Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 995–1002

STUDIES ON THE THERMAL DECOMPOSITION OF BENZOIC ACID AND ITS DERIVATIVES

M. Wesolowski and T. Konarski

Department of Analytical Chemistry, Medical University of Gdańsk, Al. Gen. J. Hallera 107
80-416 Gdańsk, Poland

Abstract

The thermal decomposition of benzoic acid and its derivatives containing –OH, $-NH_2$, –COOH and $-SO_3H$ functional groups as substituents in *ortho, meta* and (or) *para* position together with sulphanilic acid was investigated. The analyses were performed using derivatograph, sample mass ranged from 50 to 200 mg, heating rates from 3 to 15 K min^{-1} and static air atmosphere. It has been established that thermal decomposition of these aromatic acids proceeds through three common stages. In the first stage the phase transformations occur. The following two stages are due to the formation of intermediate products of the thermal decomposition and their combustion. Principal component analysis (PCA) was applied for evaluation of the results. Thanks to this method the influence of specific functional groups and their positions on the benzene ring on the thermal decomposition of the compounds under investigation was determined.

Keywords: benzoic acid, DTA, DTG, hydroxy- and aminobenzoic acids, *o*-phthalic acid, principal component analysis, sulphanilic acid, TG

Introduction

Thermal methods of analysis are widely used for investigation of the thermal decomposition of organic compounds [1–3]. These studies play an important role in the development of compounds, which are commonly used by manufacturers of drugs, cosmetics, producers of the household chemistry and other products of the chemical industry.

Generally, the thermal stability of an organic compound depends not only on the chemical structure but on the particle size, the degree of crystallinity, the purity, temperature of storage and the surrounding gas atmosphere as well [4]. Studies on stability and decomposition of chemical compounds are connected with the investigation on their thermal characteristic as a function of temperature. The stability and thermal decomposition of the large group of organic acids [5–12], along with relation between chemical structure and thermal decomposi-

---

* Presented at CETTA'97, Zakopane, Poland.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

tion of some organic compounds used in the medicine [13–16] have been studied in recent years.

All these facts led to the investigation on thermal decomposition of aromatic acids in order to define the influence of chemical structure on their thermal decomposition in addition to obtaining those thermal parameters which may be useful for defining their thermal stability.

Experimental

Materials

In this study the following acids were used (numbers of acids and manufacturers are given in the parentheses) – benzoic (1; POCh, Gliwice, Poland), salicylic (2; Hopkin & Williams Chadwell Heath, Essex, England), *p*-hydroxybenzoic (3; Koch-Light Laboratories Ltd., England), 2,6-dihydroxybenzoic (4; Aldrich-Chemie, Steinheim, Germany), acetylsalicylic (5; POCh, Gliwice, Poland), *o*-phthalic (6; POCh, Gliwice, Poland), anthranilic (7; POCh, Gliwice, Poland), *m*-aminobenzoic (8; Sojuzchimexport, Moscow, Russia), *p*-aminobenzoic (9; Pharmaceutical Works 'Polfa', Pabianice, Poland), *p*-aminosalicylic (10; Sigma Chemical Company, England), sulphosalicylic (11; Chemical Co-operative 'Unia', Warszawa, Poland) and sulphanilic (12; POCh, Gliwice, Poland).

Thermal analysis

The DTA, TG and DTG curves of the thermal decomposition of the studied acids were carried out using the OD-103 Derivatograph (MOM, Hungary). The 100 mg samples were heated in a platinum crucible at heating rates of 3, 5, 10 and 15 K min^{-1}, and additional 50 and 200 mg samples were heated at a heating rate of 5 K min^{-1}. The analyses were performed in air. As the reference α-Al_2O_3 was employed.

The interpretation of the TG and DTG curves consist of the temperature determination at the beginning of mass loss (T_i), the temperature range of reaction interval (ΔT) and loss of mass (Δm) for the second and third stage of decomposition.

Calculations

The principal component analysis (PCA), an advanced statistical method was used for complex interpretation of experimental data [17, 18]. In this method high number of variables can be reduced to two or three principal components which very often illustrate relations among objects in multidimensional space. That way problems which are difficult to imagine or interpret become easy to present in clear two or three dimensional plots.

The PCA consists of calculating of two new matrices – principal component scores and principal component loadings according to experimental data set **X** with the dimensions **np**, where **n** – is a number of observations (rows) and **p** – is a number of variables (columns). Principal component scores are set in matrix **P** with dimensions **nk**, and principal component loadings are contained in matrix **W** with the dimensions **pk**, where **k** is a number of orthogonal principal components calculated for the given set. **k** does not exceed the number of **p** variables and as a rule it is less than **p**. From the condition **k<p** one can conclude, that the number of principal components is much less than the number of the experimental variables **p**.

