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EFFECT OF ADDING METAL POWDER AND INORGANIC SALT TO A PYROLYSIS FOIL ON SELECTIVE PYROLYSIS OF PHENYL ALKYLAMINES BY CURIE-POINT PYROLYSIS-GAS CHROMATOGRAPHY

MINEMASA HIDA and TOSHIYUKI MITSUI *

Criminal Science Laboratory, Aichi Prefecture, 2-1 -1, Sannomaru, Naka-ku,
Nagoya 460 (Japan)

YOSHIKAZU FUJIMURA

Department of Industrial Chemistry, Faculty of Engineering, University of Chubu,
1200, Matsumoto-cho, Kasugai 487 (Japan)

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ABSTRACT

The purpose of this study was to determine the effects on pyrolysis of metal powder and inorganic salt additives. Aniline, benzylamine, 2-phenyl-l-ethylamine and 3-phenyl-l-propylamine were used as samples for pyrolysis, because they have a benzene ring and an amino group as common structural units, and alkyl side chains of varying length. It can be concluded that the choice of metal and inorganic salt additives is one of the most important factors in the design of procedures allowing a high degree of control over the products of pyrolysis. It is suggested that the choice of metal should be made on the basis of bond dissociation energy, and the choice of salt on the basis of cation complexation ability with amine.

Gas chromatography; phenyl alkylamines; pyrolysis, Curie-point.

INTRODUCTION

Pyrolysis-gas chromatography (Py-GC) is one of the most powerful techniques available for the study of various polymers and essentially non-volatile compounds [1]. However, ordinary pyrolysis operations are difficult to apply to quantitative analysis, since sufficient reproducibility and precision cannot be obtained. In a series of articles [2-5] we have reported the results of analysis of medicines, agrochemicals and other chemicals by Curie-point Py-GC. The analytical technique we have developed involves pyrolysis of a sample in the presence of a mixture of a metal powder and an inorganic salt on a pyrolysis foil (pyrofoil). Thus procaine hydrochloride has been determined by Py-GC at 590°C with nickel powder:potassium iodide: ammonium sulfate (10:3:2 wt.%) [2], with a relative standard deviation of about 2%. A number of local anesthetics have been determined in a similar manner. The herbicide Paraquat has been determined by Py-GC at 445°C in the presence of a mixture of nickel powder and potassium iodide (2:1 wt%) [3]. The sensitivity of the method was about 70 times greater than in the absence of the mixture. Glyphosate has been determined by Py-GC at 590°C with chromium powder and sodium carbonate (2:1 wt%) [4], with reproducibility almost equal to that achieved by gas chromatography/mass spectrometry. Although we have also shown that the molecular weight of the sample can be used as an indication as to which metal additive to choose, obtaining satisfactory results has proved difficult [5].

The objective of the present work was to determine the effects of various metal powder and inorganic salt additives. Aniline, benzylamine, 2-phenyl-1-ethylamine and 3-phenyl-l-propylamine were used as pyrolysis samples, because they have a benzene ring and an amino group as common structural units, and alkyl side chains of varying length.

EXPERI MENTAL

Apparatus and reagents

A Curie-point pyrolyzer (Japan Analytical Industry Co. Ltd., Model JHP-2) was directly coupled to a gas chromatograph (Hitachi Model 163) equipped with a flame ionization detector (FID). The temperatures of the pyrolyzer unit and the tube connecting the pyrolyzer and gas chromatograph were maintained at 150 and 200°C, respectively. The analytical column was a stainless steel tube (2 mX3 mm I.D.) packed with 10% PEG 20M supported on 80-100 mesh Chromosorb. The GC oven program used was as follows: an initial oven temperature of 40°C, an isothermal period for aniline, a 5°C/min ramp to 80°C for benzylamine, a 7.5°C/min ramp to 120°C for 2-phenyl-l-ethylamine, and a 10°C/min ramp to 130°C for 3-phenyl-l-propylamine (Table 1). FID signals were processed using a Hewlett-Packard Model 3390A integrator.

