Effect of added inorganic salts to a pyrolysis foil on pyrolysis of benzylamine by Curie-point pyrolysis-gas chromatography

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ABSTRACT

The relationship between the pyrolysis products of benzylamine and the decomposition temperatures or dehydration temperatures (D_{temp}) of several inorganic salts was investigated by means of multivariate analysis. The inorganic salts were mixed with chromium powder mounted in a pyrolysis foil. The apparent pyrolysis temperatures were calculated with multiregression analysis using the D_{temp} of the salts. The ratio of the peak area of benzene to the total area correlated with the D_{temp} of the salts. However, that of toluene tended to decrease with D_{temp}. This indicated that the inorganic salts had an effect on the pyrolysis temperature of benzylamine.

Benzylamine; gas chromatography; inorganic salt; multivariate analysis; pyrolysis.

INTRODUCTION

Pyrolysis-gas chromatography (Py-GC) has been used for studying the microstructure, degradation mechanisms and thermal stabilities of various polymers [1]. However, many pyrolysis procedures are difficult to apply to quantitative analysis because the sample is not heated with sufficient reproducibility and precision. In a series of articles we have described analytical results for medicines [2,3], agrochemicals [4,5] and other chemicals [6,7] by Curie-point Py-GC in which a sample was pyrolyzcd in the presence of a mixture of a metal powder and an inorganic salt on a pyrolysis foil (pyrofoil). This technique was used for quantitative analysis, with relative standard deviations of less than 3%, using several microgram

of the sample. In a previous work [7], we showed that the metal powder influenced the pyrolysis temperature and that the inorganic salt served as a sample supporting material. In addition, inorganic salts effected the ratio of pyrolysis products. In the present paper, the effect of the added inorganic salts on the pyrolysis products is investigated in detail using benzylamine as a sample, and benzene and toluene as the main pyrolysis products. Multivariate analysis was used to study the relationship between the pyrolysis products and such thermal properties of inorganic salts as decomposition temperature, melting point and heat content.

APPARATUS AND REAGENTS

A Curie-point pyrolyzer (model JHP-2, Japan Analytical Industry Co. Ltd) was directly coupled to a gas chromatograph (Shimadzu GC-14A) equipped with a flame ionization detector (FID). The temperatures of the pyrolyzer unit and the tube connecting the pyrolyzer to the gas chromatograph were maintained at 150°C and 200°C respectively. The analytical column was a fused silica capillary column CBP-20 (12 m X 0.53 m (inner diameter)). The GC oven was heated from 50° to 250°C at a rate of 5°C min-1, and the detector temperature was 250°C. The FID signals were processed with a Shimadzu Chromatopac C-R4A data processor. The thermal behaviour of the inorganic salts was measured by differential thermal analysis (model TG-TDA/H Rigaku Co.) using about 12 mg of the sample under a nitrogen atmosphere (50 ml min-1). The mixtures added to the pyrofoil were analyzed before and after the sample was pyrolyzed, using an X-ray diffractometer (model RINT 1100, Rigaku) with Cu Ká radiation.

Inorganic salts, listed in Table 1, and chromium powder purchased from Wako Pure Chemical Industries (Osaka, Japan), were used without further purification. Benzylamine was obtained from Tokyo Kasei Industries. (Tokyo, Japan) and reacted with hydrochloric acid to form its hydrogen chloride salt. The amine was used in its aqueous solution.

EXPERIMENTAL

The Py-GC procedure was as follows. Equal weights of chromium powder and the inorganic salt were mixed thoroughly in an agate mortar. To a piece of pyrofoil whose Curie point was 590°C (dimensions of about 9 mm X 22 mm and thickness of 0.05 mm) 30 mg of the mixture was added using a microspatula. 10 µl of the sample solution containing 5 µg of benzylamine hydrochloride was then added to it with a microsyringe. The solvent on the pyrofoil was evaporated to dryness on a hot plate at about

