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Thermal analysis of salts from 4-nitrophenol and aliphatic amines

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Abstract

Solid samples obtained from 4-nitrophenol and aliphatic amines, in excess of amine, were submitted to thermal analysis. The TGA/DTA showed two endothermic events, with exception of *tert*-butylamine, which showed three endothermic peaks. The first event was the melting of the ionic salt, which temperature does not follow a pattern, and is maxim for ethylammonium minimal for butylammonium salt. For methylammonium and ethylammonium, the fusion is followed by mass loss corresponding to one amine by 4-nitrophenol, while for the others ammonium salts, this event marks the beginning of the mass variation, that is maintained until the decomposition of the 4-nitrophenol at 485 K. The temperature of the event depends of the length of the chain of the amine, while the second occurs at the same temperature for all amines.

Keywords Ammonium salts · 4-Nitrophenol · Proton transfer · Thermal analysis

Introduction

The interaction of amines and phenols has been understood by means of hydrogen bonding and electrostatic interaction. Proton transfer yields ammonium cation and phenolate ion, but this chemical process occurs when the difference between pK_a of ammonium cation is 3 pK_a units above the phenol [1]. Below this threshold, the structure is not ionic and the aggregation is kept by hydrogen bond interaction. In both cases, the hydrogen bonds direct the relative position of the ammonium and the phenol units in order to increase the number of interactions and the optimal angle.

The 4-nitrophenol is most acidic than the majority of the phenols, with $pK_a = 7.15$ in water and 21.3 in acetonitrile [2], whereas ammonium cations are weaker acids (pK_a around 10.5 in water and 18 in acetonitrile) [3]. The difference of pK_a values from ammonium cations is slightly above the ΔpK_a threshold for ionic compounds, albeit the chemical equilibrium between hydrogen-bonded and ionic species is dependent from the dielectric constant of the solvent [4, 5], and the absorption in the UV/Vis region of aggregates formed by 4-nitrophenol with diisopropylamine, butylamine and imidazole in aprotic solvents is dependent of the temperature [6]. Complexes from amines and nitrophenols have been studied by UV/IR/Raman spectrophotometry [7] and conductivimetry, and some structures have been determined by X-ray.

We used thermal analysis to achieve information about the nature of the interaction of ammonium cations with calixarene [8] anions, when we found the effect of macrocyclic and the interactions with π-cloud of the calixarene. In the present study, we search for the effect of the role of the hydrogen bond interaction in the salts formed by amine and phenols [9], using a poor π-donor such 4-nitrophenol. Recent investigation on salts of 4-nitrobenzoic acid and alkanolamines [10] showed the role of hydrogen bond interaction.

Compounds of 4-nitrophenol are known by their nonlinear optical properties [11] by the presence of electron donor (–OH or $–O^-$) group, and electron withdrawing group and ammonium cations have attracted a lot of

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attention by their applications as drugs [12], surfactants [13], ionic liquids [14], lubricants [15] and materials for electrical applications [16]. Thermal stability is critical for some applications and allows determine thermodynamic parameters related to heat absorption, as well the possibility of side reactions. The present study seeks to establish important variables for the thermal properties of 4-nitrophenolate salts with aliphatic ammonium salts.

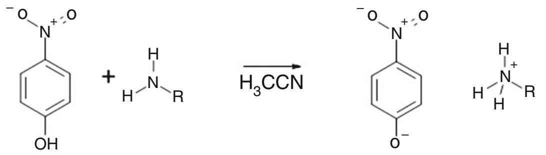
Materials and methods

The alkylammonium-4-nitrophenolate salts were obtained by adding ten times excess of alkylamine (Aldrich and Merck) to 4-nitrophenol (Aldrich) solution (100 g L^{-1}) in acetonitrile. Methylamine (VETEC) and ethylamine (VETEC) were used as aqueous solutions. Slow evaporation of the solvent gave pale yellow to orange crystals, collected and washed with hexane to remove adsorbed amine. Salts from amines with short chains (methyl, ethyl, propyl and *tert*-butyl) crystallize faster, while salts from amines with longer chains required several days to the formation of crystal samples. Infrared and ^{1}H-NMR analyses are in agreement with the proposed structure for the salts.

