Thermochimica Acta 529 (2012) 1–5

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Evaluation of thermal stability of quinones by thermal analysis techniques

Eliane Teixeira Sousa[a,b], Mateus Melo da Silva[a], Sandro José de Andrade[a,b], Manuela Pedra Cardoso[a], Luciana Almeida Silva[a,b], Jailson B. de Andrade[a,b,*]

[a] Instituto de Química, Universidade Federal da Bahia, 40170-115 Salvador, BA, Brazil
[b] Instituto Nacional de Ciência e Tecnologia, INCT, de Energia e Ambiente, Universidade Federal da Bahia, 40170-290 Salvador, BA, Brazil

ARTICLE INFO

Article history:
Received 7 October 2011
Received in revised form 3 November 2011
Accepted 8 November 2011
Available online 29 November 2011

Keywords:
Quinones
Thermal behavior
Thermal stability
TG
DSC

ABSTRACT

The thermal behavior of quinones, such as 1,4-benzoquinone; 1,2-naphthoquinone; 1,4-naphthoquinone; 9,10-phenanthraquinone and 9,10-anthraquinone, was evaluated by simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC). Headspace analysis in GC–MS in different temperatures previously identified by TG and DSC was also performed and provided information about thermal behavior of quinones and their degradation products. Results showed that 1,4-benzoquinone, 1,4-naphthoquinone and 9,10-anthraquinone are thermally stable over the range of the temperature evaluated, while 1,2-naphtoquinone and 9,10-phenanthraquinone decompose above 100 °C and 215 °C, respectively. Overall, results indicate that the molecular structure influences strongly the course of the thermal decomposition of these quinones and it is a determining factor for its thermal stability.

1. Introduction

Over the last few years, natural quinones have gained remarkable attention in the scientific community due to their several biological functions [1]. Quinones are commonly produced by oxidation of many natural products and related compounds. The usual substrates, an aromatic compound containing oxygen substituents, become quinones by the action of monooxygenase or peroxidase [2]. In the atmosphere, the most important sources of quinones are incomplete combustion of fossil fuels and photochemical reactions of polycyclic aromatic hydrocarbons (PAH) [3,4].

Quinones are present in the atmosphere both in particle-phase and gas-phase [5]. They are often toxics, featuring a variety of cytotoxic and genotoxic effects *in vivo* [2], as well as can aggravate allergic airway inflammation [6]. Owing to widespread human exposure to quinones, it is necessary to know the concentration levels of these compounds in the environmental samples in order to evaluate the potential risk to human health. Although quinones are important compounds from a toxicological point of view, only few studies have measured their atmospheric levels due to chemical analysis difficulties because the low concentrations and instability of some quinones [7,8].

Quinones analyses are, in general, performed by gas chromatography with mass spectrometry (GC–MS) [5,9] or high performance liquid chromatography (HPLC) with several detectors [10–12]. Recent analytical developments incorporate chemical derivatization to enhance GC–MS and LC–MS methodologies [13]. Since derivatized quinones are more thermal stable than original quinones, chemical derivatization allows to make use of heating without degradation.

Due to the difficulty in direct analysis of quinones using analytical techniques with heating program coupled with the fact of limited data on the thermal stability of these compounds that justify such restrictions, this paper reports on a systematic study of the thermal behavior of quinones employing thermal analysis techniques under similar conditions of typical gas chromatographic analyses, i.e., in inert atmosphere. In this work TG and DSC were employed to identify the temperatures in which thermal events take place when different quinones were submitted to heating over the typical range of temperature used in gas chromatographic analysis, under nitrogen atmosphere. We also attempted to identify by headspace analysis in GC–MS the thermal degradation products in different temperatures previously identified by TG and DSC.

2. Experimental methods

2.1. Materials

Quinones evaluated here were 1,4-benzoquinone (98%); 1,2-naphthoquinone (90%); 1,4-naphthoquinone (96.5%); 9,10-phenanthraquinone (95%) and 9,10-anthraquinone (99.4%). All

* Corresponding author. Tel.: +55 71 3283 6821; fax: +55 71 3283 6821.
E-mail address: jailsong@ufba.br (J.B. de Andrade).

