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THERMAL BEHAVIOURS OF BARIUM ORTHO-, META- AND PARA-NITROBENZOATES

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The thermal behaviours of barium ortho-, meta- and para-nitrobenzoates were studied by DTA, TG and Emanation Thermal Analysis (ETA) in the temperature range 20–300°. The application of ETA as a supplement to the classical thermoanalytical methods (DTA and TG) for the study of organic compounds in the solid state is demonstrated.

Absolute values of emanating power, measured at room temperature for samples quenched from temperatures before and after the effects in the thermoanalytical curves, provide valuable characteristics of the intermediate products of thermal treatment, especially with regard to the degree of disorder of the molecular structure. The evolution of the molecular structure of each isomer during heating is discussed, and new X-ray patterns of the different compounds are given.

Although the differences in the chemical properties of various isomers of aromatic carboxylic acids and their salts are well known in the liquid state, their behaviours in the solid state have been studied much less.

The aim of this paper is to study and compare the thermal behaviours of the barium salts of ortho-, meta- and para-nitrobenzoic acids, which are solid at room temperature.

Thermoanalytical investigations were carried out by means of DTA, TG, Emanation Thermal Analysis (ETA) and X-ray diffraction. ETA is a recommended method [1, 2], giving information not only about the structural changes in solids, but also about molecular structure and texture and about lattice forces of compounds in the solid state. The chemical compositions of the initial compounds and the intermediates of thermal treatment were followed by infrared spectroscopy and chemical analysis.

Experimental

1. *Preparation of samples*

Barium o-nitrobenzoate trihydrate

Reagents: o-nitrobenzoic acid (R.G. purity) (m.p. 147°), and $Ba(OH)_2 \cdot 8H_2O$ (A.G. purity). 0.2 M o-nitrobenzoic acid was neutralized with 0.1 M barium hydroxide. The water-soluble salt formed [3] was crystallized at 3°, washed with water and alcohol at 3° and dried in air.

Barium m-nitrobenzoate tetrahydrate
Reagents: m-nitrobenzoic acid (R.G. purity), purified by recrystallization (m.p. 140°), NaOH and $BaCl_2 \cdot 2H_2O$ (both A.G. purity). The poorly water-soluble salt [3] was prepared at 3° by addition of stoichiometric volumes of 0.1 M barium chloride and 0.2 M sodium m-nitrobenzoate, previously obtained by neutralization of 0.2 M m-nitrobenzoic acid with 0.2 M sodium hydroxide. The precipitate of barium m-nitrobenzoate was washed with water and alcohol and dried in air.

Barium p-nitrobenzoate pentahydrate
Reagents: p-nitrobenzoic acid (R.G. purity) (m.p. 242°), NaOH and $BaCl_2 \cdot 2H_2O$ (both A.G. purity). The poorly water-solublesalt [3] was prepared in an analogous way as described above for the meta-isomer.

The three salts were analyzed for barium content by volumetric and gravimetric methods. The water content was determined by drying in an oven, at 120°, and the result checked by thermogravimetry.

2. *Labelling of samples*

The barium salts of the nitrobenzoic acids were selected because of the isomorphism of barium and radium salts, this facilitating the application of emanation measurements. The introduction of the parent isotope ^{226}Ra of the emanation was made by addition of radium nitrate (kept at pH 2.5) to aqueous solutions of the barium salts of organic acids before their crystallization. The specific activity of the samples was about 5 microcurie per gram. The samples were stored for 3 months before examination, in order for ^{222}Rn to achieve radioactive equilibrium with its parent.

3. *Measurements*

For DTA and TG measurements the B.D.L. device [4] and the Adamel–Chevenard thermobalance were used, respectively. The apparatus for simultaneous ETA and DTA was described in [5]. Experimental conditions: heating rate 5° min^{-1}; gaseous medium pure nitrogen ("U" from L'Air Liquide) flowing at 60 ml. min^{-1} through sulfuric acid and silicagel; sample weight 30–50 mg for ETA, 250 mg for TG, 5 mg for DTA.