Thermogravimetric (TG) curves were performed using the Shimadzu DTG-60H equipment. The conditions were: heating temperature 30–300 °C, rate of 10 °C min^{-1}, nitrogen flow of 100 mL min^{-1} and mass of 3.16 ± 0.23 mg in aluminum crucible. The calibration of the instrument was evaluated with standard calcium oxalate monohydrate. Infrared analyses were performed in a IR Prestige 21-Shimadzu and ^{1}H-NMR in a Bruker Fourier 300 MHz.

Results and discussion

Addition of the amine to the solution of 4-nitrophenol in acetonitrile results in the formation of the ammonium salt and 4-nitrophenolate, observed by the appearance of yellow to orange color in the solution. The methyl, ethyl and *tert*-butylamine salts precipitate rapidly, while the salts of propyl, butyl, pentyl, hexyl and dodecylamine are more soluble in acetonitrile and formed solid samples after partial evaporation of the solvent. The yields were variable and higher for methyl, ethyl and *t*-butyl (around 80%) and lower for propyl, butyl, pentyl, hexyl and dodecyl (50–20%) (Scheme 1).



Scheme 1 Synthesis of ammonium salts of 4-nitrophenolate

Infrared analysis of the solid materials revealed that the presence of bands from symmetrical and unsymmetrical stretching vibration of the nitro group at 1550–1475 cm^{-1} and of the aromatic ring 1590 cm^{-1} and the stretching bands of N^+–H above 3050 cm^{-1} and the region above 3050 cm^{-1} is similar for ammonium salts, with a band above 3300 cm^{-1} and another between 3150 and 3250 cm^{-1}, with the exception of ethylammonium salt, whose infrared spectra does not show band above 3300 cm^{-1}, and two bands at 3215 and 3100 cm^{-1} for N^+–H stretching. The low frequency for stretching vibration of hydrogen bond aggregates is an evidence for strong hydrogen bond, and we consider that the ammonium group in ethylammonium is involved in three strong hydrogen bonds with phenolate or nitro groups, while other, the ammonium salts have one hydrogen bonded to nitrogen not able to interact by hydrogen bond (Fig. 1).

The analysis of ^{1}H-NMR of the products are in agreement with the ionic nature of ammonium–phenolate interaction, as seen for the ethylammonium-4-nitrophenolate spectrum shown in Fig. 2, by the shift of δ of the ammonium moiety to low fields (δ 3.7 and δ 3.0), when compared with the relative amine, while the chemical shift of the protons attached to the aromatic ring of the 4-nitrophenolate (δ 7.9 and δ 7.0) were shifted to high field, in relation with the 4-nitrophenol, mostly the proton near the phenolate. However, the most important feature was the absence of neutral 4-nitrophenol, reported in some crystal structures [7, 17].

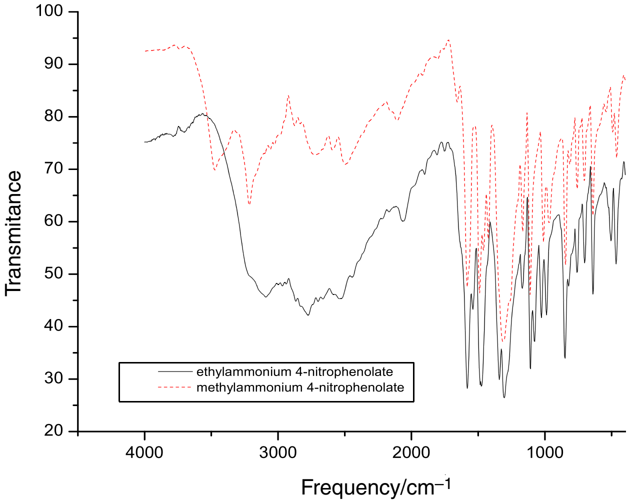
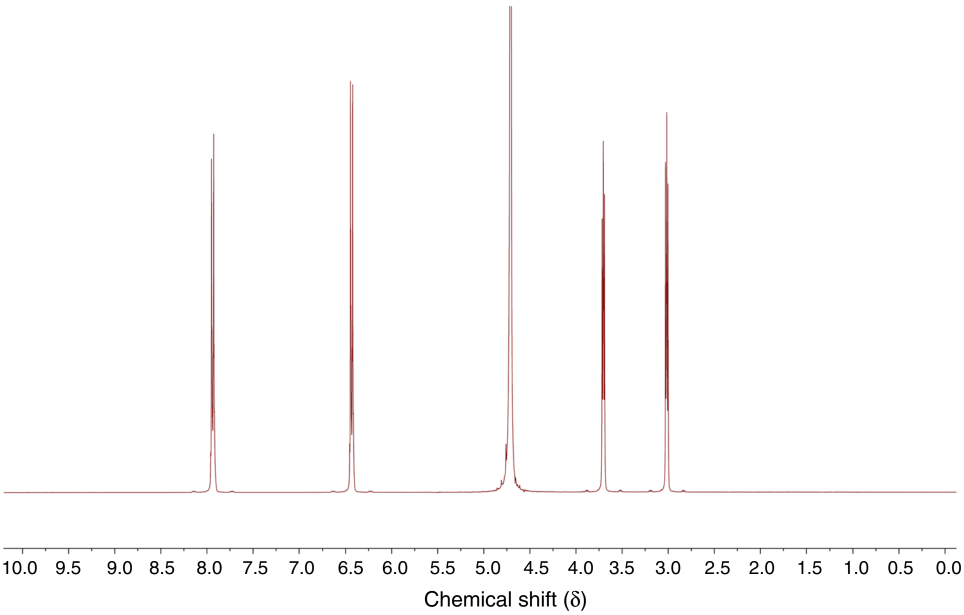