TABLE 1

Results of DTA and XRD

No	Compound	Temp (°C)	XRD *
1	$ZnCl_2$	563 0	N
2	$MnCl_2$ $4H_2O$	638 7	DH
3	$NiCl_2$ $6H_2O$	820 5	DH
4	$FeCl_3$ $6H_2O$	472 6	DH
5	$CuCl_2$ $2H_2O$	432 5–659 7	D
6	$CaCl_2$ $2H_2O$	496 3	N
7	NaCl	808	N
8	$ZnSO_4$ $7H_2O$	290 6	D
9	$MnSO_4$ $4–6H_2O$	274 4	D
10	$NiSO_4$ $6H_2O$	788 5	D
11	$Fe_2(SO_4)_3$ $3H_2O$	236 4	D
12	$CuSO_4$ $5H_2O$	233 2	D
13	$CaSO_4$ $2H_2O$	356 7	DH
14	Na_2SO_4 $10H_2O$	245 3	DH
15	$ZnCO_3$	258 1	D
16	$MnCO_3$	401 2	D
17	$NiCO_3 2Ni(OH)_2$ $4H_2O$	317 3	D
18	$CuCO_3Cu(OH)_2$ H_2O	313 4	D
19	$CaCO_3$	759 8	N
20	$NaCO_3$ $10H_2O$	850 3	N

* D, decomposition, DH, dehydration, N, no decomposition

150°C for 5 min. The pyrofoil was then loaded into the pyrolyser after it was carefully folded.

RESULTS AND DISCUSSION

The results of differential thermal analysis (DTA) and X-ray diffractometry (XRD) are summarized in Table 1. The data show that most of the sulphates and carbonates decomposed prior to the pyrolysis of benzylamine at 590°C. Sodium and calcium salts, and some chlorides did not decompose, and others became dehydrated.

Data analysis

The obtained pyrograms were transformed into computer-readable form in order to perform calculations with a personal computer. The data matrix is summarized in Table 2, and a typical pyrogram is shown in Fig. 1. There were two reasons to include in the data matrix both peak areas and heights. Firstly, it was not clear whether peak areas or peak heights would give better results. Secondly, a more reliable calculation was obtained using a

TABLE 2

Observed data for benzylamine in the presence of various salts

No. *	X_1	X_2	X_3	X_4	X_5	X_6	X_7
1	0.919	0.239	0.260	0.994	0.268	0.269	0.929
2	0.445	0.200	0.449	0.438	0.218	0.498	0.964
3	0.431	0.132	0.308	0.758	0.279	0.368	0.897
4	0.768	0.193	0.252	0.918	0.280	0.305	0.970
5	0.203	0.096	0.475	0.399	0.179	0.448	0.942
6	0.527	0.080	0.152	0.692	0.030	0.160	0.928
7	0.466	0.184	0.394	0.479	0.208	0.435	0.976
8	0.215	0.144	0.668	0.194	0.141	0.726	0.979
9	0.151	0.097	0.644	0.111	0.080	0.722	0.983
10	1.906	0.361	0.189	2.017	0.389	0.193	0.989
11	10.825	0.733	0.070	7.346	0.625	0.085	0.868
12	1.547	0.176	0.114	1.401	0.192	0.137	0.957
13	0.195	0.086	0.442	0.176	0.086	0.488	0.910
14	0.484	0.109	0.231	0.540	0.122	0.225	0.923
15	20.197	0.638	0.032	24.183	0.701	0.029	0.982
16	0.642	0.205	0.319	0.621	0.161	0.260	0.991
17	33.560	0.555	0.017	21.111	0.512	0.024	1.000
18	2.286	0.145	0.062	1.703	0.151	0.089	1.000
19	0.904	0.350	0.378	1.054	0.380	0.364	0.986
20	0.643	0.216	0.336	0.699	0.253	0.361	0.970

* The salt numbers are the same as those in Table 1.

X_1, ratio of peak area of benzene to toluene.

X_2, ratio of peak area of benzene to total.

X_3, ratio of peak area of toluene to total.

X_4, ratio of peak height of benzene to toluene.

X_5, ratio of peak height of benzene to total.

X_6, ratio of peak height of toluene to total.