Phase determination was performed with a Philips X-ray diffractometer, type 1320, using Cu K_α radiation, Ni-filtered, and a Debye–Scherrer photographic camera 114.6 mm in diameter.

Infrared spectra were obtained with a Perkin–Elmer spectrophotometer, type 237.

The ETA curves, recorded under dynamic conditions during heating of the samples, from scintillation counting of the radon in the flowing gas, are plotted as the temperature dependence of the radon emission in relative units. The absolute emanating powers E were measured at room temperature by the static "active deposit" method, suitable for E values above 0.10 and giving an accuracy of about $\pm 5\%$ for higher values of E [6].

Results

1. *Barium o-nitrobenzoate trihydrate*

The results of the thermoanalytical study of this substance are presented in Fig. 1. It follows from the TG, DTA and ETA curves that the loss of the three molecules of water occurs in the temperature range 45–110° as a one-step process. Both the trihydrate and the anhydrous product are well-crystalline, their X-ray patterns differing. Table 1 gives the corresponding diffraction lines.

At 220–240° an endothermal effect was observed in the DTA curve, together with an effect in the ETA curve, but no change of weight was found (Fig. 1). These effects can be attributed to a change in modification of anhydrous barium o-nitrobenzoate. Diffraction lines of these modifications, which we call α and β, are pre-

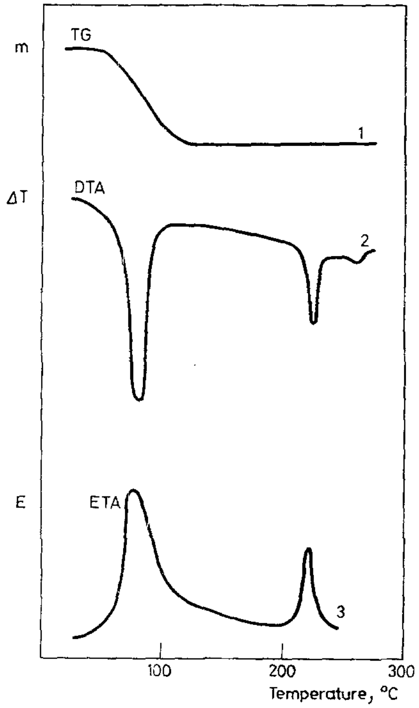

Fig. 1. TG (1), DTA (2) and ETA (3) curves of barium o-nitrobenzoate trihydrate in dry nitrogen, heating rate 5°min^{-1}

Table 1

Diffraction lines of barium o-nitrobenzoate*

Trihydrate		Anhydrous			
		heated to 200° (α variety)		heated to 240° (β variety)	
d (Å)	I	d (Å)	I	d (Å)	I
12.8	s	13.7	s	12.5	vs
7.82	vs	4.91	m	10.01	w
6.77	vs	4.75	s	7.38	w
5.73	m	4.54	m	6.72	w
5.23	m	4.41	m	5.95	w
3.92	m	3.93	m	4.69	s
3.62	vs	3.19	vs	4.22	m
3.37	m	2.26	m	3.96	m
3.12	m	2.15	m	3.63	s
2.90	m	2.04	m	3.47	m
2.62	m	1.99	w	3.29	m
2.50	m	1.60	m	2.32	w
2.07	s	1.44	w	2.09	w
1.90	s				

* visually estimated intensity I: vs = very strong, s = strong, m = medium, w = weak.

sented in Table 1. The modifications give identical infrared spectra. They are stable both in dry nitrogen and in dry air. The presence of water vapour promotes the reverse modification change from β to α. Under a partial pressure of 20 torr of water vapour at room temperature the α modification reappears after 3 hours. The β modification starts to melt incongruently at 257°; this is accompanied by an endothermic effect in the DTA curve (Fig. 1). At this time the product begins to decompose in the melt phase. After heating to 600°, well-crystalline $BaCO_3$ is formed.

