J Therm Anal Calorim (2009) 97:359–365
DOI 10.1007/s10973-009-0262-6

Thermoanalytical studies of some sweeteners

**Lucinéia Cristina de Carvalho · Milena Pinotti Segato ·
Ronaldo Spezia Nunes · Csaba Novak ·
Éder Tadeu Gomes Cavalheiro**

ICTAC2008 Conference

Abstract The thermal decomposition behavior of acesulfame-K (ACK), aspartame (ASP), sodium cyclamate (SCL), saccharine (SAC), and sodium saccharine (SSA) were investigated. After re-crystallization of the commercial samples the compounds were characterized by using elemental analysis, IR spectroscopy and thermoanalytical techniques (TG/DTG, DTA, and DSC). Evidences of hydrate water loss were observed for SSA and ASP. Melting was detected for SSA and SAC. Each compound decomposed in a characteristics way. The decomposition of APS and SAC took place completely, while ACK, SCL and SSA resulted in K_2SO_4, Na_2SO_4, and Na_2SO_4, as residues respectively. The Flynn-Wall-Ozawa method for kinetic calculations was applied for the volatilization of saccharine resulting in $E_a = 80 \pm 1$ kJ mol^{-1} and log $A = 7.36 \pm 0.07$ min^{-1}.

Keywords Non-caloric sweeteners · Thermal analysis · TG · DTA · DSC

L. C. de Carvalho · M. P. Segato · R. S. Nunes ·
É. T. G. Cavalheiro (✉)
Departamento de Química e Física Molecular, Instituto de
Química de São Carlos, USP, Av. do Trabalhador São-Carlense
400, Centro, Caixa Postal 780, CEP, 13560-970 São Carlos, SP,
Brazil
e-mail: cavalheiro@iqsc.usp.br

Cs. Novak
Hungarian Academy of Sciences, Research Group of Technical
Analytical Chemistry, Budapest University of Technology
and Economics, Szt. Gellert ter 4, H-1111 Budapest, Hungary

Present Address:
M. P. Segato
Instituto de Química, UNICAMP, Campinas, SP, Brazil

Introduction

Food additives play a distinctive role in the modern food industry, and are generally used for maintaining or improving food quality and characteristics as well as promoting food safety. The most common artificial sweeteners include sodium saccharin (SSA), aspartame (ASP), and acesulfame-K (ACK), which are all permitted for use in about 90 countries. They provide benefits to costumers offering non-caloric sweet food and beverages, an advantage for those demanding such products in order to reduce energy or sugar uptake for health reasons and to the food industry by increasing shelf life of some products compared with the sugar sweetened ones [1].

Crudely, flavor can be considered as comprising volatile components whose aroma is sensed in the nose and non-volatile components whose taste sensed on the tongue along with compounds and structures that are perceived in the mouth as mouth-feel and/or texture. It is believed that aroma is more important than taste in determining overall flavor, a generalization that can be easily demonstrated by observing the difficulties that people have identifying flavored drinks if the air flow through their noses is prevented by pinching off the nostrils [2, 3].

It is important to study the thermal behavior of sweeteners since the cooking temperature and time can cause decomposition of components during processing with new compound formation, which may be harmful or simply having undesired sweetening properties. Chemical interactions can take place during industrial processing, which may require the development of better methodologies applied to quality control and assurance [4, 5].

Saccharin has been the center of controversy in the last few decades due to its possible carcinogenic effects. However, when used into appropriate dosages it did not cause cancer in rats and it was concluded that its use under these conditions is safe [6, 7].

Among others, thermal analysis has great interest in the characterization of sweeteners and supplying analytical data for industrial process, which decreases time and costs of analyses [8–11].

In this work the thermal behavior of ACK, ASP, SCL, SAC, and SSA were evaluated in order to understand their thermal decomposition pathways and how the temperature can provoke changes in their structures. This can be useful in households or in industrial food processing in which such compounds are present as non-caloric sweeteners as well as in the identification of intermediates of thermal decomposition.