Starting point for the calculations is matrix of the data **X**. In each matrix, twelve aromatic acids were used as the rows (**n**), which were called objects, whereas T_i, ΔT and Δm denoted at different heating rates and sample masses were set as the columns (**p**) and were called variables. Matrix **X** is at first standardized, than matrix **R** is calculated according to it. After further calculations, columns in matrices **P** and **W** were obtained, which were called principal components. New matrix **P** reflects main relations among objects and makes possible classification of the investigated samples, whereas matrix **W** illustrates main relations among variables and enables their selection.

In this study three matrices were constructed. While the first grouped data set was established for the second stage of decomposition of aromatic acids, the second one contained data set for the third stage of decomposition. As the third matrix the results compiled for both stages were used.

Results and discussion

Structural formulas of the compounds studied are given in Fig. 1. There are benzoic acid and its derivatives containing –OH, $-NH_2$, –COOH and $-SO_3H$ functional groups as substituents in *ortho*, *meta* and (or) *para* position together with sulphanilic acid. The analysis of the thermal decomposition results of these acids allows to distinguish three stages of decomposition [19]. In the temperature range of the first stage, the compounds are stable. As it is displayed in Fig. 2, in the DTA curves only endothermic peaks appeared on account of the first-order phase transformations, particularly melting. This process is not accompanied by mass loss but in some cases it occurred due to evaporation of the molten compounds. This is confirmed by the second, lower and relatively broad, endothermic DTA effect.

The second stage of decomposition depends on chemical structure of the analysed acids. In this stage one or more intermediate products of the decomposition are formed. It is very difficult to establish the composition and structure of an intermediate product taking into account multidirectional course of the decomposition of organic structure. The charred residue after the decomposition of intermediate products is burned in the third stage. This process is accompanied

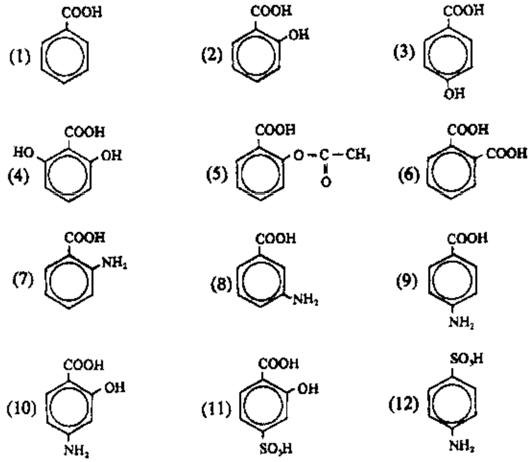

Fig. 1 Structural formulas of aromatic acids studied

both by a wide and shallow effect on the DTG curve and by an exothermic DTA effect.

For the purpose of defining the influence of the second and third functional group on thermal decomposition of the basic structure (benzoic acid), the PCA was used. The results of the first stage of decomposition were not used in calculations due to lack of the melting peak on the DTA curve of sulphanilic acid. Moreover, the second endothermic effect by reason of slight evaporation of molten compounds has not been observed for all acids.

The data matrix for the second stage of aromatic acids decomposition consists of 12 rows (aromatic acids) and 18 columns (T_i, ΔT and Δm variables at different heating rates and sample masses). The first principal component (PC1) covers 60.5% of the thermoanalytical results. The analysis of the correlation coefficients values between the T_i, ΔT and Δm variables and the PCl indicate that PC1 is strongly and negatively correlated with ΔT and Δm. In this way PC1 reflects the relationship between ΔT and Δm, and the type of functional groups substituted in the place of –H on the benzene ring of benzoic acid. It determines the distribution of aromatic acids along this vector. The second principal component (PC2) explains next 30.0% of the experimental data and is strongly and positively correlated with T_i. The remained principal components (PC3–PC18) describe only a few or even hundredth part of the total variability percentage in the data. Taking all above into account, for plotting purpose only the first two components (PC1 and PC2) may be used. They both explained 90.5% of the total variability.

As it was shown in Fig. 3, two main clusters can be extracted. In cluster A the following acids with numbers 1, 2, 3, 6, 7, 8 and 9 are included. Benzoic acid is a basic structure in all of these compounds, but they have additional –OH, $-NH_2$ or

