aqueous sodium hydroxide, 0.10ml of a 0.50M aqueous tetra-*n*-amylammonium chloride, and 1.0 ml of dichloromethane solution containing pentafluorobenzyl *p*-toluenesulfonate (8.0×10^{-2} M) and nitrobenzene (1.0×10^{-2} M) as an internal standard. Then, the vessel was sealed tightly with the stopper and shaken mechanically for 10min at room temperature. The organic layer was separated from the aqueous one, and an aliquot of it (0.4μL) was injected into the gas chromatograph.

Results and Discussion

Pentafluorobenzyl p-toluenesulfonate.

Figure 1 shows the mass and infrared spectra of pentafluorobenzyl *p*-toluenesulfonate synthesized. The mass peaks at *m/e* 352 and 181 correspond to the parent ion and base ion equivalent to the fragment $C_6F_5CH_2^+$, and infrared bands at 1170 and 1360cm^{-1} are characteristic of the symmetric and antisymmetric vibrations of $S(=O)_2$, respectively. The new compound was obtained as white needles.

In order to estimate the ability of the new compound as the derivatizing agent, *n*-butyl mercaptan was converted into its pentafluorobenzyl derivative as described in the Experimental section. After the derivatization, the organic layer was analyzed by gas chromatography with FID. The gas chromatographic peak was observed which corresponds to the pentafluorobenzyl derivative of *n*-butyl mercaptan. The peak area was measured by an internal standard method.

Optimum derivatization conditions.

In order to perform the pentafluorobenzylation of *n*-butyl mercaptan under optimum reaction conditions, we have first examined the effects of pH, of the concentration of each of the phase transfer catalyst and the reagent, and of reaction time on the derivatization of a 10.0mM *n*-butyl mercaptan solution. The results are shown in Figures 2-4. The effect of pH was examined as follows. To a 1.0-ml

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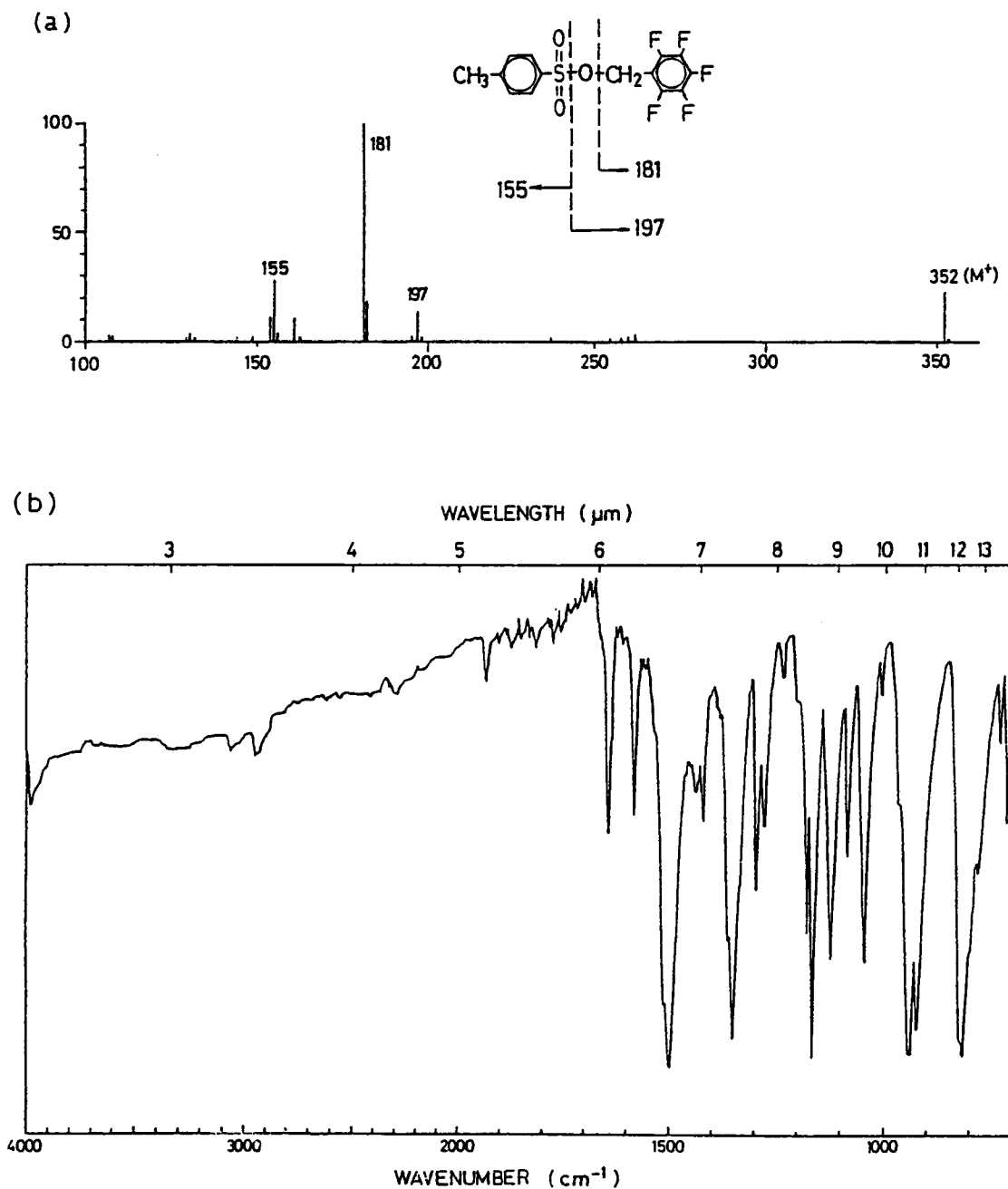