Fig. 1 Infrared spectra of methylammonium and ethylammonium 4-nitrophenolate salts

Fig. 2 ^{1}H-NMR of ethylammonium-4-nitrophenolate in D_2O



The solid samples obtained from 4-nitrophenol and aliphatic amines were submitted to thermal analysis, demonstrating total mass loss in the range of 293–500 K, as shown in Fig. 3. The curves of TGA obtained from the ammonium salts revealed two endothermic events, with the exception of *tert*-butylammonium salt, that showed three ones.

The first event occurred in different temperatures according to the chain length, and for methylamine and ethylamine salts, it coincides with the loss of mass observed by DTG curves. The losses of mass were about 18 and 25% of the initial mass, for methylammonium and ethylammonium salts, respectively, and match a 1:1 amine: phenol stoichiometry. These variations could be attributed to the loss of methylamine and ethylamine with 1:1 stoichiometry of amine/phenol. The loss of mass is associated with an endothermic peak shown by DTA curves at 387 K and 410 K for methyl and ethylamine. The increase in the leaving temperature of the amine at 299 K follows the trend of boiling temperature increase of 22 K.

This synchrony between the endothermic event and the loss of mass is an evidence to define the association between the proton transfer from the ammonium cation to the phenolate and the release of the amine from the solid. From propylammonium salt, it is no longer possible to observe a singular mass variation related to this endothermic event. The curve becomes very smooth, and the mass loss begins its descent around 373 K until the total loss of mass at 500 K. The mass lost nearby the first endothermic event corresponds to a maximum of 5% for propylamine, which cannot be attributed to the loss of one molecule of amine. Another suggested possibility was a stoichiometry of 4-nitrophenol: amine 2:1, already known for salts of secondary amines [17], but the mass loss remains insufficient to support such hypothesis. Otherwise, the use of large excesses of amine prevents such stoichiometry. The results obtained revealed a maximum in the melting temperature for ethylammonium salt, and we can attribute this result to the strong hydrogen bond interactions shown by the infrared spectrum. The sequence shows a drop in this temperature until the minimum at 322 K for butylammonium salt, followed by similar values around 348 K, as seen in Fig. 3. For the TGA, it was not possible define a plateau between both endothermic events for amines with chains longer than ethyl, and the first endothermic event marks the start of mass loss, which proceeds continuously until the total loss achieved around 493 K (Fig. 4).

This nonlinear effect behavior for the temperature of the first endothermic event should result from the contribution of different aspects related to the ammonium–phenolate interaction and related to amine departure from the solid phase. Such effects may be: ammonium acidity (or amine basicity), amine boiling point, entropy effects and other effects related to crystalline packaging. While the predominance of enthalpic factors leads to an increase in amine with the chain length, the predominance of the entropy leads to the opposite direction.

