

Short Communication

Determination of succinic acid by pyrolysis–gas chromatography in the presence of sodium sulfite and iron powder

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ABSTRACT

The determination of succinic acid was studied by Curie-point pyrolysis–gas chromatography. The recommended procedure is as follows: sample solution was added to 40 mg of the mixed powder (iron powder–sodium sulphite = 1:1), placed on a pyrolysis foil with a microsyringe and dried on a hot plate (100°C). Pyrolysis was carried out by using a gas chromatograph fitted with a Curie-point pyrolysis unit (the pyrolysis foil was maintained at 445°C for 5 s). The peak area of dimethyl sulphoxide was used for the determination of succinic acid. The measurement range was 2–102 µg and the calibration curve was a straight line with a correlation coefficient of 0.998. The relative standard deviation for the pyrolysis of succinic acid (41 µg) was 2.2% ($n=4$).

INTRODUCTION

Pyrolysis–gas chromatography (Py–GC) has been used to characterize polymers, high-boiling-point compounds and non-volatile materials [1]. This technique has been employed mainly for qualitative analysis since it is difficult to obtain sufficient reproducible pyrolysis. We have also shown that when the sample is pyrolysed in the presence of a mixture of metal powder and an inorganic salt not only are the observed peak areas larger than in the absence of the mixture but also the pyrolysis is reproducible on repeated runs. In a series of articles we have demonstrated that several amines can be

determined by means of Py–GC. For example, glyphosate [2], alkaloid narcotics [3] and aromatic amines [4] were determined by their pyrolysis products with good reproducibility and sensitivity. Further, paraquat [5] was pyrolysed in the presence of nickel powder and potassium iodide. Methyl iodide, which was obtained from the reaction of the methyl radical produced by paraquat and potassium iodide, was used to measure paraquat. Aliphatic amines [6] were determined as the corresponding alkyl chlorides that were obtained from alkyl radicals and metal chlorides. In this paper we describe the application of this technique for the determination of succinic acid, which was pyrolysed in the

presence of a mixture of iron powder and sodium sulphite. The dimethyl sulphoxide formed was used to determine succinic acid in a similar manner as above.

EXPERIMENTAL

A Curie-point pyrolyser (Japan Analytical Industry, Model JHP-2) was directly coupled to a gas chromatograph (Hitachi Model 163) equipped with a flame ionisation detector. Flame ionisation detection signals were processed using a Hewlett-Packard 3390A integrator. The temperatures of the pyrolyser unit and the tube connecting the pyrolyser and gas chromatograph were maintained at 150 and 200°C, respectively. The separations were performed on a 2 m × 3 mm I.D. stainless-steel column packed with 10% polyethylene glycol (PEG) 20M on Chromosorb W AW-DCMS (80–100 mesh). The pyrolysis products were eluted isothermally at 80°C. All chemicals used were obtained through Wako (Osaka, Japan). They were of high purity and used without further purification. Succinic acid and adipic acid were used as aqueous solutions and other acids were used as methanolic solutions.

Procedure

Equal amounts of iron powder and sodium sulphite were mixed thoroughly in an agate mortar. A 40-mg sample of the mixed powder was placed onto a piece of pyrolysis foil (about 9 mm × 22 mm, 0.05 mm thick) using a microspatula. Then 20 μl of sample solution containing about 40 μg of sample were added using a microsyringe. The solvent on the pyrolysis foil was evaporated to dryness on a hot plate at about 100°C. The pyrolysis foil was carefully folded and placed in a quartz sample tube. The tube was loaded into the pyrolyzer. About 40 μg of sample were used for each experimental determination.

RESULTS AND DISCUSSION

The pyrolysis products were separated by GC, as shown in Fig. 1. The dimethyl sulphoxide formed from the pyrolysis product of succinic acid and sodium sulfite was used for the determination of succinic acid. Sodium carbonate deca-hydrate, potassium iodide and nickel chloride hexa-hydrate, which were

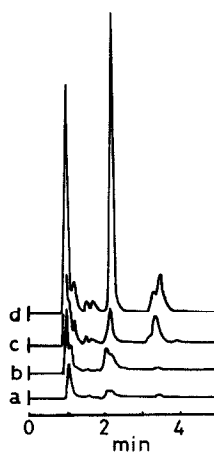


Fig. 1. Typical pyrograms of succinic acid (a) without any additives, (b) with 20 mg of sodium sulphite, (c) with 20 mg of iron powder and (d) with a mixture of sodium sulphite and iron powder. The pyrolysis temperature was 445°C. The amount of succinic acid was 41 μg.