Metal powders, metal chlorides and aniline purchased from Wako Pure Chemical Ind. (Osaka, Japan) were used without further purification. Benzylamine, 2-phenyl-l-ethylamine and 3-phenyl-l-propylamine were obtained from Tokyo Kasei Ind. (Tokyo, Japan). Benzylamine and 3-phenyl-l-pro-

TABLE 1

Operating conditions of the instrument

Pyrolyzer	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) 3 mm I.D.X2 m
Column temperature *	(a)40°C (b)40-80°C, 5°C/min (c) 40-120°C, 7.5 °C/min (d) 40-130° C, 10° C/min
Carrier gas	N2
Detector	FID Range 102, 103

* (a) Aniline hydrosulfate, (b) benzylamine hydrochloride, (c) 2-phenyl-l-ethylamine hydrochloride, (d) 3-phenyl-l-propylamine hydrochloride.

hydrosulfate and hydrochloride salts, respectively. The amines were used as aqueous solutions. The metal chlorides were used as their hexahydrates, except for manganese chloride, which was used as a tetrahydrate.

Procedure

The following procedure was used. Adequate amounts of metal powder and metal chloride were mixed thoroughly in an agate mortar. The mixture was placed onto a piece of pyrofoil (about 9 mm X 22 mm, 0.05 mm thick) using a micro-spatula. The sample solution was added using a micro-syringe, the needle head of which had been flattened so that the whole sample solution could be injected onto the pyrofoil. The solvent on the pyrofoil was evaporated to dryness on a hot plate at about 100°C. The pyrofoil was loaded into the pyrolyzer after careful folding. The Py-GC conditions are shown in Table 1. About 40 ì/g of sample were used for each experimental determination. The experiments were then developed as follows.

(1) Metal powder. 20 mg samples of metal powder were added to the pyrofoil. The metals used were aluminum, chromium, manganese, iron, nickel, copper and zinc. The optimum metal was chosen so as to maximize the yield of aromatic hydrocarbons (e.g. benzene, toluene) as measured by the peak area of largest detector response, and so as to obtain a simple pyrogram.

(2) Inorganic salt. Mixtures of 4 mg of metal chloride and 20 mg of the optimum metal powder were added to the pyrofoil. The salts used were magnesium chloride, aluminum chloride, manganese chloride, ferric chloride, cobaltous chloride and nickel chloride. The optimum salt was chosen in the same manner as was the optimum metal.

(3) Amount of salt added. Mixtures of 1-20 mg of the optimum salt and 10 mg of the optimum metal were added to the pyrofoil. The optimum amount of salt was chosen in the same manner as was the optimum metal.

(4) Pyrolysis temperature. The optimum mixture of salt and metal was added to seven kinds of pyrofoil (333, 386, 445, 500, 590, 670 and 764ºC), in order to observe the effect of pyrolysis temperature. The optimum temperature was chosen in the same manner as was the optimum metal.

RESULTS AND DISCUSSION

Effects on pyrolysis of metal additives

The effects of the metal additives on the pyrolysis of benzylamine hydrochloride are shown in Fig. 1. From Fig. 1 and Table 2, it can be seen that when a metal of high Curie point was used, the sample amines decomposed into small fragments. If the metal had a Curie point, the pyrolysis temperature was close to that Curie point temperature for the apparatus used. When the Curie point of the metal was higher than the temperature of the pyrofoil, the pyrolysis temperature was achieved at the Curie point. The relationships between the metal added and the production yields of benzene, toluene, ethylbenzene and propylbenzene are summarized in Table 2. As can be seen from Table 2, the maximum total production for all the amines was observed when chromium powder was added to the pyrofoil. The pyrolysis temperature was close to the temperature of the pyrofoil when chromium was used as the metal additive, because chromium does not have a Curie point. Chromium powder was chosen as the optimum