Experimental

In this work, acesulfame-K ($C_4H_4KNO_4S$–Fluka, analytical grade), aspartame ($C_{14}H_{18}N_2O_5$—Natural Pharma, technical grade), sodium cyclamate ($C_6H_{12}NNaO_3S$—Natural Pharma, technical grade) and sodium saccharine ($C_7H_4NNaO_3S \cdot 2H_2O$—Natural Pharma, technical grade) were used.

The analytical grade acesulfame-K and the aspartame were used without further purification. The technical grade sodium cyclamate and sodium saccharine sweeteners were re-crystallized before use. The re-crystallization was performed by dissolving the sweetener in a minimum amount of water followed by addition of five times more related to the water volume of cold acetone (sodium cyclamate) and ethyl alcohol (sodium saccharine).

The acidic saccharine (SAC) was obtained by dissolving 15.0 g of sodium saccharine in 30.0 mL of distilled water. To this solution drop by drop concentrated HCl was added until a precipitate was formed. Then the solution was placed in a refrigerator overnight. The resulting precipitate was filtered, washed with cold water and dried in a vacuum oven at 30 °C for 24 h.

The compounds were characterized by FTIR spectroscopy (1% in KBr pellets) using a Nicolet 5SXC FTIR spectrophotometer.

The TG/DTG and DTA curves were recorded using a SDT-Q600 simultaneous TG-DTA thermal analyzer controlled by Thermal Advantage (4.2.1) software; both from TA-Instruments. The best experimental conditions were optimized as 10 °C min^{-1} heating rate, dynamic air atmosphere with 100 mL min^{-1} flow rate in the 25–900 °C temperature range. All the runs were performed in an alumina sample holder with sample masses of c.a. 4 mg.

Results and discussion

Elemental analysis (EA)

The elemental analysis (C, N, H) results are presented in Table 1. The measured C, N, and H contents (as well as the amount of hydrate water) are in a good agreement with the chemical structures/composition of the compounds.

FTIR studies

The IR spectra for all the sweeteners investigated in this work are presented in Fig. 1. In SCL the imino group showed a narrow NH stretching band at 3278 cm^{-1} and the imino hydrogen deformation (δ NH) is assigned to the strong band at 1446 cm^{-1}. Asymmetrical SO_2 stretching was attributed to bands at 1244 and 1215 cm^{-1}, and symmetrical SO_2 stretching to the band at 1173 cm^{-1}, in agreement with the findings of Neville et al. [12].

The spectrum of SSA shows the stretching bands of C=O at 1644 cm^{-1}, C=C at 1584 cm^{-1}, the SO_2 asymmetrical stretching at 1258 cm^{-1} and symmetrical one at 1148 cm^{-1}. The CS stretching appeared at 1050 cm^{-1}, while the CN deformation coupled to the HCC is presented at 1120 cm^{-1} [13].

The IR spectrum of ASP is presented in Fig. 1, in which the following bands can be highlighted. The CO and CN stretching in the amide portion could be responsible for exhibiting strong IR absorption in the regions around 1669 and 1548 cm^{-1}, respectively. The ester group characterized by carbonyl bonds could be accounted by strong IR absorption bands in the region of 1737 cm^{-1}. In addition, the strong IR band in the region of 1150–1300 cm^{-1}, might be attributed to (O=C)–O stretching. This band constitutes a high-frequency single-bond stretch involving CC and OC bonds. The IR bands around 3000 cm^{-1} may be assigned to OH stretching vibration in the carboxyl moiety. Similarly, strong wagging of aromatic CH belonging to the monosubstituted benzene might have led to the occurrence of bands

Table 1 Elemental analysis data for all sweeteners

Sweeteners	Experimental (calculated) (%)		
	C	H	N
ACK	22.14 (23.85)	2.09 (2.01)	7.04 (6.96)
ASP. 0.75 H_2O	55.08 (54.62)	6.08 (6.39)	9.30 (9.10)
SCL	35.83 (35.81)	5.52 (6.01)	7.00 (6.96)
SAC	45.74 (45.89)	3.09 (2.75)	7.66 (7.65)
SSA. 0.75 H_2O	38.43 (37.66)	1.67 (2.71)	6.52 (6.27)