2. *Barium m-nitrobenzoate tetrahydrate*

Fig. 2 presents the TG, DTA and ETA curves for barium m-nitrobenzoate tetrahydrate. Dehydration occurs in the range 50 – 135°. It was confirmed by DTA, using the lower heating rate of 2° min^{-1}, that no intermediate hydrates are formed. The dehydrated product (sample heated to 180°) is very poorly crystalline, no lines being observed in the X-ray pattern. An exothermic effect appears at 218 – 230° in the DTA curve on further heating, but no discontinuity is observed in the ETA curve in this temperature range. No difference is found between the infrared spectra of samples heated to 180° and to 260°, i.e., before and after the DTA effect. The X-ray pattern of the sample heated to 260°, however, consists of rare and diffuse lines. It is assumed that a slight physical change, e.g., a lattice rearrangement of the poorly-crystalline anhydrous product takes place at 218 – 230°.

Table 2

Diffraction lines of barium m-nitrobenzoate*

Tetrahydrate		Anhydrous salt heated to 260°	
d (Å)	I	d (Å)	I
8.53	s	13.9	w
7.54	s	7.43	w
5.73	s	5.74	w
4.47	m	5.18	w
3.81	m	4.23	w
3.73	s	3.80	w
3.57	m		
3.50	m		
3.29	s		
3.23	s		
2.64	s		
2.50	m		
2.39	m		
2.30	s		

* visually estimated intensity I: vs = very strong, s = strong, m = medium, w = weak.

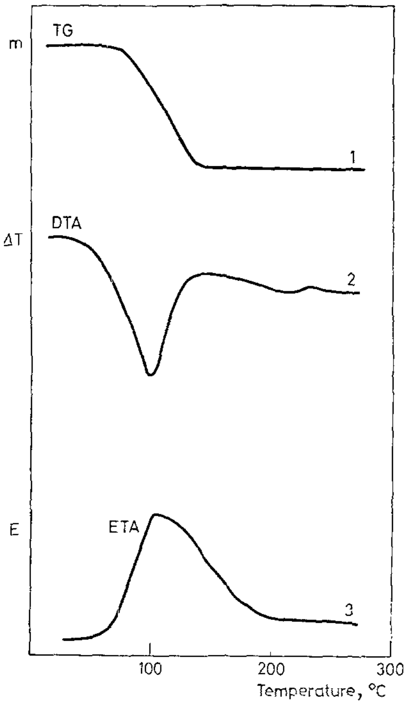

Fig. 2. TG (1), DTA (2) and ETA (3) curves of barium m-nitrobenzoate tetrahydrate in dry nitrogen, heating rate 5°min^{-1}

Diffraction lines of the initial, well-crystalline hydrated sample and of the sample heated to 260° are presented in Table 2.

Decomposition of the anhydrous salt without melting starts at 350°. If a higher heating rate (10° min^{-1}) is used, a melting process can be observed at 366°. The exothermic effect to the decomposition starts at 375°. The presence of a $BaCO_3$ residue from the sample heated up to 600° was proved via its X-ray pattern.

3. *Barium p-nitrobenzoate pentahydrate*

The TG, DTA and ETA curves in Fig. 3 show two dehydration steps in the range 60–150°. The first step corresponds to the loss of 80% hydrate water. Similarly to the initial pentahydrate, the intermediate monohydrate (sample heated to 108°) is well-crystalline according to its X-ray pattern. The diffractogram of the fully dehydrated salt (sample heated to 170°), however, exhibits no lines. In the interval 190–200° an exothermic effect is observed in the DTA curve, and a slight effect on the ETA curve. Sharp lines occur in the diffractogram of the sample heated to 210°. The infrared spectra of samples heated to 170° and to 210° are identical. A physical change, e.g., a rearrangement of the molecular lattice is assumed to occur in this temperature range.