0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2011.11.012

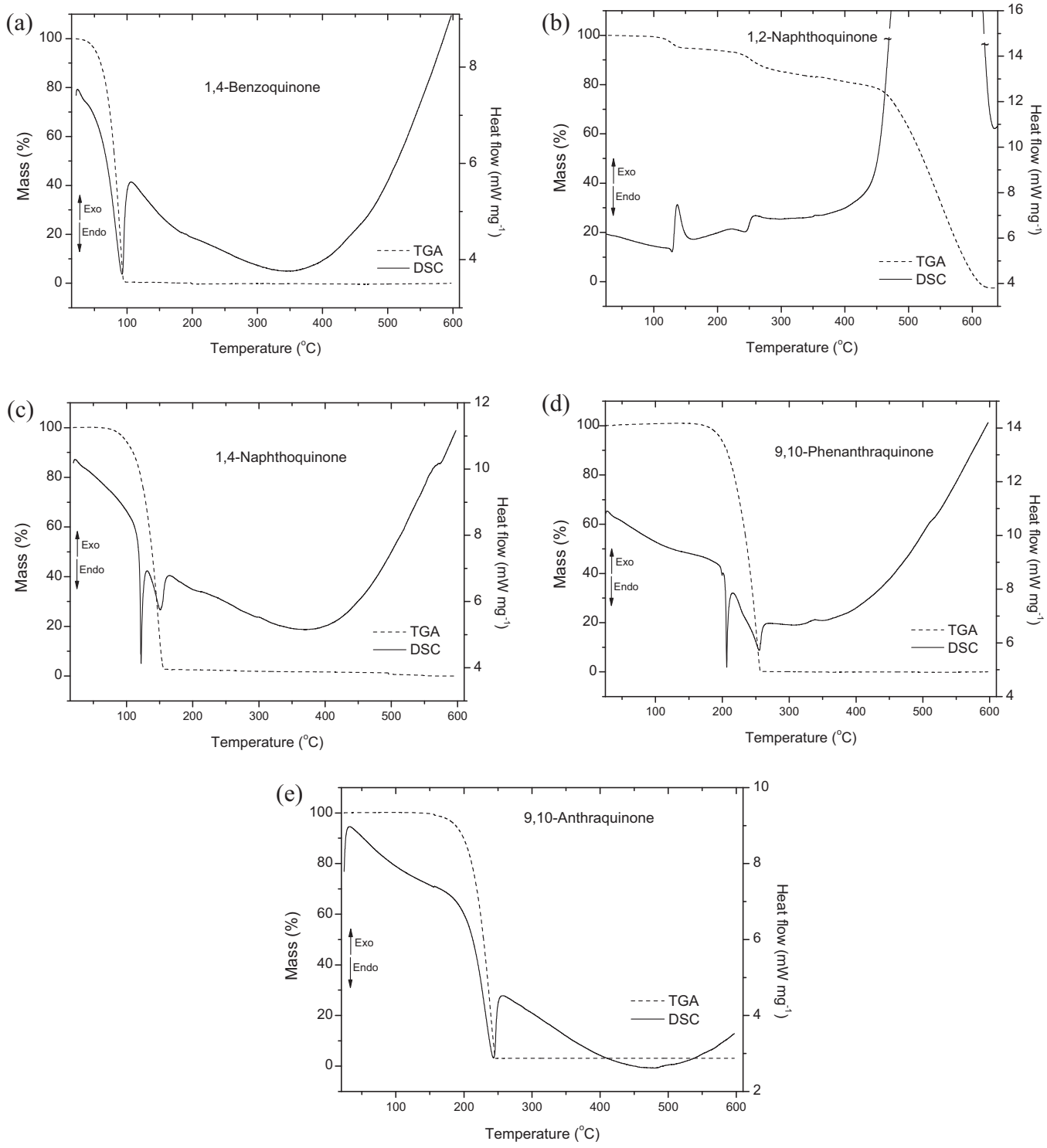

Fig. 1. Simultaneous TG and DSC curves **(a–e)**: **(a)** 1,4-Benzoquinone; **(b)** 1,2-Naphthoquinone; **(c)** 1,4-Naphthoquinone; **(d)** 9,10-Phenanthraquinone; **(e)** 9,10-Anthraquinone.

quinones were purchased from Sigma–Aldrich and the solids were used without further purification.