X_7, ratio of total peak area detected from 0–4 min to total.

larger-dimension data matrix. Data analysis was performed with multivariate analysis from a program written in basic using a personal computer (NEC PC-9801VX). This program was developed in our laboratory.

Cluster analysis

Figure 2 presents the dendrogram obtained by applying Ward's method to the whole samples. This dendrogram indicates four groups (clusters) as follows: class 1, nos. 1, 3,4, 6, 14, 16, 19, 20; class 2, nos. 2,5, 7, 8, 9, 13; class 3, nos. 10, 12, 18 and class 4, nos. 11, 15, 17. In class 4, the benzene peak overlapped with some decomposition products of the inorganic salt on the pyrogram, because all of the pyrolysis products were introduced to the separation column to avoid poor reproducibility. Therefore the class 4 salts

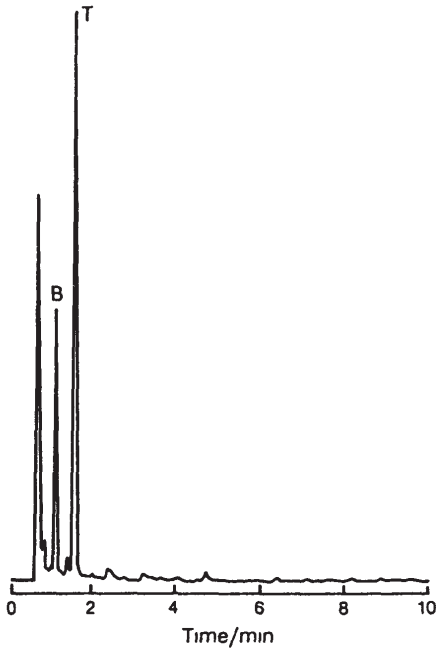

Fig 1 Pyrogram of benzylamine HCl 30 mg of the mixture (Cr NaCl = 1 1) was added to a pyrolysis foil (B benzene T toluene)

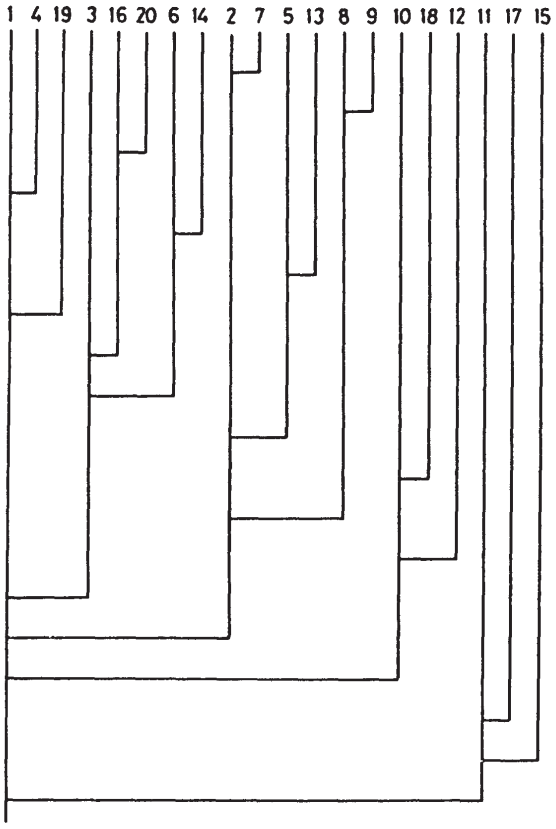

Fig 2 Dendrogram of cluster analysis

were not used to study their effect on pyrolysis. Furthermore, the class 3 salts were similar to class 4.