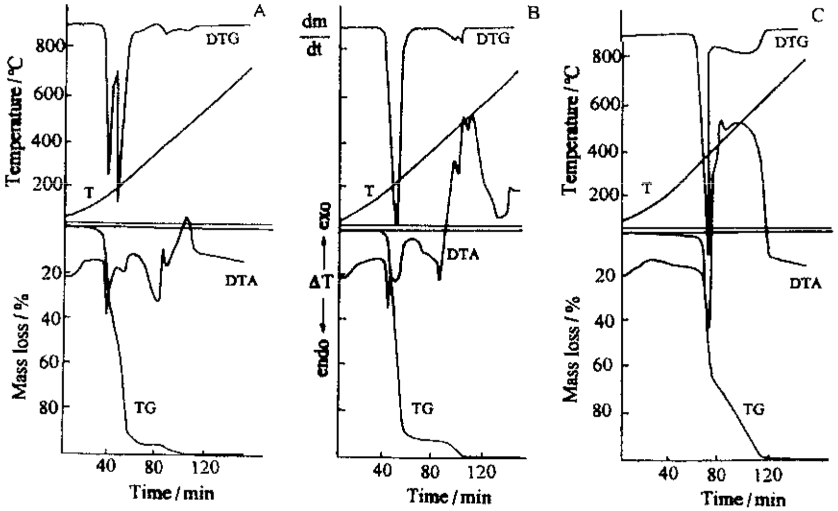

Fig. 2 DTA, TG and DTG curves of the thermal decomposition of – (A) 2,6-dihydroxybenzoic, (B) *p*-aminobenzoic and (C) sulphanilic acids. 100 mg samples were heated at a rate of 5 K min^{-1}

–COOH groups in the *ortho*, *meta* or *para* position as the second functional group. Yet, acids including three functional groups can be found in cluster B. There are acids numbered 4, 10 and 11 in this cluster. Two of acids numbered 5 and 12, which are basically different from others because of their chemical structure, are not included in any clusters.

The data matrix for the third stage of the thermal decomposition also consists of 12 objects and 18 variables. Three significant principal components (PC1, PC2 and PC3) have been extracted and they explain 92.0% of the total variability. PC1 is positively correlated with T_i and ΔT, whereas Δm is negatively correlated. The conclusion can be drawn that PC1 reflects a ratio of T_i and ΔT to Δm as a measure of the influence of substituents on the thermal decomposition of basic structure (benzoic acid). It explains 61.7% of the variability in thermoanalytical data. On the other side, only a certain tendency exists between PC2 and Δm, whereas T_i and ΔT are not correlated. Altogether PC2 covers 21.6% of the variability. Next PC3 is generally not correlated, especially with the thermal variables denoted for higher heating rates and for 200 mg sample. It explains 8.7% of variability and its eigenvalue is greater than 1. For these reasons PC3 has been taken into consideration.

The PCA results for the third stage of the thermal decomposition are presented in Fig. 4. It can be said that there are two subgroups within cluster A. These are connected with the addition of second substituent to benzoic acid. Acids with numbers 1, 2 and 3 are grouped in values of PC1 from 0.1 to 1.8, whereas acids numbered as 7, 8 and 9 from 2.7 to 3.0. Place of linkage of the second sub-

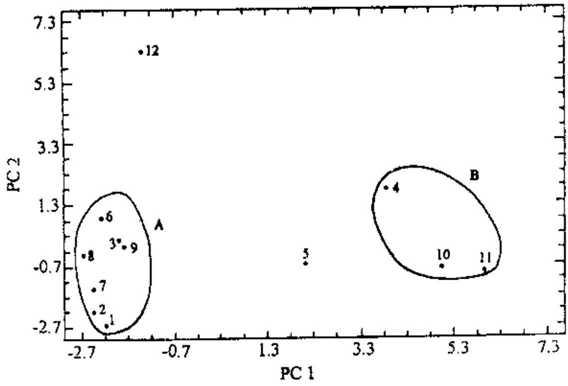

Fig. 3 Scatterplots of the first two principal component vectors (PC1 and PC2) for the second stage of thermal decomposition of organic acids. Numbers in the figure denotes studied aromatic acids

stituent is determined by PC3 which value decreases when functional group is substituted alternately in *ortho*, *meta* and *para* position.

In acids grouped in cluster B (PC1 values from –4. 1 to –5.6), their distribution is also mainly determined by PC3. As it is shown for salicylic acid derivatives with the third functional group in *para* position, the addition of $-NH_2$ group into this particular place sets the *p*-aminosalicylic acid (10) into higher positive PC3 value. In case of $-SO_3H$ group PC3 value is close to one for 2,6-dihydroxybenzoic acid (4) whose –OH group is localized in the *ortho* position.

The calculations performed for compiled results which were achieved from the second and third stage of the aromatic acids thermal decomposition revealed that PC1, PC2 and PC3 cover 59.5, 21.8 and 6.3% of the total variability, respectively. Clusters A and B are distinctly separated from one another and acids included in these clusters are distributed according to the conclusions drawn previously. Only a few differences have been noticed. Place of linkage of the second substituent with the acids located in cluster A causes the increase of PC3 value when functional group is substituted alternately in *ortho*, *meta* and *para* position.