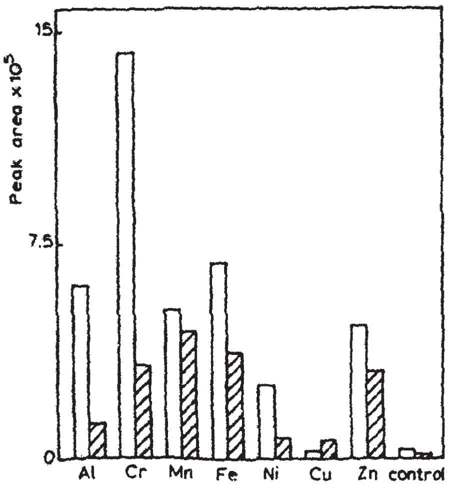


Fig. 1. Effects of metals on the pyrolysis of benzylamine hydrochloride. To the pyrofoil (590 °C) was added 20 mg metal powder with 41.2 μg benzylamine hydrochloride. Dashed areas, benzene; plain areas, toluene.

TABLE 2

Effects of metal powders on peak areas of pyrolysis products (X 10^3)

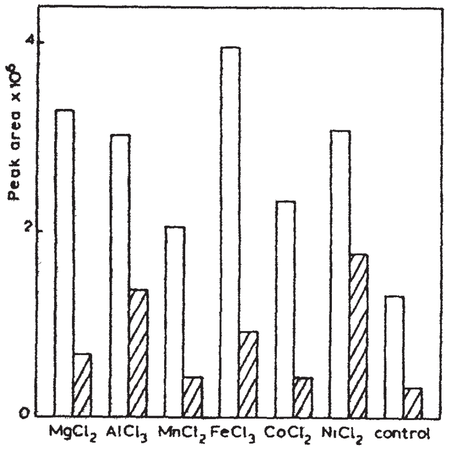
Amines *	Products	Al	Cr	Mn	Fe	Ni	Cu	Zn
Aniline	Benzene	8	68	9	7	3	48	7
Benzylamine	Benzene	123	330	459	375	67	61	305
	Toluene	610	1432	526	689	258	21	469
2-Phenyl-1-ethylamine	Benzene	113	173	384	299	113	192	28
	Toluene	529	906	445	342	297	124	505
	Ethylbenzene	118	161	11	71	15	65	128
	Benzene	21	29	54	38	13	15	12
3-Phenyl-1-propylamine	Toluene	23	30	94	30	5	1	10
	Ethylbenzene	8	115	9	5	1	7	43
	Propylbenzene	3	24	2	5	0	7	28

To the pyrofoil (500°C) was added 20 mg metal powder for 41.1 μg aniline sulfate and 40.2 μg 3-phenyl-l-propylamine hydrochloride. To the pyrofoil (590°C) was added 20 mg metal powder for 41.2 μg benzylamine hydrochloride and 41.5 μg 2-phenyl-l-ethylamine hydrochloride.

metal powder, to be used in the subsequent experiments. Further, dissociation of the amino groups was predominantly observed when chromium was used. On the other hand, manganese promoted dissociation of the sample amine into the benzene ring and methylene group. This can be explained by the fact that manganese has a Curie point of 1131°C and the sample was pyrolyzed at about 1131°C, which was higher than the temperature of the pyrofoil. It seems that the results obtained were related to the Curie points of the metal powder additives [6].