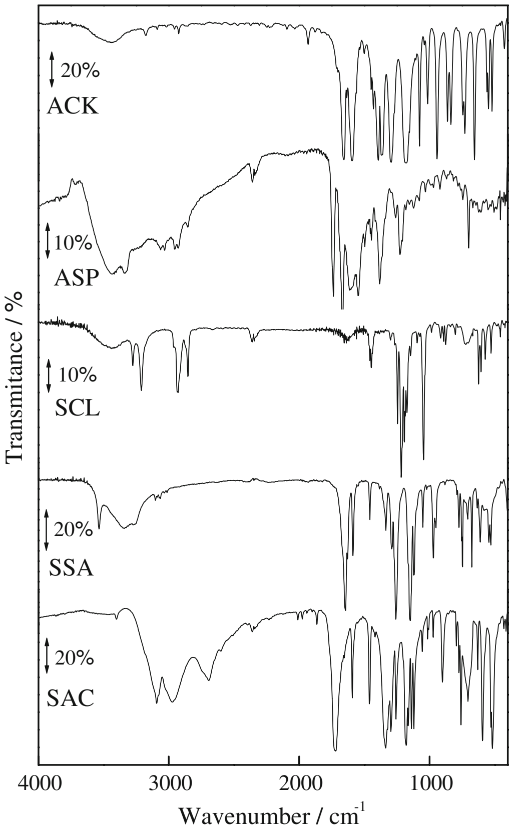

Fig. 1 IR spectra for all the sweeteners

around 700–800 cm^{-1} region. In addition, the bands around 1050 and 1600 cm^{-1} could be assigned to CN stretching and NH_2 scissoring, respectively. These observations are in agreement with those described by Khurana et al. [14].

The most intense bands of ACK are located at 1680 and 1150 cm^{-1} due to C=O stretch and NH_2 rock in amides. Other less intense absorption bands are located at 1600 and 1356 cm^{-1} due to SO_2 stretch and C=C stretch in cyclohexenes. The bands observed in this work are in agreement with those described by Armenta et al. [15].

As expected most of the bands observed in the acidic form of SAC are also observed in the sodium salt spectra and are present in the 1563–700 cm^{-1} range. Most significant changes could be noticed between 3500–1772 cm^{-1} and 1500–700 cm^{-1}. This is an evidence of the conversion of the sodium salt to its acidic form with changes in the hydration of the molecule as well as in the C=S and C–N bonds [16].

Thermogravimetric studies and characterization of intermediates by TG-DTA

The TG/DTG curves of the sweeteners are presented in Fig. 2a, while the DTA curves are in Fig. 2b. The thermal events observed in each case at air are described below and summarized in Table 2, in which is possible to see the temperature intervals, mass losses (in %) and DTA peak temperatures.

The solid residues were characterized also by X-ray diffraction after preparation of the samples under conditions similar to those in which they appeared in the thermal balance and compared with standard XRD database (diffractograms here are not presented).

Acesulfame-K (ACK)

According to the TG/DTG curves the decomposition takes place from 258 to 450 °C. The DTG curve indicates that the process starts with a sudden mass loss between 258 and 340 °C that generates a thermally non-stable residue and then the process continues slowly up to 450 °C, producing carbonaceous material that burns between 450 and 658 °C. The residue at 660 °C was characterized by infrared spectroscopy and X-ray diffraction, which was K_2SO_4.

Aspartame (ASP)

The thermal behavior of ASP can be characterized with five steps in its TG/DTG. The first and the second ones were related to the loss of water. According to Leung et al. [17] aspartame exists in two hemihydrate solid forms that loose water at different temperatures. Form I looses water around 58 °C, while Form II at 113 °C.