The thermal decomposition of compounds with number 5 and 12 differs from all other acids. The replacement of acid group from –COOH to $-SO_3H$, while at the same time $-NH_2$ is the second functional group in *para* position, brings about the significant increase of PC2 value with very small change of PC1 and PC3 values. That situation is observed for acids numbered from 9 to 12. On the other hand, acetylation of –OH group of salicylic acid decreases PC1 value, increasing at the same time value of PC2. This fact causes shifting of acid numbered 5 to the group of acids gathered in B cluster.

The analysis of the first two principal components loading factors (W1 and W2) shows that all studied thermoanalytical variables may be used in the assess-

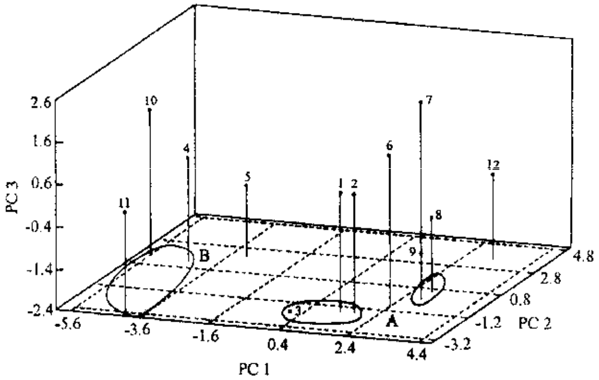

Fig. 4 Scatterplots of the first three principal component vectors (PC1, PC2 and PC3) for the third stage of thermal decomposition of organic acids. Numbers in the figure denotes studied aromatic acids

ment of the influence of functional groups on the thermal decomposition of aromatic acids. The most useful are ΔT for the second and third stage, Δm for the second stage and T_i for the third stage. The utility of T_i for the second stage and Δm in the case of the third stage of the thermal decomposition have the lower significance in describing the distribution of acids along PC1.

Conclusions

Similar physicochemical properties of the aromatic acids make their thermal decomposition courses comparable and go via three stages. Thermal methods of analysis can be useful for determination of the temperature ranges corresponding with the thermal stability of organic compounds.

As a result of PCA calculations it has been shown that the thermal decomposition of organic acids depends on the type and position of substitution of the second and third functional group. Due to the ability of the PCA to reduce a large number of variables (18 thermoanalytical variables for 12 aromatic acids), the scatterplot of two or three principal components clear reflects differences in the thermal decomposition of acids studied, which are difficult to imagine and interpret by means of multidimensional plots. In this way it has been recognised that better discrimination among acids is obtained for the data set of the second decomposition stage. The distribution of acids in two-dimensional space is determined by higher percentage of the total variability than at the same time for the third stage.

Generally, all determined thermal parameters may be useful for the assessment of influence of substituents on the thermal decomposition of basic structure.

References

1 M. Wesołowski, Thermochim. Acta, 21 (1977) 243.
2 M. Wesołowski, Thermochim. Acta, 31 (1979) 133.
3 M. Wesołowski, Drug. Dev. Ind. Pharm., 11 (1985) 493.
4 E. Pawełczyk and T. Hermann, Basic principles of drug stability, PZWL, Warsaw 1982.
5 W. W. Wendlandt and J. A. Hoiberg, Anal. Chim. Acta, 28 (1963) 506.
6 W. W. Wendlandt and J. A. Hoiberg, Anal. Chim. Acta, 29 (1963) 539.
7 J. Györe and M. Ecet, J. Thermal Anal., 2 (1970) 397.
8 K. Nagata, Bull. Nat. Res. Inst. Polymer Res., 2 (1973) 13.
9 Y. C. Lien and W. W. Nawar, J. Food Sci., 39 (1974) 911.
10 K. Rajeshwar and E. A. Secco, Can. J. Chem., 54 (1976) 2509.
11 F. González-Vilchez, M. C. Puerta Vizcaino and M. F.Gargallo Esteban, Thermochim. Acta, 42 (1980) 295.
12 M. F. Gargallo Esteban, M. C. Puerta Vizcaino and F. González-Vilchez, Thermochim. Acta, 62 (1983) 257.
13 J. Martin-Gil, F. Martinez Villa, M. C. Ramos-Sanchez and F. J. Martin-Gil, J. Thermal Anal., 29 (1984) 1351.
14 M. Uher, M. Košik and A. Martvoň, VIII Konf. Term. Anal., Vysoke Tatry, 2-5. X. 1979, Termanal 79, 273.
15 L. E. Cook and D. A. Hildebrand, Thermochim. Acta, 9 (1974) 129.
16 M. Bachratá, Ž. Bezákova and M. Blešova, Acta Fac. Pharm., 38 (1984) 97.
17 S. Wold, Pattern Recognition, 8 (1976) 127.
18 B. R. Kowalski, Anal. Chem., 52 (1980) 112R.
19 M. Wesołowski and T. Konarski, J. Thermal Anal., 43 (1995) 279.