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GAS CHROMATOGRAPHIC DETERMINATION OF SMALL AMOUNTS OF FORMIC ACID IN MIXTURES CONTAINING PHENOL, ACETONE AND AROMATIC HYDROCARBONS

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SUMMARY

A method for determining small amounts of formic acid in mixtures from the synthesis of phenol from cumene, in particular those obtained after the decomposition of cumene hydroperoxide, is described. The determination consists in extraction of formic acid as the sodium salt, acidification and esterification to methyl formate followed by gas–liquid chromatography with an internal standard.

INTRODUCTION

Formic acid is formed in small amounts as one of the side-products in the synthesis of phenol and acetone by cleavage of cumene hydroperoxide[1]. It appears in the so-called decomposition mixtures obtained by the action of sulphuric acid on cumene hydroperoxide, in crude phenol, distillation residues of phenol, in phenolate solutions and other mixtures from phenol production. The presence of formic acid in these intermediates is undesirable as it is corrosive towards apparatus made of stainless steel containing chromium[2] and nickel[3].

Because of the variety of substances present in the decomposition mixtures and the small content of formic acid, a gas chromatographic method was sought.

Formic acid has been determined in different mixtures by gas–liquid chromatography both directly and after the formation of derivatives. The direct determination of formic acid in addition to other acids has been carried out by employing an argon detector[4] or a thermalconductivity detector using a column containing a microporous polymer[5] (such as Porapak Q) or a column containing a fluoronated polymer coated with polyethylene glycol and azelaic acid[6] or a porous polymer coated with stearic acid[7]. It is generally considered that formic acid gives no response in a flame-ionization detector, as has been confirmed by recent work[8]. However, the possibility of determining formic acid by using this type of detector has been reported[9]. During the determination of formic acid by gas chromatography, thermal decomposition occurs[10], giving carbon monoxide, carbon dioxide, hydrogen and water if the injector or column temperature is above 150°, which might cause too low results. It is also possible to determine formic acid as carbon monoxide[11].

A number of papers have described methods involving the formation of deriva-

tives. Formic acid has been determined in aqueous solution by gas chromatography of formanilide[12] or of benzyl formate[13]. Free formic acid, acetic acid or their salts in cigarette smoke have been determined as methyl esters[14] formed by esterification with methanol containing dry hydrogen chloride followed by gas chromatographic separation on a polyethylene glycol column. Trimethylsilyl esters have also been used as derivatives in the determination of formic acid[15].

The purpose of this paper is to describe a combination of extraction and concentration of formic acid, preparation of the methyl ester and gas chromatography, which permits the determination of formic acid in the required range of 0.01–0.1 % in mixtures containing phenol, acetone, aromatic hydrocarbons and other compounds formed in the decomposition of cumene hydroperixide.

EXPERIMENTAL

Apparatus

A Giede Model GCHF 18.3 gas chromatograph with a flame-ionization detector was used. Argon was employed as the carrier gas, and electrolytic hydrogen from an Elhygen hydrogen generator and compressed air as auxiliary gases. A 3 m × 4 mm O.D. stainless-steel column packed with 10% Carbowax 20M on 60–80 mesh Chromosorb W AW was used.

Reagents

The following reagents, mainly of reagent grade, were used in the determination: benzene, diethyl ether, methanol (dehydrated), sodium hydrogen carbonate, hydrochloric acid (sp. gr. 1.19), sulphuric acid (90%), 0.2 *N* sodium hydroxide solution, formic acid (99%) and ammonium chloride.

Anhydrous methanol–hydrogen chloride solution. The solution was prepared by bubbling through methanol (final drying with molecular sieve 4A) hydrogen chloride evolved from concentrated hydrochloric acid with 10% ammonium chloride to which 90% sulphuric acid was added dropwise. The operation was carried out in laboratory glass apparatus commonly used for this type of evolution of gases and their drying and absorption in liquids. Addition of ammonium chloride to hydrochloric acid[16] was used to prevent the formation of chlorine. Before entering the methanol, the gas stream was passed through a wash bottle containing sulphuric acid and a tower loosely packed with anhydrous calcium chloride. The concentration of the methanolic solution of hydrogen chloride should be about 2 *N* (checked by titration with 0.2 *N* sodium hydroxide solution). It was prepared in a volume sufficient for a number of analyses.