2.2. Thermal analysis

Thermogravimetric and DSC analyses were performed simultaneously using a DSC TGA SDT Q600 system (TA Instruments), in nitrogen dynamic atmosphere with a flow rate of 50 mL min^{-1} at a heating rate of 5 °C min^{-1} over the range 25–650 °C and using 1.0–2.0 mg of sample in a open platinum cell. The reference was a pure platinum cell. The conventional DSC analysis was performed using a Shimadzu DSC-50 thermal analyzer. DSC curves were obtained in a closed aluminum cell with 2 mg of sample in nitrogen dynamic atmosphere, flow rate of 50 mL min^{-1} and heating rate

Table 1
Mass loss and respective range of temperature obtained from TG curves.

Quinone	Mass loss (%)		Melting point[16] (°C)	Vapor pressure[13a] (mmHg)
	25–160 °C	160–300 °C		
1,4-Benzoquinone	100	–	115.7	9.0×10^{-1}
1,2-Naphthoquinone	6	9	146	1.47×10^{-3}
1,4-Naphthoquinone	100	–	128.5	1.8×1^{-4}
9,10-Phenanthraquinone	–	100	208.5	2.33×10^{-6}
9,10-Anthraquinone	–	100	286	1.16×10^{-7}

[a] Vapor pressures are given at 298 K

of 5 °C min^{-1} from ambient temperature to 500 °C. The reference was a pure aluminum cell.

2.3. Headspace analysis

Samples of quinones (1.0–2.0 mg) were heated up to the temperatures previously identified by thermal analysis, in sealed vials, during 10 min and 250 μL of headspace vapor were injected in CG–MS system.

2.4. GC–MS analysis

The analyses were performed using a GC–MS system (Shimadzu GC-2010/QP-2010 Plus, Kyoto, Japan) equipped with a split/splitless injector in the splitless mode and at 280 °C during the chromatographic run. Samples were injected with a Combi Pal autosampler using a 2.5 mL syringe. Compounds were separated in a capillary column (DB-5 MS 5%-phenyl-methylpolysiloxane; 30 m × 0.25 mm ID × 0.25 μm, Agilent Technologies, Palo Alto, USA) using helium (99.9999%) as carrier gas at a 0.98 mL min^{-1} flow rate. The oven temperature was varied as follows: 120 °C (2 min), then warmed to 280 °C at 5 °C min^{-1} and held at 280 °C for 10 min. The mass detector conditions were: transfer line temperature of 250 °C, ion source temperature of 260 °C and ionization mode with electron impact at 70 eV. The analysis was done in the SIM (selected ion monitoring) mode.

3. Results and discussion

3.1. Thermogravimetric and differential scanning calorimetric analyses of quinones

Fig. 1 shows the TG and DSC curves obtained simultaneously for all quinones evaluated. According to TG curve of 1,4-benzoquinone (Fig. 1a), the mass is totally lost in one step until 96 °C. At the same range of temperature, one can observe a single sharp endothermic peak (92.3 °C) in DSC curve (Fig. 1a), typical of phase transition [14,15]. This behavior suggests a sublimation event without further decomposition or phase transition steps.

Available data [16] about phase transitions for all target quinones are showed in Table 1 and used as parameter to evaluate the results obtained in this work from thermal analysis. According to literature data, 1,4-benzoquinone melts at 115.7 °C. Nevertheless, under conditions evaluated here, TG and DSC curves provide evidence that such quinone sublimated at 93 °C. Due to the low molar mass of 1,4-benzoquinone, the small amount of sample used and the heating carried out under nitrogen dynamic flow, we observe a sublimation event instead a melting. This conclusion is also in agreement with the vapor pressure data of quinones obtained from literature (Table 1) [13], that confirms a too high vapor pressure for 1,4-benzoquinone compared with the other quinones.

On the other hand, the thermal decomposition of 1,2-naphthoquinone takes place in three steps until 630 °C, as can be seen in TG curve (Fig. 1b). In the first step, the quinone loses 6% of mass between 103 °C and 155 °C. This mass loss is associated with an exothermic peak at 137 °C in DSC curve (Fig. 1b). Besides, another mass loss (∼9%) associated with a set of successive endothermic and exothermic peaks appear at 243 °C and 260 °C in DSC curves, followed by continual mass loss until 623 °C. There is no evidence about any phase transition in the course of the heating. In summary, according to TG and DSC curves, 1,2-naphthoquinone is thermally stable only until about 100 °C, above this temperature the quinone is decomposed.

Table 2
Headspace analysis results under diferent temperatures.