At our experiments two dehydration processes are attributed to the presence of a mixture of Forms I and II (see in Table 2). According to the stoichiometric calculations 2:1 ratio of Form I and Form II can be supposed and of 0.75 hydrate water molecules per mol of the ASP (see Table 2). Cheng and Lin [18] also described the existence of a dihemihydrate, but our findings did not show the presence of this form in our sample.

The third event was an intramolecular reaction of aspartame with release of methanol that generates a diketopiperazine (DKP). After that penylalanine methylesther is lost by decomposition of the DKP (fourth event) generating a carbonaceous material that burns in the fifth step. This is in agreement with the findings of Simencio [19], Conceição et al. [20] and Cheng and Lin [18].

However, according to the Merck Index [21] diketopiperazine begins to sublime at 260 °C and sinters at 305 °C, which could explain the DTA peak at 250 °C, which was not discussed in [20], but was reported in [19] and confirmed by our experiments. Under dynamic heating the decomposition of DKP seems to take place as represented by the TG curve. Cheng and Lin [18] comment that the endothermic peak at 249 °C should be assigned to the melting of DKP, however they did not show TG curves.

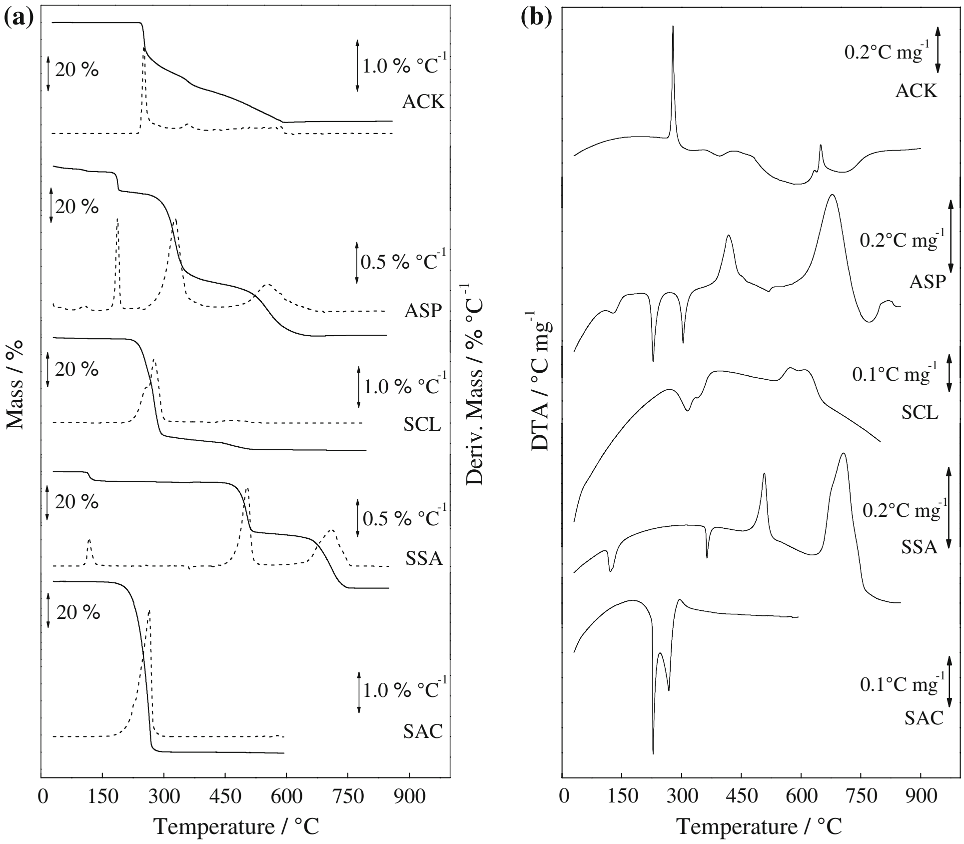

Fig. 2 **a** TG/DTG curves and **b** DTA curves of sweeteners obtained in dynamic air atmosphere. Exo up