Multiple regression analysis and canonical correlation analysis

From multiple regression analysis, the pyrolysis products were correlated with the decomposition temperatures or dehydration temperatures (D_{temp}) of inorganic salts rather than with the melting points and heat contents. The multiple regression equation obtained from 14 samples is represented in eqn. (1)

$$Y = -2190X_1, 4- 5370X_2 - 4260X_2 - 626X_4 + 46.3X_5 + 2350X_6 + 725X_7 -336 \quad (1)$$

where Y is a calculated D_{temp} and Xi(i= 1, 2,...,7) are the data defined as follows: X_1 is the ratio of peak area of benzene to toluene; X_2 is the ratio of peak area of benzene to total; X_3 is the ratio of peak area of toluene to total; X_4 is the ratio of peak height of benzene to toluene; X5 is the ratio of peak height of benzene to total; X6 is the ratio of peak height oftoluene to total and X_7 is the ratio oftotal peak area detected from 0-4 min to total. The multiple correlation coefficient and the coefficient of determination were 0.863 and 0.745 respectively. Table 3 shows the calculated D_{temp} for the salts using this equation. As can be seen in Table 3, several D_{temp} values were greater than that of the pyrofoil utilized (590°C),

TABLE 3

Multiple regression analysis of decomposition temperatures

No [a]	Decomposition temperature (C)		
	DTA	Calculated	Error
1	563	443	120
2	639	678	−39
3	821	794	27
4	473	628	−155
5	433	379	54
6	496	449	47
7	808	667	141
8	291	338	−47
9	274	267	7
13	357	410	−53
14	245	421	−176
16	401	400	1
19	760	876	−116
20	850	860	10

[a] The samples 10 11 12 15 17 and 18 were omitted The salt numbers are the same as those in Table 1

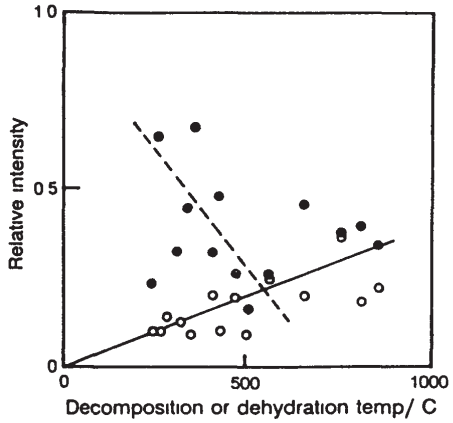

Fig 3 Relationship between the decomposition or dehydration temperature of the salt and the peak areas of benzene or toluene ○ Benzene peak area/total peak area ● toluene peak area/total peak area

so that multiple regression analysis was performed using the decomposition temperatures obtained by DTA. Manganese chloride, nickel chloride, sodium chloride, calcium carbonate and sodium carbonate decomposed at temperatures higher than 590°C, as summarized in Table 1. These data suggest that pyrolysis temperatures in this technique vary depending on the D_{temp} of tne inorganic salts. The coefficients of X_2 and X_3 were larger than the other coefficients. This means that the ratio of the peak area of benzene to total (X_2) and toluene to total (X_3) are very important in analyzing the pyrolysis profiles. In addition, X_2 is a useful factor resulting from the canonical correlation analysis (correlation coefficients with equal variances were used for the calculations). The canonical correlation coefficient was 0.863, and the structure vectors of X_2 and X_5 were 0.640 and 0.793 respectively. Figure 3 illustrates the relationship between D_{temp} of the salts and the relative peak intensities of benzene (solid line) and toluene (broken line) against the total peak area on the pyrograms. The ratios of peak area of benzene to total area increased with an increase in Dtemp of the inorganic salts, and that of toluene tended to decrease. These results are consistent with the bond dissociation energy of the carbon-carbon bond, which is generally larger than that of the carbon-nitrogen bond [8]. It is therefore reasonable to conclude that the inorganic salts effected the pyrolysis products. It is reasonable that this phenomenon should occur with variation in the pyrolysis temperature in the presence of inorganic salts.

CONCLUSION

It can also be concluded from this study that the pyrolysis products were dependent upon the Dtemp of the inorganic salts. In the presence of salts

which decomposed at lower temperatures, a smaller amount of benzene and a larger amount of toluene were produced. In particular, the formation of benzene was favoured using salts which decomposed at higher temperatures. This phenomenon suggests that the pyrolysis temperature is influenced by the inorganic salt.

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