Quinone	Temperature (°C)	*m/z*[a]
1,4-Benzoquinone	Room temperature	**108**
	100	**108**; 110
	114	**108**; 110
	150	**108**;110
1,2-Naphthoquinone	Room temperature	**158**
	80	72
	100	72, 151
	125	–
	260	148
1,4-Naphthoquinone	Room temperature	–
	80	**158**; 208
	100	**158**; 208
	125	**158**; 208
9,10-Phenanthraquinone	Room temperature	–
	160	72; 73; 276; 148
	210	–
	250	–
9,10-Anthraquinone	Room temperature	–
	160	**208**
	185	**208**
	248	–
	286	**208**

[a] *m/z* of molecular ion: 1,4-benzoquinone = **108**; 1,2-naphtoquinone and 1,4-naphtoquinone = **158**; 9,10-phenanthraquinone and 9,10-anthraquinone = **208**.

For 1,4-naphthoquinone, TG curve (Fig. 1c) shows total mass loss in a single step in temperatures of 70–156 °C. In this temperature range, the DSC curve (Fig. 1c) shows two successive endothermic peaks. The first one is a typical transition phase peak that could be assigned to a melting step at 122 °C. The second broader endothermic peak (130–165 °C) in DSC curve (Fig. 1c) can be due to thermal degradation or simply an evaporation process that starts immediately after melting. Nevertheless, the former hypothesis was rejected after headspace analysis (see discussion in Section 3.2.).

TG and DSC curves (Fig. 1d and e) do not show any thermal event below 160 °C for 9,10-phenanthraquinone and 9,10-anthraquinone; after that, the mass loss begins for both. Fig. 1d shows a set of endothermic peaks in DSC curve for 9,10-phenanthraquinone. The first one, at 200 °C, is a too small peak, like a shoulder, probably due to some contamination. The next one is a sharp endothermic peak at 206.5 °C, assigned to the melting point. In temperature range of 215 °C and 265 °C, DSC curve shows an overlap of peaks, probably due to simultaneous events such as evaporation and thermal decomposition. For

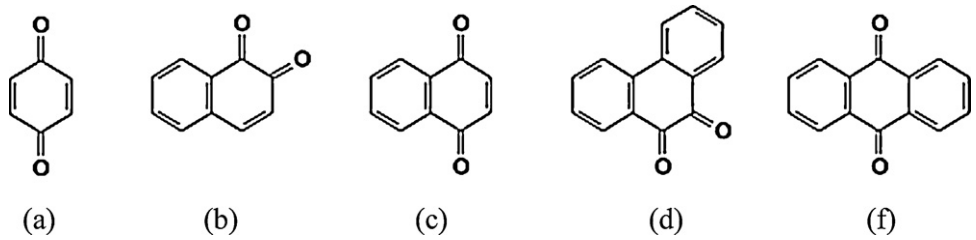

Fig. 2. Molecular structures of quinones: **(a)** 1,4-Benzoquinone; **(b)** 1,2-Naphthoquinone; **(c)** 1,4-Naphthoquinone; **(d)** 9,10-Phenanthraquinone; **(e)** 9,10-Anthraquinone.

9,10-anthraquinone, simultaneous TG and DSC curves show, respectively, 100% of mass loss and an endothermic peak in the same range of temperature (160–247 °C), suggesting a sublimation event similar to 1,4-benzoquinone behavior. However, in this case, the event takes place in higher temperature (243.5 °C) than in 1,4-benzoquinone (92.3 °C), probably, due to the higher molar mass of 9,10-anthraquinone.

Since the simultaneous TG/DSC analyses carried out in an open cell, we could not obtain information about thermal behavior of quinones above temperatures of total mass loss. In order to better understand the behavior of quinones above this temperature, conventional DSC curves were acquired in a closed cell. The profile of all curves are very similar to those obtained from simultaneous TG/DSC analysis showed in Fig. 1(a–e) and no thermal events were detected above the temperature of total mass loss.

3.2. Headspace analysis

Headspace analysis in GC–MS of the solid quinones were carried out at room temperature and in temperatures near thermal events identified in TG and DSC curves (Table 2) in order to identify the compounds present in each temperature condition.

