

CURIE-POINT PYROLYSIS-GAS CHROMATOGRAPHY OF ALIPHATIC AMINES IN THE PRESENCE OF METAL POWDER AND INORGANIC SALT

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ABSTRACT

A fundamental investigation has been undertaken to determine the optimum conditions for the addition of metal powder and metal chloride to a pyrolysis foil for the analysis of aliphatic amines by means of Curie-point pyrolysis-gas chromatography. It is suggested that the effectiveness of the addition of a suitable inorganic salt to the pyrolysis foil is associated with the ability of the metal ion to complex with amines. Nickel powder was useful when the pyrolysis was carried out at lower temperatures and chromium was preferred at higher temperatures. The suitable pyrolysis temperature was related to the molecular weight of the amine samples. The optimum conditions for the pyrolysis of three butylamines resembled one another. The recommended conditions for dibutylamine hydrochloride are that the pyrolysis be carried out at 333°C in the presence of a mixture of nickel powder and cobaltous chloride hexahydrate (10 : 3 w/w). The calibration curves for dibutylamine hydrochloride, constructed by using the peak area method, were linear over the sample size range of 2.1-41.2 µg. The relative standard deviation (n = 4) was 2.56 % for 20.6 µg

Amines, aliphatic; Curie-point pyrolysis; gas chromatography; metal powder; pyrolysis.

INTRODUCTION

Although pyrolysis-gas chromatography (Py-GC) has been widely used to characterize various polymers [1] and other essentially nonvolatile compounds [2], relatively few studies have involved quantitative analysis. One of the reasons for this is that it is difficult to establish a reproducible method for the pyrolysis of a sample. Many attempts have been made to improve the

reproducibility and sensitivity of Py-GC, including the development of new pyrolysers and columns [3]. We have shown that the addition of a metal powder or a mixture of a metal powder and an inorganic salt to a sample for Curie-point pyrolysis is effective in improving the reproducibility and sensitivity in the analysis of pharmaceuticals [4] and agrochemicals [5]. The nature and amount of metal powder and inorganic salt have been determined empirically rather than through systematic studies. In this work we have conducted a fundamental Curie-point Py-GC investigation of aliphatic amines, detected as the corresponding alkyl chlorides, in order to optimize conditions for their pyrolysis in the presence of metal powder and inorganic salt additives. We also discuss the determination of dibutylamine hydrochloride.

APPARATUS AND REAGENTS

Apparatus

Pyrolysis was conducted using a Curie-point pyrolyser (Model JHP-2) supplied by Japan Analytical Industry Co., which was combined with a Hitachi Model 163 gas chromatograph.

Reagents

Metal powders and metal chlorides purchased from Wako Pure Chemical Ind. (Osaka, Japan) were used without further purification. All amines were obtained from Tokyo Kasei Ind. (Tokyo, Japan). Monobutylamine, dibutylamine, dihexylamine, dioctylamine and didecylamine were treated with hydrochloric acid to give the corresponding hydrogen chloride salts. Tributylamine was used as received. Monobutylamine and dibutylamine were dissolved in distilled water and the other amines were dissolved in methanol. The metal chlorides were used as their hexahydrates, with the exception of manganese chloride, which was used as the tetrahydrate.

EXPERIMENTAL

The procedure is as follows: adequate amounts of metal powder and metal chloride were mixed thoroughly in an agate mortar. To a piece of pyrolysis foil (pyrofoil; about 9 mmX22 mm and 0.05 mm thick), the mixture was added with a microspatula. The sample solution was added to the foil by a microsyringe of which the needle head was flattened so that the sample solution was injected completely onto the pyrofoil. The solvent on the pyrofoil was evaporated to dryness on a hot plate at about 100°C. The

TABLE 1

Instrumental operating conditions

Pyrolyser	Japan Analytical Ind. JHP-2
Oven temperature	150°C
Pipe temperature	200°C
Pyrolysis time	5s
Gas chromatograph	Hitachi 163
Column	10% PEG 20M Chromosorb (AW-DMCS)2mX3mm ID
Column temp.	40°C
Carrier gas	Nitrogen
Detector	Flame ionization, range 102

pyrofoil was loaded into the pyrolyser after it had been carefully folded. The Py-GC conditions are shown in Table 1. About 40 μg of sample were used for each experimental run. Fig. 1 illustrates typical pyrograms for dibutylamine hydrochloride. The observed area of the peak emerging at about 3 min under the optimum conditions (Fig. 1d) was about 65 times as large as that obtained without any additives (Fig. 1a).