Table 2 The thermal events, temperature intervals, mass losses in %, and DTA peak temperatures for sweeteners

Sweeteners	Event	Temperature intervals (°C)	Mass loss/%		DTA peak (°C)
			Exp	(Calc)	
ACK	Decomp	258.5–450.2	39.7	–	278.0 (exo)
	CM burn	450.2–658.3	18.7	–	633.1 (endo)
	Residue	>658.3	42.1	(43.0)	650.2 (exo)
ASP	Dehydration Form I	24.8–75.7	2.69	(2.93)	–
	Dehydration Form II	75.7–127.3	1.66	(1.46)	109.7 (endo)
	Sublimation	127.3–209.3	11.76	–	190.3 (endo)
	Burn decomp	209.3–440.1	53.31	–	340.3 (exo)
	CM burn	440.1–681.0	30.58	–	548.2 (exo)
SCL	Decomp	180.0–260.0	22.3	–	258.7(endo)
	Burn decomp	260.0–323.8	36.2	–	–
	CM burn	323.8–795.0	7.5	–	463.5 (exo)
	Residue	>795.0	34.8	(35.3)	–
SSA	Dehydration	21.5–153.8	5.51	(5.6)	121.8 (endo)
	Melting	–	–	–	361.1 (endo)**
	Decomp	436.3–537.2	29.38	–	508.2 (exo)
	CM burn	537.2–768.0	32.2	–	–
	Residue	>768.0	31.79	(32.4)	706.6 (exo)
SAC	Total process	152.8–372.3	100	–	–
	Melting	–	–	–	226.8 (endo)**
	Volatilization	246.0–295.0	–	–	254.1 (endo)**

**CM* carbonaceous material

**Onset temperature

Since at our experiments in this temperature interval mass loss was observed, in our opinion it cannot be a simple melting process.

Conceição et al. [20] reported a volatilization processes between 30 and 150 °C for ASP, however we believe that this is rather related to a two-step dehydration as stated above.

Sodium cyclamate (SCL)

The TG-DTA curve revealed the first thermal event, which can be related to the decomposition of the sample, resulting 58.5% of mass loss and a carbonaceous residue. According to the DTG curve (Fig. 2a) decomposition undergoes by successive steps without the formation of a stable intermediate products prohibiting their characterization. The DTA curve did not show any evidences of melting or polymorphic transformations.

After burning of the carbonaceous residue the stable decomposition product was identified as sodium sulphate by IR spectra, in which bands between 1100 and 1200 cm^{-1} attributed to S=O stretching [16] and the ones in the 600–700 cm^{-1} range are also characteristic for Na_2SO_4 (see Fig. 3). X-ray diffraction also confirmed the presence of Na_2SO_4 as residue (TG: 34.8% and calc.: 35.5%).

Sodium saccharin (SSA)

In agreement with the findings of Naumov et al. [22] the water release resulted of 0.75 mol of H_2O (TG: 5.7%; calc.: 5.6%). After dehydration the DTA peak can be observed is related to the melting of the sample and the decomposition took place in two steps leading to sodium sulphate as residue (found = 31.45, calc = 32.48%).

The presence of Na_2SO_4 in the residue was confirmed by IR and X-ray diffraction analyses. Since relatively stable intermediates were found, IR spectra were taken from the decomposition products at different temperatures. By the evaluation of the resulted IR spectra (Fig. 3) one can conclude that the sweetener is stable up to 200 °C and the Na_2SO_4 is formed even at 550 °C but some organic compound is still remain. At 750 °C the organic matter is released and only bands for Na_2SO_4 appeared in the spectra [23].

Saccharin (SAC)

Bernal et al. [24] described when SAC is heated it undergoes at first melting followed by volatilization. This was confirmed by heating a saccharin sample in a long test tube, collecting the condensate and recording its IR spectrum. The DTA curve of the condensate is presented in Fig. 4, while Fig. 5 presents the spectra of the sample and the condensate for comparison.