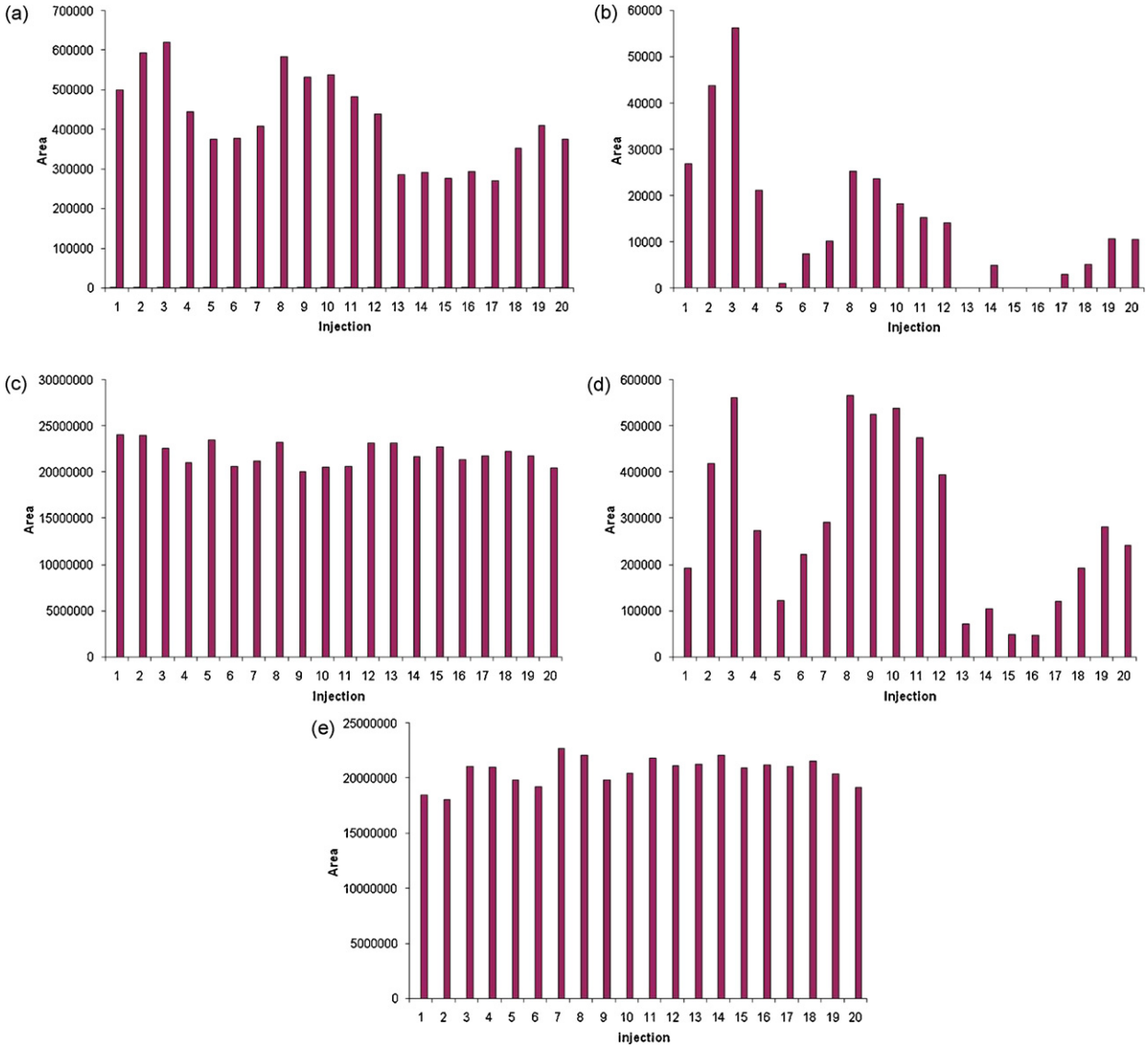

Fig. 3. Successive injections of quinones solutions: **(a)** 1,4-Benzoquinone (15.9 mg L^{-1}); **(b)** 1,2-Naphthoquinone (55.4 mg L^{-1}); **(c)** 1,4-Naphthoquinone (19.9 mg L^{-1}); **(d)** 9,10-Phenanthraquinone (68.8 mg L^{-1}); **(e)** 9,10-Anthraquinone (19.6 mg L^{-1}).

Headspace analysis at room temperature detected only 1,4-benzoquinone (molecular ion of $m/z = 108$) and a very small sign of 1,2-naphthoquinone (molecular ion of $m/z = 158$). This fact is consistent with TG and DSC results, that identified a low sublimation temperature for 1,4-benzoquinone, which means high vapor pressure at room temperature. Headspace analysis of benzoquinone were also carried out at 100, 114 and 150 °C. In all cases, 1,4-benzoquinone was detected, but the ion of $m/z = 110$ was always present. Such molecular ion match to hydroquinone, the reduction product of 1,4-benzoquinone [17], that can be present as impurity.