Effects on pyrolysis of metal chloride additives

The effects of the salt additives on the pyrolysis of benzylamine hydrochloride are shown in Fig. 2. The relationships between the metal chloride added and the production yields of benzene, toluene, ethylbenzene and propylbenzene are presented in Table 3. In general, yields of pyrolysis products were higher when ferric chloride, nickel chloride and aluminum chloride were used than when other salts were used. Dissociation of the amines into the benzene ring and methylene group was predominantly observed with nickel chloride and aluminum chloride. Further, ferric chloride and nickel chloride were superior to the other salts in terms of their effect on the dissociation of the amino groups. The exact weight of aluminum chloride used was difficult to determine because of its high deliquescence. As a result, ferric chloride was used for the pyrolysis of aniline and benzylamine, and nickel chloride was used for 2-phenyl-l-ethylamine and 3-phenyl-l-propylamine. In the presence of only chromium powder, the most abundant products obtained from pyrolysis of 2-phenyl-l-ethylamine



Fig, 2. Effects of inorganic salts on the pyrolysis of benzylamine hydrochloride To the pyrofoil (590°C) was added a mixture of 4 mg salt and 20 mg chromium powder with 41.2 µg beruylamine hydrochloride. Dashed areas, benzene; plain areas, toluene.

and 3-phenyl-l-propylamine were toluene and ethylbenzene, respectively. By contrast, in the presence of a mixture of chromium and nickel chloride, the most abundant products were ethylbenzene and benzene, respectively (Tables 2 and 3).

Effects on pyrolysis of the amount of metal chloride added

Figures 3a and 3b illustrate the effects of the amount of nickel chloride hexahydrate on, respectively, peak area and formation ratio of pyrolysis

TABLE 3

Effects of salts on peak areas of pyrolysis products (× 10^3)

Amines *	Products	$MgCl_2$	$AlCl_3$	$MnCl_2$	$FeCl_3$	$CoCl_2$	$NiCl_2$
Aniline	Benzene	6	222	10	567	98	253
Benzylamine	Benzene	649	1429	447	936	479	1797
	Toluene	3295	3052	2070	3996	2380	3135
2 Phenyl 1 ethylamine	Benzene	227	1609	199	800	929	1245
	Toluene	241	668	688	977	1586	1347
	Ethylbenzene	569	1334	199	1067	400	2390
3 Phenyl 1 propylamine	Benzene	31	262	34	131	109	215
	Toluene	22	66	37	49	45	60
	Ethylbenzene	34	54	19	26	10	79
	Propylbenzene	37	73	9	19	9	31

* To the pyrofoil (500 ° C) was added a mixture of 20 mg metal powder and 4 mg salt for 41 1 µg aniline sulfate and 40 2 µg 3 phenyl 1 propylamine hydrochloride To the pyrofoil (590 ° C) was added a mixture of 20 mg metal powder and 4 mg salt for 41 2 µg benzylamine hydrochloride and 41 5 µg 2 phenyl 1 ethylamine hydrochloride

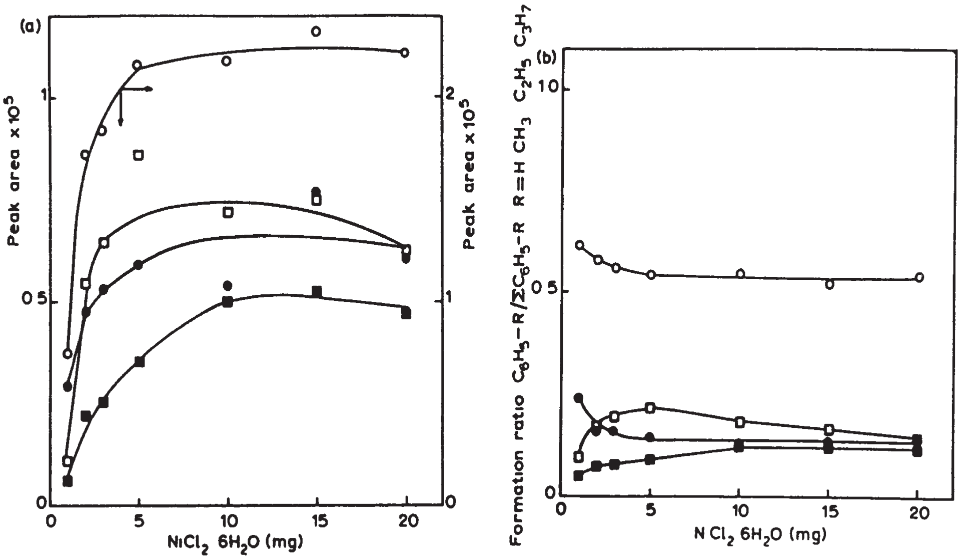


Fig 3 (a) Effects of the amount of nickel chloride hexahydrate added on the peak areas of pyrolysis products of 3 phenyl 1 propylamine hydrochloride