Figure 1 Mass (a) and infrared (b) spectra of pentafluorobenzyl *p*-toluenesulfonate

of *n*-butyl mercaptan solution, sodium hydroxide or sulfuric acid (0.90ml) of different concentration was added before derivatization. On the addition of sulfuric acid, however, the peak area of the derivative decreased down to zero. Therefore, Figure 2 shows only the effect of the addition of sodium hydroxide. The peak area of the derivative becomes constant when the concentration of sodium hydroxide added exceeds 0.01M. Further work was carried out by adding 0.10M sodium hydroxide. Figure 3 shows the effects of the concentration of tetra-*n*-amylammonium chloride and pentafluorobenzyl *p*-toluenesulfonate. The yields reach constant values when the concentrations of tetra-*n*-amylammonium chloride and pentafluorobenzyl *p*-toluenesulfonate are higher than 0.05M and 0.075M, respectively. Figure 4 gives the effect of reaction time; the pentafluorobenylation completes within 10min. From the results mentioned above, the optimum reaction conditions described in the Experimental section were chosen.

Calibration curve and gas chromatogram.

Six samples containing the reference standard at about 1-6mM *n*-butyl mercaptan were analyzed to construct a calibration curve of the *n*-butyl mercaptan concentration (X) against the peak area ratio of the derivative to the internal standard (Y).

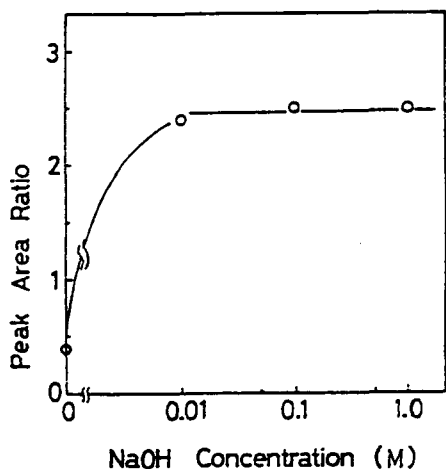


Figure 2 Effect of concentration of NaOH added on pentafluorobenylation.

A linear regression equation ($Y=0.251X+0.094$) was obtained with a correlation coefficient of 0.990. A linear calibration curve was also constructed in the range of 0.1-1.0mM with a correlation coefficient of 0.990, by analyzing ten reference standard solutions.