In this procedure there are four variable parameters: metal powder, inorganic salt, ratio of mixture, and pyrolysis temperature. The effect of the

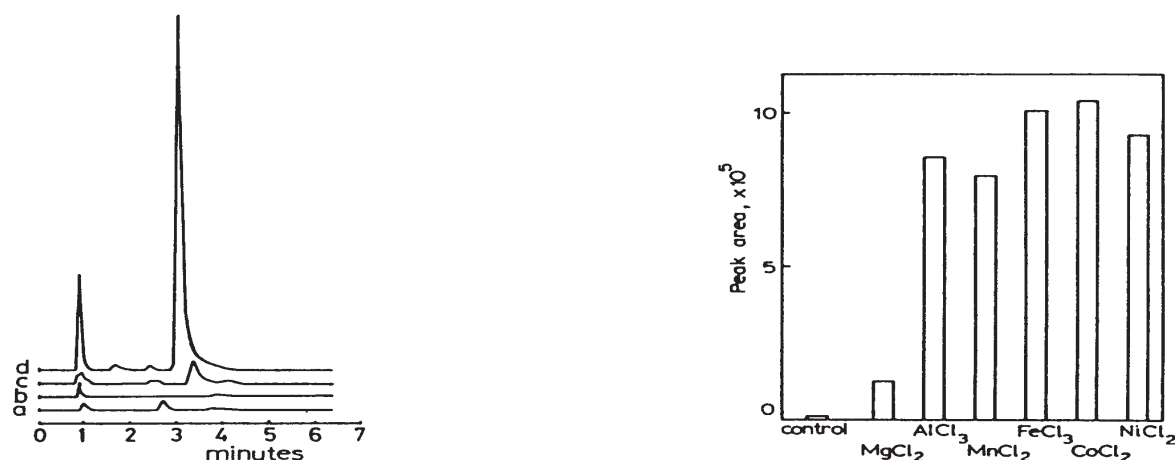


Fig. 1. Typical pyrograms of dibutylamine hydrochloride. (a) Without any additives. (b) 10 mg of nickel powder. (c) 3 mg of cobaltous chloride hexahydrate. (d) Mixture of (b) + (c). The pyrolysis temperature was 333°C. The amount of dibutylamine hydrochloride used was 20.2 μg .

Fig. 2. Effect of the added salt on the pyrolysis of monobutylamine hydrochloride. A mixture of 4 mg of salt and 20 mg of nickel powder was added to the pyrofoil at 386°C. The amount of monobutylamine hydrochloride used was 41.2 μg .

variation of these parameters on the pyrolysis is a very interesting phenomenon which can be followed quantitatively by Curie-point Py-GC. We therefore examined their effect in the following manner. The amines were detected as the corresponding alkyl chlorides which were identified by mass spectrometry. The addition of metal chloride was thus studied first.

Inorganic salt

A mixture of 4 mg of metal chloride and 20 mg of nickel powder were added to the pyrofoil in order to study the effect of the addition of inorganic salt. The salts used were magnesium chloride, aluminium chloride, manganese chloride, ferric chloride, cobaltous chloride and nickel chloride. The metal chloride which gave a simple pyrogram and the largest peak area of alkyl chloride was called the 'optimum' salt and was used in subsequent studies.

Metal powder

A mixture of 20 mg of metal powder and 4 mg of the optimum salt were added to the pyrofoil in order to examine the effect of the addition of metal powder. The metal powders used were aluminium, chromium, manganese, iron, nickel, copper and zinc. The 'optimum' metal was discovered and used in the same manner as the optimum salt.