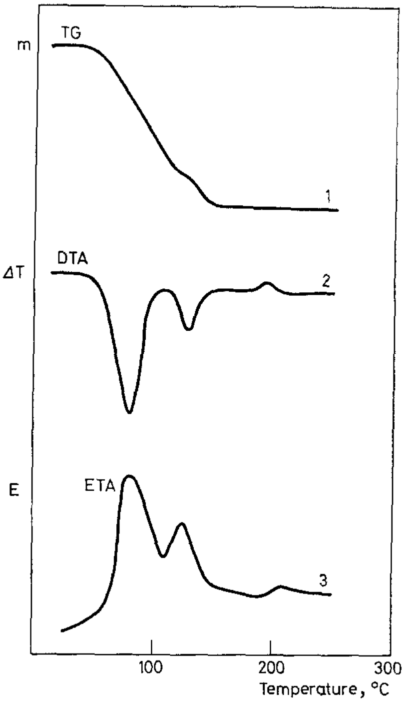

Fig. 3. TG (1), DTA (2) and ETA (3) curves of barium p-nitrobenzoate pentahydrate in dry nitrogen heating rate 5°min^{-1}

Diffraction lines of the initial pentahydrate and of the sample heated to 210° are presented in Table 3.

Table 3

Diffraction lines of barium p-nitrobenzoate*

Pentahydrate		Anhydrous salt heated to 210°	
d (Å)	I	d (Å)	I
13.5	m	13.1	vs
7.06	s	7.95	vs
5.91	s	6.83	s
5.48	vs	5.91	s
5.34	vs	5.18	s
4.82	s	4.18	s
4.31	s	3.80	m
4.16	m	3.53	m
4.01	m	3.43	m
3.80	m	3.33	s
3.45	m	2.86	s
3.35	m		
3.23	vs		
3.11	vs		
2.74	s		
2.62	s		
2.51	s		
2.34	vs		

* visually estimated intensity I: vs = very strong, s = strong, m = medium, w = weak.

The anhydrous product starts to decompose without melting at 370°. The final product of pyrolysis (sample heated to 540°) is well-crystalline $BaCO_3$.

The infrared spectra of the ortho-, meta- and para-isomers of anhydrous barium nitrobenzoate exhibit characteristic bands [6]:

– in the regions 710–760 cm^{-1}, 780–800 cm^{-1} and 810–850 cm^{-1}: bands characterizing γ-CH groups of ortho-, meta- and para-carboxylate isomers, respectively;

– in the regions 1330–1370 cm^{-1} and 1520–1540 cm^{-1}: bands characteristic of the NO_2 group and of all three isomers;

– in the regions 1410 cm^{-1} and 1590 cm^{-1}: bands characterizing symmetric and asymmetric COO^- groups, respectively.

Comparison of the I.R. spectra of the hydrates and heated samples indicates the release of hydration water for all three isomers. No change was observed in the I.R. spectra of samples of any anhydrous isomer on heating up to melting or pyrolysis.

Discussion

The thermoanalytical curves presented above show that the dehydration of all isomers is accompanied by changes of weight, endothermal effects in the DTA curves and effects in the ETA curves. The temperatures of the effects in the TG, DTA and ETA curves coincide well.

The dehydration of the ortho-, meta- and para-isomers starts at about 50° and is finished at 115°, 140° and 150°, respectively, under the experimental conditions used. The ortho- and meta-isomers are dehydrated in one step, and the para-isomer in two steps. The dehydration is increasingly more difficult, therefore, in the sequence: ortho – meta – para.

The melting points of the isomers increase in the same sequence: ortho m.p. = 257°, meta m.p. = 366°, para m.p. was found by DTA to be greater than 370°, when the anhydrous salt starts to decompose.

The X-ray study of the isomers (see diffraction lines in Tables 1 – 3) permits

Table 4

Characteristics of o-, m- and p-isomers of barium nitrobenzoate

Sample (heated to)	Absolute emanating power, (%)	Crystallinity X-ray pattern	I.R. spectra
ortho			
trihydrate (20°)	18	sharp lines (see Table 1)	no difference
anhydrous (200°)	80	sharp lines α modification (see Table 1)	
anhydrous (240°)	70	sharp lines β modification (see Table 1)	
meta			
tetrahydrate (20°)	15	sharp lines (see Table 2)	no difference
anhydrous (180°)	75	no lines	
anhydrous (260°)	71	diffuse lines	
para			
pentahydrate (20°)	28	sharp lines (see Table 3)	no difference
anhydrous (170°)	86	no lines	
anhydrous (210°)	67	sharp lines (see Table 3)	
anhydrous (330°)	58	id.	

the general conclusion of the low symmetry of their crystalline lattices, in both initial hydrated and dehydrated states.