The factor from the ammonium acidity is related with the proton transfer between the ammonium cation and phenol, and can be obtained from the relation with the Gibbs free energy and the difference of pK_a ($\Delta pK_a = pK_a$ ammonium − pK_a phenol).

$$\Delta G = -2.303RT\Delta pK_a$$

Since the pK_a is nearly constant for all amines used in this experiment and ΔpK_a is nearby constant in the linear

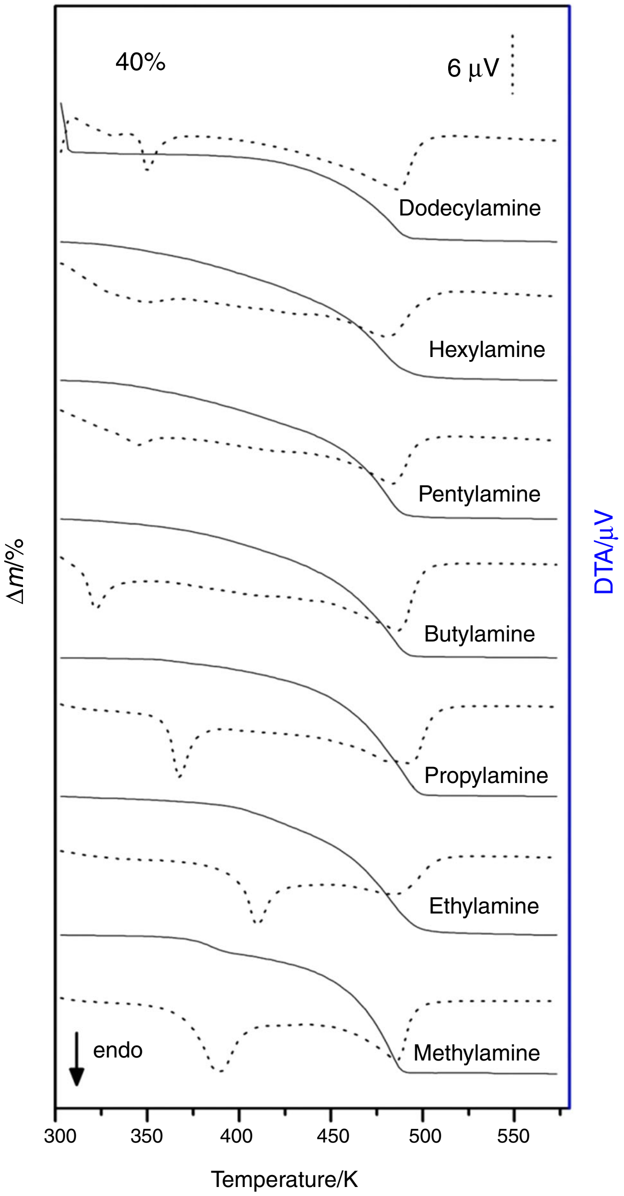


Fig. 3 TG/DTA curves for salts of 4-nitrophenol with aliphatic amines

amine series, we concluded that the free energy associated with the transfer of the proton is practically the same in the series. This effect alone should result in values of temperature for the events constants.

The second effect to be considered is the boiling point of amines, shown in Table 1, that increases for larger chain lengths by the increase in the molecular mass of the amine, and once that the proton transfer regenerates the amine, the contribution of this effect should be important for the profile of thermal analysis.

Another effect is the entropy related with translation modes by vaporization, as well the variation of vibrational and rotational modes from the aliphatic chain. The effect from longer chains should result as an increase in the entropic factor related to amine vaporization, similar to alkanes with different aliphatic chains [18], whereas the packing effect is related with the correct geometry to find the minimal energy in the solid phase and is hard to predict and find correlations.

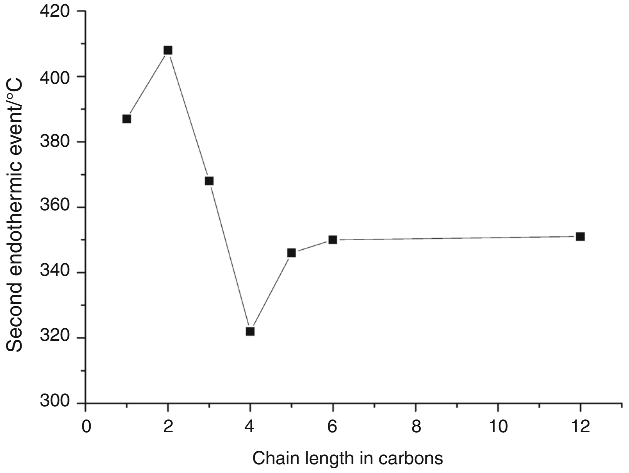
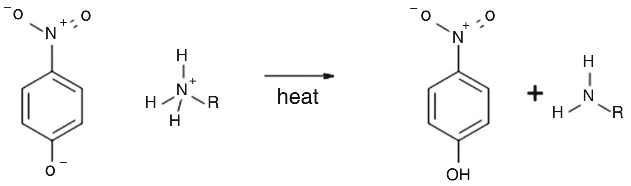