Amount of salt addition

A mixture of 1-20 mg of the optimum salt and 10 mg of the optimum metal was added to the pyrofoil and the effect of the amount of salt added was studied. The amount of the optimum salt was determined and used in the same manner as the optimum salt.

Pyrolysis temperature

An optimum mixture of the salt and metal was chosen to study the effect of pyrolysis temperature. The pyrofoil temperatures used were 333, 386, 445, 500, 590, 670 and 764°C. The optimum temperature was found in the same manner as the optimum salt.

RESULTS AND DISCUSSION

Effect of the added metal chloride on the pyrolysis

The effect of the added salt on the pyrolysis of monobutylamine hydrochloride is shown in Fig. 2. A similar behaviour was observed for all three

butylamines. The addition of cobaltous chloride hexahydrate gave the best condition for the pyrolysis of the three butylamines, and nickel chloride hexahydrate and manganese chloride tetrahydrate provided the largest peak area for butyl chloride. Cobaltous chloride hexahydrate was the optimum salt for the three butylamines. Ferric chloride hexahydrate was the optimum salt for dioctylamine, while nickel chloride hexahydrate gave better results with dihexylamine and didecylamine. Although aluminium chloride hexahydrate gave a larger peak area for didecylamine, it was difficult to weigh accurately as a consequence of its deliquescence. It is suggested that the selection of an optimum salt is correlated with its ability to complex amines.

Effect of the added metal on the pyrolysis

The effect of the added metal on the pyrolysis of monobutylamine hydrochloride is shown in Fig. 3. Since nickel was used, the peak area of butyl chloride was relatively large. The peak area of the chlorides of dibutylamine and tributylamine were maximised when copper was used as the added metal. When an aqueous solution of the sample was added to the mixture of fine copper powder and cobaltous chloride hexahydrate, the powder floated on the surface rather than penetrating homogeneously into the mixture. Consequently, nickel was used rather than copper as the optimum metal for the three butylamines. Manganese powder was used for

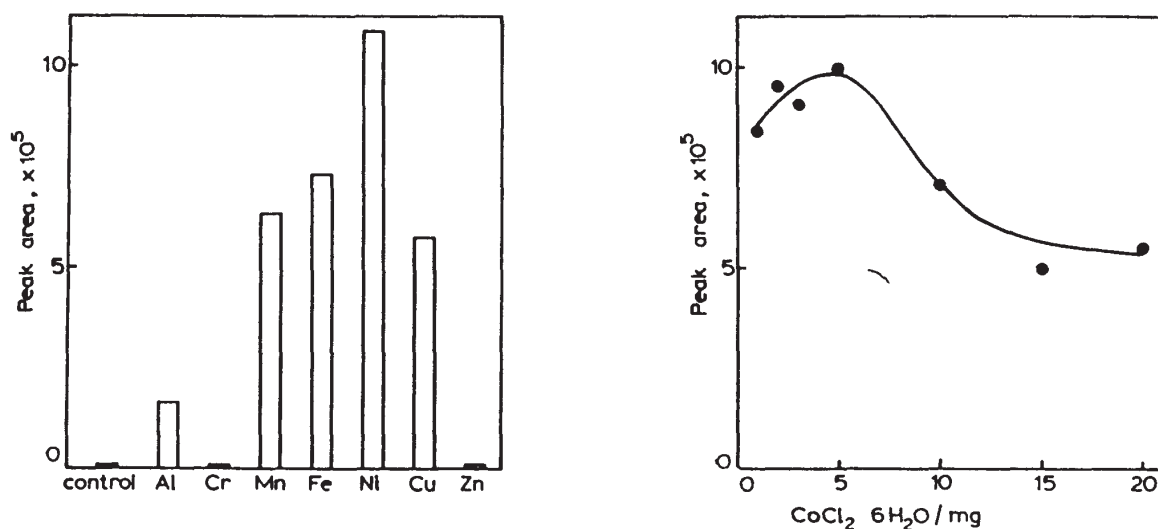


Fig 3 Effect of the added metal on the pyrolysis of monobutylamine hydrochloride A mixture of 20 mg of metal and 4 mg of the optimum salt was added to the pyrofoil at 386 °C The amount of monobutyl amine hydrochloride used was 41.2 μg