Kinetics studies for SAC

Since in the DTG curves of SAC well defined thermal profiles were found, the Flynn-Wall-Ozawa isoconversional method was used to evaluate the solid state kinetic of

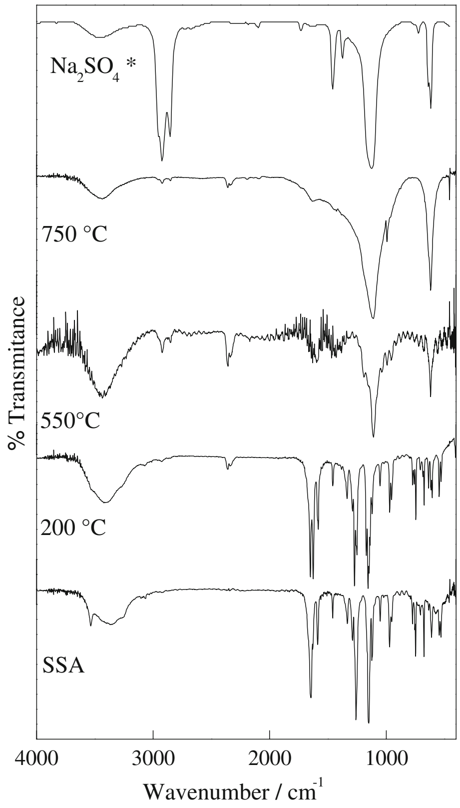

Fig. 3 The spectral evolution of the sodium saccharin decomposition. *Peaks c.a. 3000 cm^{-1} due to the mineral oil

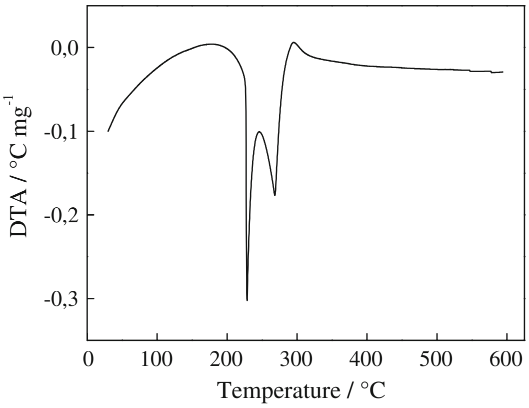

Fig. 4 DTA curve of the volatile matter condensed in the top of the test tube when saccharine is heated. Exo up