(b) Effects of the amount of nickel chloride hexahydrate added on the formation ratios of pyrolysis products of 3 phenyl 1 propylamine hydrochloride To the pyrofoil (500 °C) was added a mixture of 10 mg chromium and 1–20 mg nickel chloride hexahydrate with 40 2 µg 3 phenyl 1 propylamine hydrochloride ○ benzene ● toluene □ ethylbenzene ■ propylbenzene

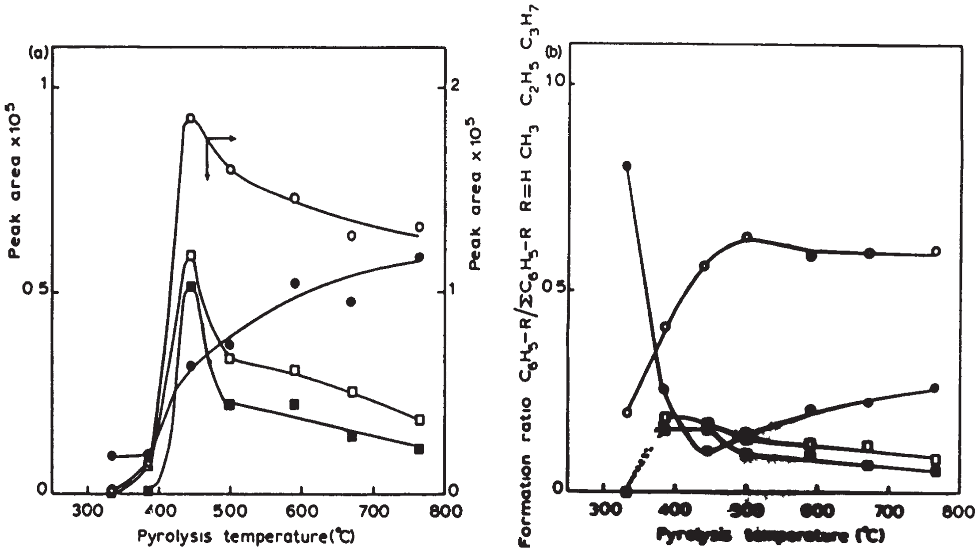


Fig 4 (a) Effects of pyrolysis temperature on peak areas of pyrolysis products of 3-phenyl-1 propylamine hydrochloride

(b) Effects of pyrolysis temperature on formation ratios of pyrolysis products of 3-phenyl-1 propylamine hydrochloride To the pyrofoil was added a mixture of 15 mg nickel chloride hexahydrate and 10 mg chromium powder The amount of 3-phenyl-1-propylamine hydrochloride used was 40 2 µg ○ benzene, ● toluene, □ ethylbenzene, ■ propylbenzene

TABLE 4

Recommended pyrolysis conditions

Amines	Detecting product	Metal. Salt	(w/w)	Temp (°C)
Aniline	Benzene	$Cr.FeCl_3$	10 3	590
Benzylamine	Toluene	$Cr\ FeCl_3$	2·1	590
2-Phenyl-1-ethylamine	Ethylbenzene	$Cr\cdot NiCl_2$	2 3	445
3-Phenyl-1-propylamine	Benzene	$Cr\ NiCl_2$	2 3	445

products obtained from 3-phenyl-l-propylamine hydrochloride. Figure 3a shows that the peak area of the products increased up to 5 mg and remained almost constant about 5 mg. Figure 3b shows that the formation ratios of benzene and toluene decreased and that of propylbenzene increased up to 5 and 10 mg, respectively, and that the ratios thereafter remained almost constant. Ethylbenzene increased up to 5 mg, and then gradually decreased. Figures 3a and 3b combined indicate that the same reactions would occur in the range 10-20 mg of nickel chloride hexahydrate.