useful salts in previous investigations, and sodium sulphite were studied in this work. The salts served as pyrolysis temperature controllers and sample supports. In the presence of the mixed powder of sodium sulphite and iron powder (through 100 mesh, electrolytic), the dimethyl sulphoxide peak area was about twenty times higher than in its absence. The metal powder was mixed with sodium sulphite in order to improve the conduction of heat from the pyrolysis foil to the sample. The metals used were aluminum, chromium, manganese, iron, nickel and zinc. The maximum total production was observed when chromium or iron powder was used. The effect of the mixed ratio of inorganic salt and metal powder on the peak area of dimethyl sulphoxide was studied using a mixture of 3–30 mg of sodium sulphite and 15 mg of chromium or iron powder. The optimum added mixture was sodium sulphite and iron (1:1, w/w). The amount of the mixture added to the pyrolysis foil varied from 10 to 60 mg. The peak area of dimethyl sulphoxide considerably increased up to 20 mg and slightly increased in the range of 20 mg up to 60 mg. The optimal sensitivity and handling were obtained from addition of 40 mg. With further addition of mixture it was difficult to fold the foil without spilling powder. The pyrolysis temperature was studied by using different Curie-point pyrolysis foils (333, 386,

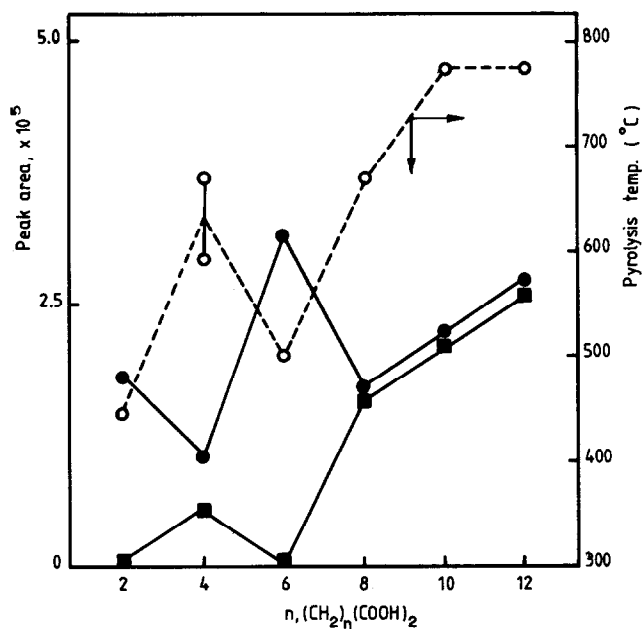


Fig. 2. Effect of additives on succinic acid and its homologues. ■ = no additives; ● = 40 mg of iron powder and sodium sulphite (1:1); ○ = optimal pyrolysis temperature.

445, 500, 590, 670 and 764°C) which are commercially available. The maximum peak was observed when succinic acid was pyrolyzed at 445°C.

The peak area of dimethyl sulphoxide was used to study the effect of addition of succinic acid and its homologues, as shown in Fig. 2. The peak areas of dimethyl sulphoxide pyrolysis of succinic acid and suberic acid in the presence of iron powder–sodium sulphite (1:1, w/w) were about 20 and 35 times

greater than without additives. This effect related to the pyrolysis temperature of each acid. Succinic acid and suberic acid were pyrolysed below 500°C and the others above 500°C. Because sodium sulphite decomposed at a higher temperature, improvements in sensitivity were not observed with adipic acid, sebacic acid, 1,10-decanedicarboxylic acid and 1,12-dodecanedicarboxylic acid. Adipic acid formed the anhydride.

The pyrolysis of succinic acid was therefore carried out as follows: pyrolysis temperature was 445°C; the mixture ratio of sodium sulphite and iron was 1:1 (w/w); the amount of mixture was 40 mg. The measurement range was 2–102 µg and the calibration curve was a straight line with a correlation coefficient of 0.998. The relative standard deviation for the pyrolysis of succinic acid (41 µg) was 2.2% ($n = 4$). Using Py-GC the quantitative analysis of succinic acid was established.

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