It follows from Tables 1 – 3 that the structures of the samples change during dehydration. Changes in structure or surface area of the studied isomers during dehydration were assumed on the basis of the effects in the ETA curves (see Figs 1 – 3).

It was quantitatively shown by Flügge and Ziemens [8] that the emanating power of any substance is influenced by two principal factors: a) rate of diffusion of emanation through the solid structure, b) recoil ejection of radon atoms from disintegrations occurring near the surface. Both phenomena depend on the surface of the solid. ETA is therefore a sensitive method, giving indirect information about processes related to the magnitude of the surface area or to conditions for diffusion of the inert gas in the solid [9]. The significance of an effect in the ETA curve depends on the structural or surface-area difference between the two states of the solid, before and after the discussed effect. The information obtained from the ETA curves under dynamic experimental conditions is supplementary to that from the classical thermoanalytical methods.

Quantitative conclusions about the rates of diffusion of emanation through the solid lattices which are closely related to the molecular structures of the organic substances, can be obtained from the absolute values of the emanating power of the samples.

Table 4 lists these E values, measured at room temperature by the "active deposit method" for initial hydrates and anhydrous products heated to various temperatures, their crystallinity data obtained by X-ray, and the differences in chemical configuration observed via I.R. spectra.

Emanating power and molecular structure of samples

It is well known (see for instance reference [9]) that the emanating power depends on the composition of the solid, its structure and its texture. Inorganic compounds of coarse texture usually have a low emanating power, about 1 % or less, whereas long-chain organic compounds commonly process a higher emanating power, even in large grains. Strassmann [10], Gregory and Moorbath [2] showed that in a homologous series of barium salts of monocarboxylic acids the emanating power increases with increasing chain length: from barium acetate to laurate and palmitate it rises progressively from a few per cent to 100%. Gregory and Moorbath also stated that the high radon emanating powers at room temperature of barium palmitate or other fatty acid salts are almost entirely due to the very high rate of diffusion of radon at room temperature and not to a high specific surface area.

A correlation was found too between the emanating power and the composition of the organic salts [10, 2]. Strassmann [10] stated that even geometric isomers differ greatly in emanating power. He studied, among other compounds, barium o-, m- and p-nitrobenzoates and found the emanating powers at room temperature to be 14%, 1.5% and 0.4%, respectively. We found higher values: 18%, 15% and 28%, respectively, for the same isomers (see Table 4).

Only the two latter differ significantly from the previously determined values; one reason could be different degrees of hydration, as it appears that the E values for the dehydrated salts are higher by a factor of 3 or 4 than those for the hydrates.

The influence of the isomeric configuration is difficult to assess, because these hydrates do not contain the same number of water molecules, and have different structures and particle sizes. Comparison of the dehydrated samples cannot provide a clear-cut conclusion, because of the very different degrees of crystallinity (see remarks on X-ray patterns in Table 4) and particle sizes (see below). As a rule, however, it can be said that the para-isomer has a somewhat higher emanating power than the others.

Let us now discuss the emanating powers of dehydrated compounds heated up to different temperatures in order to investigate their molecular structures.

The ETA curves (Figs 1–3) show that for each isomer the maximum radon release rate occurs at the temperature corresponding to the maximum dehydration rate. Though this is not a true emanating power, because stationary conditions no longer exist, it gives a good picture of the defect structure created by evolution of water.

Values of the absolute emanating power measured at room temperature decrease when the dehydrated samples of all three isomers are heated (Table 4).