In the case of 1,2-naphthoquinone, headspace analysis at 80, 100, 125 and 260 °C did not detect this quinone in any temperature, probably due to thermal decomposition, as predicted previously by thermal analysis. For 1,4-naphthoquinone and 9,10-anthraquinone, headspace analysis identified the respective quinone in all temperatures evaluated; however, 9,10-anthraquinone (molecular ion of $m/z = 208$) always appears as contaminant. Similar to 1,2-naphthoquinone, headspace analysis of 9,10-phenanthraquinone did not detect this quinone in any temperature evaluated, suggesting thermal degradation, as predicted previously by TG and DSC.

Taking into account the molecular structures of quinones evaluated here (Fig. 2), a relationship between thermal stability and the position of carbonyl groups can be observed. The carbonyl groups in the thermally unstable quinones, such as 1,2-naphthoquinone and 9,10-phenanthraquinone, are much closer (ortho position, Fig. 2b and d) than in the others. Carbonyl group concentrates high electronic density on oxygen atom. Since the two carbonyl groups are too close in ortho position, it can result in high electronic replusion, decreasing the stability of molecular structure, which can favor the thermal degradation reactions. Both 9,10-phenanthraquinone and 1,2-naphthoquinone are ortho-quinones; however, our results provide evidences that the former is more thermal stable than the last one. It must be a consequence of molecular stabilization by more effcient mesomeric effects in 9,10-phenanthraquinone. The presence of two benzene rings attached to the quinone group, in the case of 9,10-phenanthraquinone, instead only one, in the case of 1,2-naphthoquinone, provides better charge distribution by delocalization of π orbitals (Fig. 2).

3.3. Stability under chromatographic conditions

In order to evaluate the quinones stability in acetonitrile solutions under chromatographic conditions, a series of successive injections of standard solutions was performed and the responses showed in Fig. 3.

The results demonstrated a good repeatability in peak area for 1,4-naphthoquinone and 9,10-anthraquinone, with relative standard deviation (RSD) of 6.10 and 5.63%, respectively. The thermal and headspace analyses did not reveal any evidence about thermal decomposition for both quinones in temperature range of the chromatographic analysis. Meanwhile, despite the good thermal stability, 1,4-benzoquinone showed a reasonable repeatability with RSD of 26.5%. This lower repeatability, when compared to 1,4-naphthoquinone and 9,10-anthraquinone is probably due to the interference of hydroquinone (molecular ion of $m/z = 110$) detected in headspace analysis over the range of temperature evaluated. On the other hand, there is no repeatability in successive injections of 1,2-naphthoquinone and 9,10-phenanthraquinone solutions. In these cases, TG and DSC as well as headspace analysis showed clearly evidence of thermal degradation of these quinones.

4. Conclusions

The quinones studied here showed different thermal behavior. 1,4-Benzoquinone, 1,4-naphthoquinone and 9,10-anthraquinone are thermally stable over the range of the temperatures evaluated with respect to decomposition and they demonstrated to be stable under chromatographic conditions. Otherwise, 1,2-naphthoquinone and 9,10-phenanthraquinone decompose above 100 °C and 215 °C, respectively, and no repeatability in chromatographic analysis was observed. Overall, results indicate that the molecular structure influences strongly the course of the thermal decomposition of these quinones. The intramolecular interaction of carbonyl groups in ortho position seems to favor the thermal degradation and the mesomeric effects seem to contribute for increasing the thermal stability of ortho-quinones, giving to the compound with more π clouds (9,10-phenanthraquinone) more stabilization by resonance. These results provide helpful informations about thermal stability of quinones that can give support in development of methods for quinones determination by GC–MS.

Acknowledgements

Authors wish to thank CAPES, CNPq, PRONEX, FAPESB and FINEP for financial support, Prof. Dr Heloysa Andrade, Prof. Dr. Ednildo Torres and Prof. Marcos Fábio de Jesus for thermal analysis support and Prof. Dr Vilma Mota for helpful discussions.