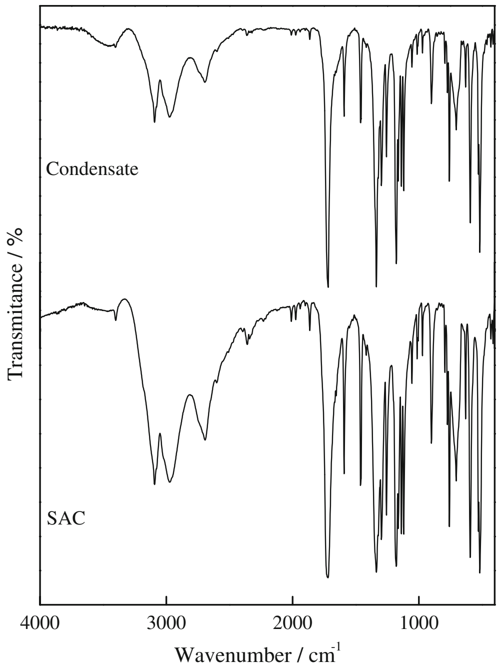

Fig. 5 IR spectrum of saccharin and condensate product in wall tube

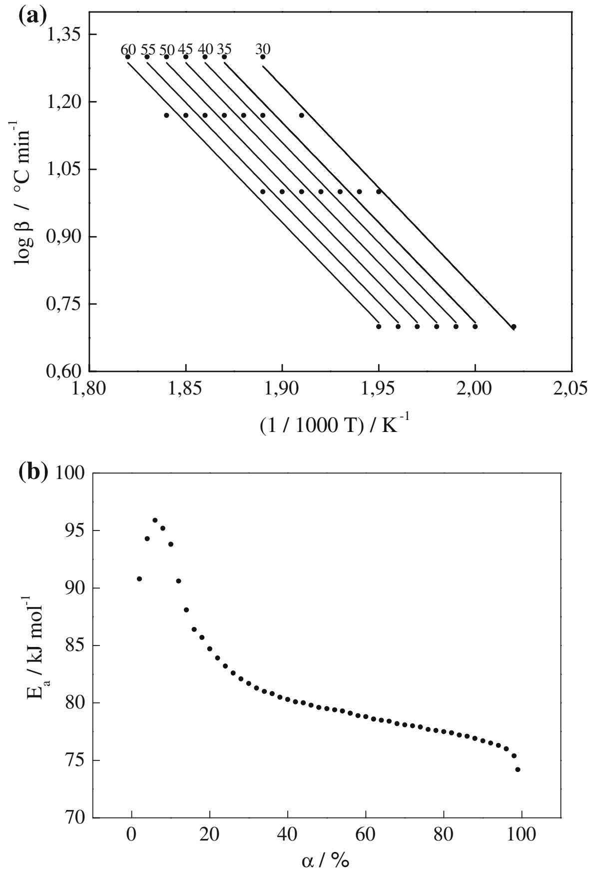

Fig. 6 **a** log *β* vs. 1/1000*T* plots for saccharin at *a* 30.0, *b* 35.0, *c* 30.0, *d* 45.0, *e* 50.0, *f* 55.0, and *g* 60.0% conversion. **b** E_a vs. α plots for saccharin at all range of conversion

Table 3 Data used in the obtaining of log *β* vs 1/*T* graphs for SAC volatilization

α (%)	E_a (kJ mol^{-1})	log *A*	$t_{1/2}$ 60 min (°C)
30.0	81.7	7.48	180.1
35.0	80.9	7.41	178.9
40.0	80.3	7.37	177.7
45.0	79.8	7.34	176.5
50.0	79.5	7.32	175.3
55.0	79.1	7.31	174.0
60.0	78.7	7.29	172.6

volatilization of SAC at different heating rates (*β*, at 5, 10, 15, and 20 °C min^{-1}) under N_2 (50 mL min^{-1} flow rate), at conversion degrees of (α) 30, 35, 40, 45, 50, 55, and 60%.

Figure 6a presents the log *β* vs. 1/*T* curve for SAC volatilization which generates the results for E_a, log A and half-life time, presented in Table 3. The dependence of E_a vs. α is presented in Fig. 6b and confirms that melting has some influence in the volatilization at the beginning of the process and the decomposition of residue influences the process at the end. However, for α 30–60% the process of volatilization was a single event. The suggested kinetic parameters are $E_a = 80 \pm 1$ kJ mol^{-1} and $\log A = 7.36 \pm 0.01$ min^{-1} (from data in Table 3).

Conclusions

All the compounds were subjected to thermal analysis (TG/DTG and DTA) showing characteristic thermal decomposition pathways as described above. In some cases, decomposition takes place only after dehydration. After their dehydration the investigated sweeteners presented the following thermal stability order: ASP < SSA < SCL < ACK. The acidic form of saccharin evaporated completely without decomposition.

The thermal decomposition kinetic studies for all the compounds could not be performed, because of the overlapping thermal events. Only saccharin exhibited such a thermal curve that allowed the determination of the kinetic parameters for its volatilization.

References

1. Noble AC. Taste-aroma interactions. Trends Food Sci Technol. 1996;7:439–44.
2. Taylor AJ, Linforth RST. Flavour release in the mouth. Trends Food Sci Technol. 1996;7:444–48.
3. Fatibello-Filho O, Vieira IC, Gouveia ST, Calafatti SA, Guaritá-Santos AJM. Artificial sweeteners. Quim Nova. 1996;3:248–60.