Fig. 4 Variation of temperature of the first endothermic event with the length chain of the amine

Table 1 Boiling point (b.p.) of amines

Amine	b.p./K
Methylamine	267
Ethylamine	289
1-Propylamine	321
tert-butylamine	318
1-Butylamine	351
1-Pentylamine	377
1-Hexylamine	405
1-Dodecylamine	520

We proposed a simple model to rationalize the results, based in the early evidences characterized by thermochromism phenomenon. Ammonium cations and 4-nitrophenolate interact by electrostatic and hydrogen bonding through the phenoxide and nitro groups with the positive hydrogen of the ammonium group along the $O^{-}–H^{+}–N$ axis. When the temperature reaches the first endothermic event, the solid melts, and the ammonium cation



Scheme 2 Proton transfer of the ammonium cation to 4-nitrophenolate promoted by heat

transfers back the proton to the phenolate, resulting in the original amine and 4-nitrophenol (Scheme 2).

Both methylamine and ethylamine have lighter chains and lower boiling points and leaves the solid when their salts melt, whereas for other amines with heavier chains, the loss of mass corresponding to the reverse proton transfer occurs after the melting of the salts. The amine remains in the liquid phase, but it is loosely bonded and vaporized by further heating. Amines with longer chains also have higher boiling points, and the variation of mass after the aggregation change results in a slower loss of mass corresponding to the departure of the amine with high molecular weight, which explains the variations in TG analysis.

The profile of the melting temperature seems almost erratic. First, we observe an increase from methyl to ethyl, followed by a drop until to reach a minimum for butylamine, followed by a new increase until a plateau after hexylamine.

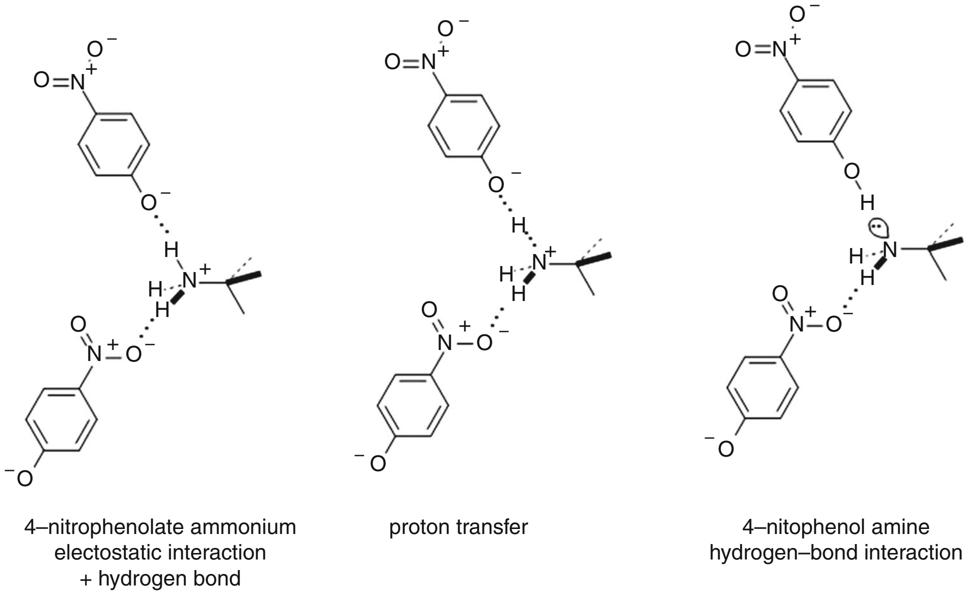
In order to explain the profile, we propose the change in the form of interaction between 4-nitrophenol and amine from ionic to hydrogen-bonded in liquid phase, resulting in loose aggregates. The hydrogen-bonded amine gains additional vibrational and rotational modes with the phase change and the entropy variation depends of the length chain of the amines, whereas changes in enthalpy promoted by the proton transfer should be almost the same for all amines. However, the highest value for the temperature of proton transfer for ethylammonium salt is attributed to strong hydrogen bonds observed by infrared spectrum of this compound (Scheme 3).