The specific surface areas of α and β anhydrous o-nitrobenzoates, obtained by heating the hydrate at 200 and 240°, respectively, were measured. The former was found to be 2.9 $m^2 \cdot g^{-1}$, whereas the second was lower than 0.1 $m^2 \cdot g^{-1}$ and not measurable by physical adsorption of nitrogen. Thus, a factor of more than 30 in grain size is associated with a comparatively small change (80 to 70%) in the emanating power. Such specific surface areas and a density of 1.875 [10] mean particle sizes larger than 10^4 Å, while the recoil range, calculated according to Flügge and Zimens [8] and well verified for barium salts of fatty acids [2], is 570 Å. Thus, the recoil fraction of the emanating power cannot exceed 3%. It can therefore be stated that E is due entirely to a high rate of diffusion of radon in the lattices of these aromatic compounds, as was concluded by Gregory and Moorbath for long-chain aliphatic substances [2].

The decrease of the radon-diffusion rate therefore permits the conclusion that the degree of disorder of the molecular lattice of the studied isomers decreases on heating. This conclusion is in an excellent agreement with the results of the X-ray, diffraction study (Table 4), which has shown the lattices of the samples to become more arranged with increasing temperature up to melting or pyrolysis.

Conclusion

It has been shown that the ortho-, meta- and para-isomers of barium nitrobenzoate differ in chemical and physical behaviour in the solid state during heating. The characteristics of the isomers heated to different temperatures (up to melting point or pyrolysis) are given by the values of the emanating power at room temperature, X-ray diffraction lines and characteristic bands in the I.R. spectra. The degree of disorder of the molecular lattices of all three isomers decreases on heating, as estimated from the values of the emanating power at room temperature.

Two modifications of the anhydrous ortho-isomer called α and β, are described. The melting points of the ortho- and meta-isomers were determined by DTA as 257° and 366°, respectively; the para-isomer decomposes before melting.

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Résumé — Par TG, ATD et ATE on a étudié, dans le domaine compris entre 20 et 300°C, le comportement thermique des nitrobenzoates de baryum (isomères ortho, méta et para) et on a montré l'intérêt de l'ATE utilisée comme technique complémentaire de la TG et de l'ATD pour l'étude de composés organiques à l'état solide.

En mesurant, pour chaque composé, les valeurs absolues du pouvoir émanateur avant et après chaque effet endothermique ou exothermique, on a pu mettre en évidence les caractéristiques des produits intermédiaires qui apparaissent au cours du traitement thermique, notamment en ce qui concerne le degré de désordre de la structure moléculaire. On a discuté l'évolution de cette structure pour chaque isomère au cours du chauffage. Les diagrammes de diffraction X présentés sont tous nouveaux.

Zusammenfassung — Das thermische Verhalten von Ortho-, Meta- und Para-Isomerem des Bariumnitrobenzoats wurde durch DTA, TG und Emanations-Thermoanalyse (ETA) im Temperaturbereich von 20—300°C untersucht. Die Anwendung der ETA als Ergänzung klassischer thermoanalytischer Verfahren (DTA und TG) zum Studium organischer Verbindungen wird beschrieben.

Die absoluten Werte der Emanationskraft, gemessen an Mustern, welche von Temperaturen vor und nach den Effekten abgekühlt worden waren, werden an Hand thermoanalytischer Kurven gezeigt. Sie stellen wertvolle Charakteristika von Zwischenprodukten der thermischen Behandlung dar, besonders hinsichtlich des zerstörten Ordnungsgrades der Molekularstruktur. Die Entwicklung der Molekularstruktur jedes Isomers während der Aufheizung wird erörtert und neue Röntgenspektra der verschiedenen Verbindungen werden angeführt.

Резюме — Изучено термическое поведение орто-, мето- и пара-изомеров нитробензоата бария в области температуры 20—300° методами ДТА, ТГ и эскаляционного термического анализа (ЭТА). Использование ЭТА продемонстрировало для изучения органических соединений в твердой фазе. На термодинамических кривых представлены абсолютные значения эманирующей способности, измеренной при комнатной температуре для образцов, охлажденных от температур до и после эффектов. Предложен ценный метод для характеристики промежуточных продуктов термообработки, с учетом степени разрушения молекулярного строения. Дискутируются структурные превращения молекулы каждого из изомеров при нагревании.