Effects on pyrolysis of the pyrolysis temperature

The effects of varying the temperature for the pyrolysis of 3-phenyl-l-propylamine hydrochloride (40.2 µg) with a mixture of 10 mg of chromium

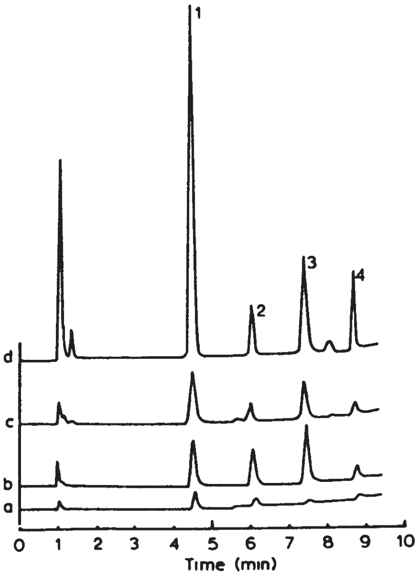


Fig 5 Typical pyrograms of 3 phenyl 1 propylamine hydrochloride (a) without any additives (b) with 15 mg nickel chloride hexahydrate (c) with 10 mg chromium (d) mixture of (b) and (c) The amount of 3 phenyl 1 propylamine hydrochloride used was 40 4 μg and the pyrolysis temperature was 445°C (1) Benzene (2) toluene (3) ethylbenzene (4) propylbenzene

and 15 mg of nickel chloride hexahydrate are shown in Figs. 4a and 4b. Figure 4a shows that yields of benzene, ethylbenzene and propylbenzene were highest at 445° C, while the yield of toluene increased with increasing temperature. The peak areas of benzene, ethylbenzene and propylbenzene decreased above 445° C, because of the decomposition of the 3-phenyl-l-propylamine into small fragments. The formation ratio of benzene was roughly constant above 445° C, and those of ethylbenzene and propylbenzene decreased slightly above 500° C, as can be seen from Fig. 4b. Figures 4a and 4b suggest that the formation reaction of toluene differs from the formation reactions of the other products. The recommended pyrolysis conditions for the amines considered are summarized in Table 4.

Figure 5 shows typical pyrograms of 3-phenyl-l-propylamine hydrochloride. The observed benzene peak area at about 4.5 min from the optimum condition (Fig. 5d) was about 30 times as large as that observed without any additives (Fig. 5a).

CONCLUSIONS

It can be concluded from this study that the choice of metal and inorganic salt additives is one of the most important factors in the design of procedures allowing a high degree of control over the products of pyrolysis. Our findings suggest that the metal powder and inorganic salt chosen affect the pyrolysis temperature and the ratio of pyrolysis products, respectively. The peak areas of the pyrolysis products and the formation ratios are important factors in the determination of the amines considered. Future publications will address the results of further studies in this area.

REFERENCES

1 S. Tsuge and H. Ohtani, Pyrolysis-Gas Chromatography of Polymers: Fundamentals and Data Compilation, Tekunoshisutem, Japan, 1989.
2 Y. Minami, T. Mitsui and Y. Fujimura, Bunseki Kagaku, 37 (1988) 259.
3 T. Mitsui, Y. Minami and Y. Fujimura, Bunseki Kagaku, 36 (1987) 821.
4 M. Hida, T. Mitsui and Y. Fujimura, Bunseki Kagaku, 38 (1989) 87.
5 M. Hida, T. Mitsui and Y. Fujimura, J. Anal. Appl. Pyrolysis, 17 (1990) 181.
6 Metal Data Book, 1974, Japan Metals Society, Maruzen, p. 10.