To this solution diethyl ether was carefully added, preferably by weighing in an ampoule to obtain an approximately 0.3% solution. The solution was stored in a tightly stoppered flask in a cool place. The chromatogram of this solution obtained under the conditions of analysis described below should show only the peaks of diethyl ether and methanol after the initial peak of hydrogen chloride.

Procedure

Extraction and methylation. A 50-ml volume of the sample of the decomposition mixture was measured into a 250-ml separating funnel and 150 ml of benzene

were added with mixing. A 0.2-g amount of sodium hydrogen varbonate and 2 ml of distilled water were added and the mixture was shaken vigorously for about 3 min. After the layers had separated, the lower layer was carefully transfered into a 25-ml flask with a ground-glass joint. The benzene layer was washed with two 2-ml portions of water and the washings were combined with the solutions in the flask.

Water was evaporated from the solution by heating on a water-bath and aspirating the vapour from above the liquid by placing in the neck of the flask a glass tube connected to a water pump. Then 2 ml of methanol were added and evaporation was continued to dryness. The flask containing the residue (sodium formate, salts of other acids and excess of sodium hydrogen carbonate) was connected with a reflux condenser and 10.0 ml of the solution for methylation were introduced through the condenser. The contents of the flask were then mixed for 1 h using a magnetic stirrer. After removing the condenser, the flask was closed with a ground-glass stopper.

Gas chromatographic analysis. The conditions of separation were as follows: oven temperature, 50°; injector and detector temperature, 60°: carrier gas (argon) flow-rate at the outlet, 20 ml/min; hydrogen flow-rate, 20 ml/min; air flow-rate, *ca.* 200 ml/min; chart speed, 1 cm/min; amplifier range, $\times$ 10 at 10^9 of input resistance.

The size of the sample of the solution after esterification injected into the chromatograph was 3 μl. The following peaks were obtained on the chromatograms: hydrogen chloride, diethyl ether, methyl formate, methyl acetate (if acetic acid was present in the sample) and methanol (above the chart scale). The areas of the methyl formate and diethyl ether (internal standard) peaks were measured and their ratio calculated. The amount of formic acid in the sample taken was then read from the calibration graph.

Preparation of calibration graph. A standard solution consisting of 0.2 *N* formic acid in benzene was prepared; 2.0 ml of the solution were measured into a 250-ml separating funnel and benzene was added to a volume of 200 ml. Then 0.2 g of sodium hydrogen carbonate was added and the procedure as for the sample was followed as far as the production of the chromatogram. The areas of the methyl formate and diethyl ether peaks were measured, and the ratio was calculated.

Similar chromatograms were prepared using 0.5, 1.0, 3.0 and 5.0 ml of the 0.2 *N* formic acid solution in benzene and the ratios of the peak areas were calculated, and plotted against the amount of formic acid in milligrams in each volume of standard solution. A calibration graph was prepared for each methylation solution.

RESULTS AND DISCUSSION

Preliminary tests, carried out in order to determine formic acid in the samples directly with the use of a thermalconductivity detector, did not give satisfactory results. For this purpose a Porapak Q column was used at 160° and at an injector temperature 200° necessary for flash evaporation of the sample. The recovery of formic acid was much too low because of possible decomposition. Large acetone and water peaks made it difficult to achieve an acceptable resolution. It was evident that it was necessary to separate the formic acid and other acids from the bulk of the other compounds, mainly acetone and phenol. This was accomplished by extraction with sodium hydrogen carbonate solution from a benzene solution of the sample. The recovery of formic acid in the whole procedure, including esterification, was complete within the limits of

experimental error. This was established by an independent gas chromatographic determination of methyl formate in solution after methylation and comparison with the starting concentration of formic acid in the benzene solution.

The calibration graph was linear in the range required for control analysis (0.005–0.1 % of formic acid). The relative standard deviation of the results in this range was 10–5%, respectively.

It was also possible to determine the acetic acid content, either from the methyl acetate peak using a suitable calibration graph for acetic acid or from the ratio of both ester peaks by employing a theoretical correction factor. In addition to the analysis of decomposition mixture obtained from cumene hydroperixode, the method has also been used to determine formic acid in crude phenols and distillation residues.

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