Fig 4 Effect of the amount of the optimum salt on the pyrolysis of monobutylamine hydrochloride A mixture of 1–20 mg of the optimum salt and 10 mg of the optimum metal was added to the pyrofoil at 386 °C The amount of monobutylamine hydrochloride used was 41.2 μg

dioctylamine since nickel, chromium and iron powder gave complex pyrograms. Chromium was the optimum metal for dihexylamine and didecylamine.

Effect of the amount of the added metal chloride on the pyrolysis

Fig. 4 illustrates the effect of the amount of the optimum salt on the pyrolysis of monobutylamine hydrochloride. The peak area of butyl chloride from monobutylamine decreased with addition of more than 5 mg of the salt. It appeared that an excess of the salt prevented pyrolysis of the amine. Monobutylamine and dibutylamine required several milligrams of the optimum salt in the presence of 10 mg of nickel. Dioctylamine required 5-10 mg and dihexylamine and didecylamine required 10-15 mg of the optimum salt in the presence of 10 mg of the optimum metal. With increasing molecular weight (M.W.) of the amine, the amount of the salt added showed a tendency to increase. Tributylamine is the only sample containing a tertiary amino group. The peak area of butyl chloride obtained from tributylamine increased uniquely according to an increase in the amount of optimum salt added up to 20 mg. This phenomenon might be attributed to the reaction of the cobaltous chloride hexahydrate with tributylamine to depress the evaporation of tributylamine before pyrolysis.

Effect of the pyrolysis temperature

The effect of the pyrolysis temperature of monobutylamine hydrochloride is shown in Fig. 5. The peak area of butyl chloride from monobutylamine

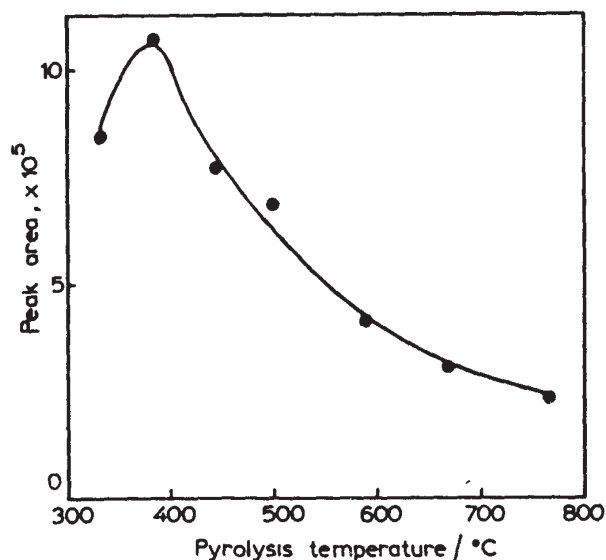


Fig 5 Effect of the pyrolysis temperature of monobutylamine hydrochloride A mixture of 5 mg of cobaltous chloride hexahydrate and 10 mg of nickel powder was added to the pyrofoil The amount of monobutylamine hydrochloride used was 41.2 μ g

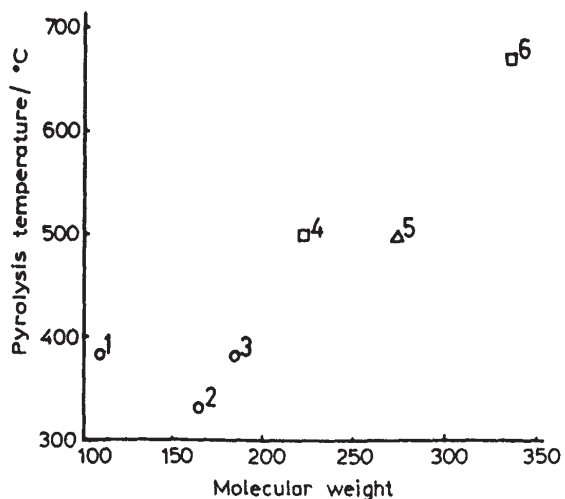


Fig. 6. Relationship between molecular weight and pyrolysis temperature. (1) Monobutylamine hydrochloride; (2) dibutylamine hydrochloride; (3) tributylamine; (4) dihexylamine hydrochloride; (5) dioctylamine hydrochloride; (6) didecylamine hydrochloride. (o) Nickel powder; (i%) chromium powder; (a) manganese powder.