The entropy variation would raise the maximum for butylamine, and further increase in the carbonic chain does not result in large entropy variation because the rest of the chain already has some rotational freedom in the ionic form, and there is no additional entropic gain with the change from the ionic form to molecular form. Early reports for the melting point of symmetrical quaternary ammonium salts exhibit a sudden drop with the increase in the alkyl chain length [19].

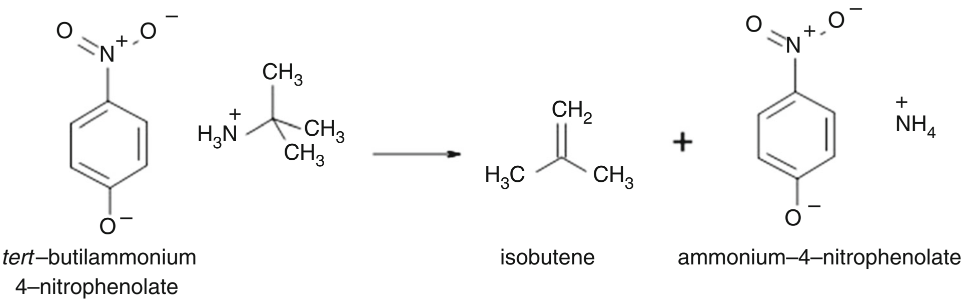
The salt with *tert*-butylamine displayed a unique curve with three endothermic events. The first occurs at 355 K, followed by another at 397 K and the last at 485 K. The value of mass loss matches with the decomposition of the *tert*-butylammonium into isobutene and ammonium, which remains in solid phase. This result was not expected, but can be explained by the relative stability of the *tert*-butyl cation, formed by the breaking of the ammonium–carbon bond, followed by proton transfer from the *tert*-butyl cation to ammonia, resulting in isobutene and the ammonium salt of 4-nitrophenol. This proposal is likely an E1-type reaction promoted by heat. Identical results were reported [20] by thermal decomposition of *tert*-butylamine promoted by HBr (Scheme 4, Fig. 5).

The last step is the complete vaporization of the mass left over nearly 485 K and is coincident with the complete loss of mass for all samples analyzed. This is an evidence that the ammonium cation or the amine does not have influence in this event, and this event was attributed to the decomposition of 4-nitrophenol, already reported in such temperature [21]. The range of the loss of mass matches the boiling point of nitrobenzene, although we could not devise nor find any reliable mechanism to yield nitrobenzene from 4-nitrophenol.

Scheme 3 Proton transfer pathway of ammonium salt to 4-nitrophenolate



Scheme 4 Proposed reaction for decomposition of *tert*-butylammonium 4-nitrophenolate salt



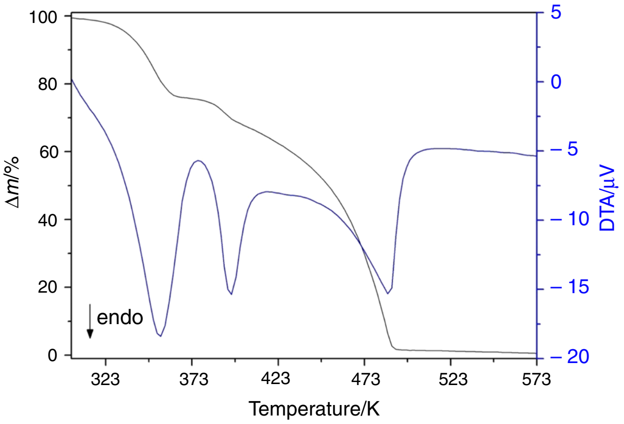


Fig. 5 TG/DTA curve of salt of *tert*-butylamine and 4-nitrophenol

Conclusions

Thermal analysis of the 4-nitrophenol salts with linear aliphatic amines reveals two endothermic processes with mass loss:, a) fusion of the salt followed by proton transfer from the ammonium cation to 4-nitrophenolate anion; for methylammonium and ethylammonium salt the proton transfer occurs simultaneously with fusion, while for other amines the protons transfer occurs slowly in higher temperatures; b) the second endothermic peak is attributed to vaporization of nitrobenzene, formed by decomposition of nitrophenol.

There is no linear behavior between the temperature of the amine output and the carbon chain length, and this was attributed to contribution from the variation of boiling point of the amines and variation in the entropic contribution with the increase in the length of chain of amines. In addition, *tert*-butylamine has one more endothermic peak, attributed to the breaking of the C–N^{+} bond and formation of isobutene and ammonium.

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