4. Curini R, Ascenzo FD, Lucchetti MC, Wendlandt WW. Thermoanalytical techniques applied to the analysis of an Italian soft cheese—a critical comparison with the official methods of analysis. Thermochim Acta. 1989;144:301–12.
5. Dollimore D. The application of thermal-analysis in studying the thermal-decomposition of solids. Thermochim Acta. 1992;203: 7–23.
6. Simão AM. Aditivos Para Alimentos Sob o Aspecto Toxicológico. São Paulo: Nobel; 1985. p. 231.
7. Chen QC, Wang J. Simultaneous determination of artificial sweeteners, preservatives, caffeine, theobromine and theophylline in food and pharmaceutical preparations by ion chromatography. J Chromatogr. 2001;937:57–64.
8. Conceição MM, Melo AML, Narain N, Santos IMG, Souza AG. Isothermal kinetic study of corn and its derivatives. J Therm Anal Cal. 2002;67:373–9.
9. Silva SA, Conceição MM, Souza AG, Cavalheiro JMO, Alencar ALS, Prasad S. Calorimetry and thermogravimetric study of algaroba [*Prosopis juliflora* (SW) D. C.]. Quim Nova. 2001;24: 460–4.
10. Silva SA, Conceição MM, Souza AG, Macedo RO. Calorimetric and kinetic parameters of manioc derivatives. Thermochim Acta. 1999;328:177–81.
11. Souza FS, Macedo RO, Veras JWE. Studies of cimetidine preformulated and tablets for TG and DSC coupled to the photovisual system. Thermochim Acta. 2002;99:392–3.
12. Neville GA, Ethier JC. J AOAC Int. 1971;54:1200.
13. Imai Y, Kamada J-I. Vibrational spectra of saccharin nitranion and its orientation on the surface of silver metal particles. Spectrochim Acta A. 2005;61:711–5.
14. Khurana HK, Cho IK, Shim JY, Li QX, Jun S. Application of multibounce attenuated total reflectance Fourier transform infrared spectroscopy and chemometrics for determination of aspartame in soft drinks. J Agric Food Chem. 2008;56:778–83.
15. Armenta S, Garrigues S, de la Guardia M. FTIR determination of aspartame and acesulfame-K in tabletop sweeteners. J Agric Food Chem. 2004;52:7798–803.
16. Silverstein RM, Bassler GC, Morrill TC. Spectrometric identification of organic compounds. 5th ed. New York: John Willey; 1991.
17. Leung SS, Padden BE, Munson EJ, Grant DJW. Hydration and dehydration behavior of aspartame hemihydrate. J Pharm Sci. 1998;87:508–13.
18. Cheng YD, Lin SY. Isothermal Fourier transform infrared microspectrosopic studies on the stability kinetics of solid-state intramolecular cyclization of aspartame sweetener. J Agric Food Chem. 2000;48:631–5.
19. Simencio RL. Potencialidade do uso de tratamentos quimiométricos de dados termogravimétricos: formulação farmacêutica e adoçante artificial. Msc Dissertation, Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brasil; 2005.
20. Conceição MM, Fernandes VJ Jr, Souza AG, Nascimento TC, Aragão CFS, Macedo RO. Study of thermal degradation of aspartame and its products of conversion in sweetener using isothermal thermogravimetry and HPLC. Thermochim Acta. 2005;433:163–9.
21. Budavari S (ed). The Merck Index, 13th edn, Merck, Whitehouse Station; 1996.
22. Naumov P, Jovanovski G, Abbrent S, Tergenius LE. Thermal behavior of the saccharinates of K^+, Na^+, Rb^+, Cs^+ and NH_4^+: structural inferences. Thermochim Acta. 2000;359:123–30.
23. Pouchert CJ. The Aldrich Library of FT-IR Spectra, v. 2. Milwaukee, Wisconsin, USA: Aldrich Chemical Company; 1985.
24. Bernal C, Couto AB, Breviglieri ST, Cavalheiro ETG. Influence of some experimental parameters on the results of differential scanning calorimetry-DSC. Quim Nova. 2002;25:849–55.