The typical gas chromatogram of the conversion product in dichloromethane layer is shown in Figure 5, when 10.0mM *n*-butyl mercaptan solution was made to react with pentafluorobenzyl *p*-toluenesulfonate in the presence of tetra-*n*-amylammonium chloride and sodium hydroxide under the optimum reaction conditions. The peak of the derivative from *n*-butyl mercaptan (i. e., peak a in Figure 5) was identified by gas chromatography combined with mass spectrometry. The mass spectrum obtained exhibited the derivative was *n*-butyl pentafluorobenzyl thioether ($\text{CH}_3(\text{CH}_2)_3\text{SCH}_2\text{C}_6\text{F}_5$).

Conclusion

It is found that *n*-butyl mercaptan can be derivatized to *n*-butyl pentafluorobenzyl thioether by the reaction with pentafluorobenzyl *p*-toluenesulfonate and tetra-*n*-amylammonium chloride and subsequently determined by flame ionization gas chromatography. As *n*-butyl mercaptan was selected as the model aliphatic mercaptan, this technique will be applicable to other aliphatic mercaptans such as methyl, ethyl, and *n*- and isopropyl mer-

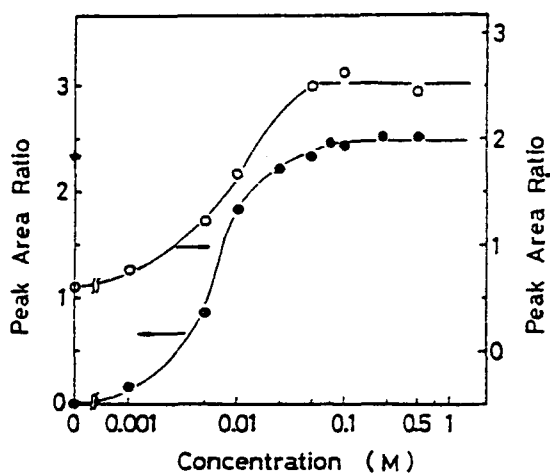


Figure 3 Effects of concentrations of tetra-*n*-amylammonium chloride (○) and pentafluorobenzyl *p*-toluenesulfonate (●) on pentafluorobenylation.

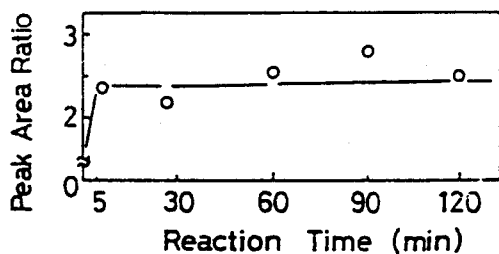


Figure 4 Effect of reaction time on pentafluorobenzylation.

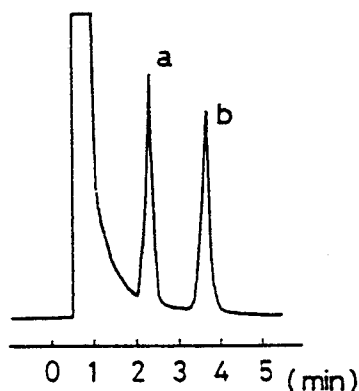


Figure 5 Gas chromatogram for the determination of *n*-butyl mercaptan.

Peak a = derivative of *n*-butyl mercaptan (*n*-butyl pentafluorobenzyl thioether), b = internal standard (nitrobenzene).

captans, which are one of the main groups of evil-smelling compounds. Furthermore, the present technique based on pentafluorobenzylation is an ECD-oriented derivatization designed to enhance the sensitivity. The development of this method is under investigation for the determination of trace amounts of mercaptans by gas chromatography with ECD. Work is also continuing on the application of the new derivatizing agent, pentafluorobenzyl *p*-toluenesulfonate, to the gas chromatographic determination of other organic materials; for example, fatty acids and phenols.

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