decreased as the pyrolysis temperature increased beyond 386°C. This indicated that the monobutylamine was pyrolysed to some small degree at high temperature. Fig. 6 shows the relationship between the M.W. of the amine and the optimum pyrolysis temperature. In general, a larger amine M.W. was related to a higher optimum pyrolysis temperature. The optimum pyrolysis temperature of didecylamine was 670°C; this compound has the highest M.W. of the six amines studied.

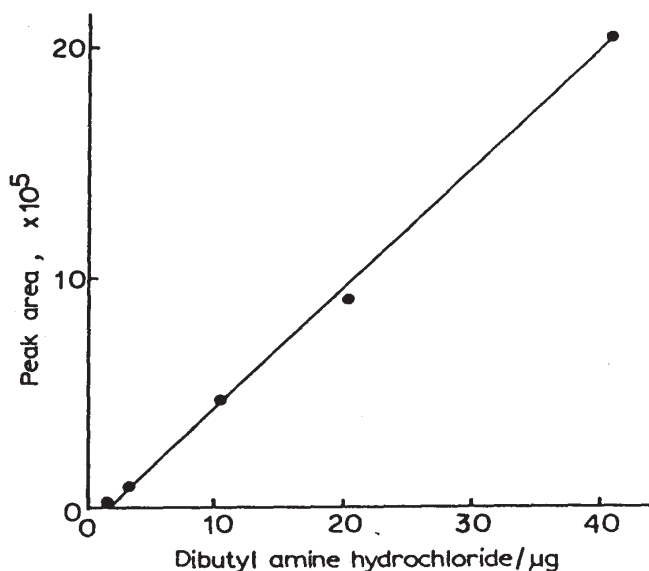


Fig. 7. Calibration curve for dibutylamine hydrochloride. The pyrolysis temperature was 333°C; 40 mg of a mixture of nickel powder and cobaltous chloride (10:3) was used.

Determination of dibutylamine hydrochloride

A maximum and constant peak area was obtained for the sample containing between 30 and 50 mg of the mixture of the nickel powder and cobaltous chloride hexahydrate (10:3 w/w) to the pyrofoil (333°C). About 40 mg of the mixture was used for the determination of dibutylamine hydrochloride in the sample range of 2.1-41.2 µg. The calibration curve is shown in Fig. 7. The relative standard deviation was 2.56% for four repeat measurements using 20.6 µg of dibutylamine hydrochloride under optimum conditions.

CONCLUSION

We can summarize the optimum conditions for the pyrolysis of the aliphatic amines as follows. (1) Inorganic salt: salts of cobalt(II), nickel(II) and iron(III), which have the ability to complex the amines studied in an efficient manner, provided the larger peak areas of alkyl chloride. (2) Metal: nickel powder gave the largest peak area with butyl chloride obtained from the three butylamines, and chromium gave good results for the other amines. (3) Amount of salt added: monobutylamine and dibutylamine required metal-to-salt ratios of 1 : 0.5 and those amines which have a larger M.W. than dibutylamine required ratios of 1 : 1-1 : 1.5. Tributylamine required a ratio of 1 : 2 or higher. (4) Pyrolysis temperature: it was discovered that the pyrolysis temperature of aliphatic amines is related to their M.W. At higher pyrolysis temperatures, amines of high M.W. gave good results. Dibutylamine hydrochloride can be determined by Curie-point Py-GC in the range of 2.1-41.2 µg with a relative standard deviation less than 3% under optimum conditions.

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