References

[1] M.N. da Silva, V.F. Ferreira, M.C.B.V. de Souza, An overview of the chemistry and pharmacology of naphthoquinones with emphasis on β-lapachone and derivatives, Quim. Nova 26 (2003) 407–416.
[2] Q. Zhang, T. Tu, D.A. d'Avignon, M.L. Gross, Balance of beneficial and deleterious health effects of quinones: a case study of the chemical properties of genistein and estrone quinones, J. Am. Chem. Soc. 131 (2009) 1067–1076.
[3] J. Sasaki, S.M. Aschmann, E.S.C. Kwok, R. Tkinson, J. Arey, Products of the gas-phase OH and NO_3 radical-initiated reactions of naphthalene, Environ. Sci. Technol. 31 (1997) 3173–3179.
[4] M.R. Sienra, Oxygenated polycyclic aromatic hydrocarbons in urban air particulate matter, Atmos. Environ. 40 (2006) 2374–2384.
[5] A. Eiguren-Fernandez, A.H. Miguel, E. de Stefano, D.A. Schimitz, A.K. Cho, S. Thurairatman, E.L. Avol, J.R. Froines, Atmospheric distribution of gas- and particle-phase quinones in Southern California, Aerosol Sci. Technol. 42 (2008) 854–861.
[6] K. Hiyoshi, H. Takanow, K.-I. Inouew, T. Ichinosez, R. Yanagisawaw, S. Tomura, Y. Kumagai, Effects of phenanthraquinone on allergic airway inflammation in mice, Clin. Exp. Allergy 35 (2005) 1243–1248.
[7] A. Eiguren-Fernandez, A.H. Miguel, R. Lu, K. Purvis, B. Grant, P. Mayo, E. de Stefano, D.A. Schimitz, A.K. Cho, S. Thurairatman, E.L. Avol, J.R. Froines, Atmos. Environ. 42 (2008) 2312–2319.
[8] N. Kishikawa, M. Nakao, Y. Ohba, K. Nakashima, N. Kuroda, Concentration and trend of 9,10-phenanthrenequinone in airborne particulates collected in Nagasaki city, Japan, Chemosphere 64 (2006) 834–838.
[9] A.K. Cho, E. Di Stefano, Y. You, C.E. Rodriguez, D.A. Schimitz, Y. Kumagai, A.H. Miguel, A. Eiguren-Fernandez, T. Kobayshi, E. Avol, J. Froines, Determination of four quinones in diesel exhaust particles, SRM 1649, and atmospheric PM 2. 5, Aerosol Sci. Technol. 38 (2004), 68-.
[10] S. Paramapojn, M. Ganzera, W. Gritsanapan, H. Stuppner, Analysis of naphthoquinone derivatives in the Asian medicinal plant Eleutherine Americana by RP–HPLC and LC–MS, J. Pharm. Biomed. Anal. 47 (2008) 990–993.
[11] X. Zhou, J. Zhang, X. Qin, X. Hu, Determination of Pyrroloquinoline Quinone in DNA binding by LC, Chromatographia 73 (2011) 1027–1030.
[12] N. Kishikawa, N. Ohkubo, K. Ohyama, K. Nakashima, N. Kuroda, Selective determination of ubiquinone in human plasma by HPLC with chemiluminescence reaction based on the redox cycle of quinone, Anal. Bioanal. Chem. 400 (2011) 381–385.
[13] C. Jakober, S.G. Riddle, M.A. Robert, H. Destaillats, M.J. Charles, P.G. Green, M.J. Kleeman, Quinone emissions from gasoline and diesel motor vehicles, Environ. Sci. Technol. 41 (2007) 4548–4554.
[14] L.A. Silva, J.R. Matos, J.B. de Andrade, Synthesis, identification and thermal decomposition of double sulfites like $Cu_2SO_3.MSO_3.2H_2O$ (M = Cu, Fe, Mn or Cd), Thermochim. Acta 360 (2000) 17–27.
[15] V.M. da Silva, L.A. Silva, J.B. de Andrade, M.C.C. Veloso, G.V. Santos, Determination of moisture content and water activity in algae and fish by thermoanalytical techniques, Quim. Nova 31 (2008) 901–905.
[16] D.R. Lide (Editor-in-Chief), Handbook of Chemistry and Physics, 78th ed., CRC Press, Inc., Cleveland, 1997–1998.
[17] J. Kim, T.D. Chung, H. Kim, Determination of biologically active acids based on the electrochemical reduction of quinone in acetonitrile + water mixed solvent, J. Electroanal. Chem. 499 (2001) 78–84.