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Piezoelectric crystal microbalance measurements of enthalpy of sublimation of C_2–C_9 dicarboxylic acids

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PCM measurements of enthalpy of sublimation

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Abstract

We present here a novel experimental setup able to measure the enthalpy of sublimation of a given compound by means of Piezoelectric Crystal Microbalances (PCM).

This experiment was performed in the TG-Lab facility in IAPS-INAF, dedicated to the development of TGA sensors for space measurements, such as detection of organic and non-organic volatile species and refractory materials in planetary environments.

In order to study physical-chemical processes concerning the Volatile Organic Compounds (VOC) present in atmospheric environments, the setup has been tested on Dicarboxylic acids.

Acids with low molecular weight are among the components of organic fraction of particulate matter in the atmosphere, coming from different sources (biogenic and anthropogenic). Considering their relative abundance, it is useful to consider Dicarboxylic acid as "markers" to define the biogenic or anthropogenic origin of the aerosol, thus obtaining some information of the emission sources.

In this work, a temperature controlled effusion cell was used to sublimate VOC, creating a molecular flux that was collimated onto a cold PCM. The VOC re-condensed onto the PCM quartz crystal allowing the determination of the deposition rate. From the measurements of deposition rates, it was possible to infer the enthalpy of sublimation of Adipic acid, i.e. ΔH_{sub}: $141.6 \pm 0.8 \, \mathrm{kJ \, mol^{-1}}$, Succinic acid, i.e. $113.3 \pm 1.3 \, \mathrm{kJ \, mol^{-1}}$, Oxalic acid, i.e. $62.5 \pm 3.1 \, \mathrm{kJ \, mol^{-1}}$ and Azelaic acid, i.e. $124.2 \pm 1.2 \, \mathrm{kJ \, mol^{-1}}$ (weight average values). The results obtained are in very good agreement with literature within 10 % for the Adipic, Succinic and Oxalic acid.

1 Introduction

A large number of aerosol species is present in atmosphere and many physical-chemical processes occur to create/destroy compounds, therefore monitoring and characterizing some of them is a tricky task.

The primary atmospheric aerosol is composed of particles coming from processes such as rocks erosion and fire and from anthropogenic processes (such as the fossil fuels combustion or by the industrial activity). Volatile organic compounds (VOC) in primary aerosol can generate the secondary organic aerosol (SOA, composed of fine particles) from photo-oxidation reactions with compounds in Earth's atmosphere, in particular hydroxyl radical, ozone and nitrate radical. For example, hydrocarbons are enriched carboxylic (-COOH), carbonyl (-CO) or hydroxides (-OH) functional groups and are transformed in ketones or carboxylic acid after several reactions.

Because of the wide number of VOC transformation processes it is crucial to know the chemical-physical properties (i.e. enthalpy, entropy, free energy) in order to characterize the organic fraction of the atmospheric aerosol. In detail, specific substances (*markers*) or class of substances should be identified in order to provide some information on the atmospheric aerosol sources, e.g. evaluating the transformation degree of the organic compound and their release by primary sources (Pietrogrande et al., 2014).

Carbohydrates and Dicarboxylic acids with low molecular weight (subclass of carboxylic acid) are among the most important groups of molecules identified in the atmospheric aerosol. It could be useful to consider these substances as molecular tracers providing information on the aerosol origin (biogenic or anthropogenic) and on the processes that the organic substances undergo in the atmosphere. Dicarboxylic acids are present with various concentrations in different terrestrial environments, e.g. marine, rural, urban (Kawamura et al., 2005; Yu and Fraser, 2004; Limbeck et al., 2001), and their formation in atmosphere is likely due to photochemical reactions in gaseous phase involving VOC (in particular aliphatic and aromatic hydrocarbons) of biogenic and anthropogenic origin. In addition they represent an important component of the atmospheric aerosol particles, both in remote and urban areas (Rohrl and Lammel, 2001): the Oxalic acid is the most abundant Dicarboxylic acid in the tropospheric aerosol and comprises 41–67 % of the total diacids whereas the Succinic and Malonic acid are less abundant and reach peaks of 4–8.7 % during the summer (Kawamura and Ikushima, 1993).

Adipic, Succinic and Oxalic have been identified in laboratory (Hatakeyama et al., 1985) studies as SOA products (reaction of O_3 with cyclohexene) whereas, the Azelaic acid is produced from the oxidation of unsaturated fatty acids in atmosphere (Rozaini, 2012).

In order to characterize Dicarboxylic acids different methods are used, based on measurement of the evaporation rates and calculation of the enthalpy of sublimation/evaporation, e.g. Thermal Desorption Particle Beam Mass Spectrometry Method (TPTD, Chattopadhyay and Ziemann, 2007), Knudsen Effusion Mass-loss (da Silva et al., 2001), Knudsen Effusion Mass Spectrometry (Booth et al., 2009), Tandem Differential Mobility Analyzer technique (TDMA, Bilde et al., 2003) and effusion method, EM (Davies and Thomas, 1960; Granovskaya, 1948). Discrepancies between results obtained by the different methodologies were found to be up to two orders of magnitude, and this makes the acids characterization even more difficult.

In this study low molecular weight Dicarboxylic acids (carbon chains from C_2 to C_9, see Fig. 1) were analyzed by means of a new experimental set-up, based on Piezoelectric Crystal Microbalances (PCM) that is commonly used to detect mass variations, density, viscosity, absorption/desorption processes, by means of transformation of mass change into fundamental resonance frequency variation. The PCM oscillation frequency goes as $1/m$, being m the mass deposited on the microbalance, as stated by the Sauerbrey equation (Sauerbrey, 1959). Therefore, in principle it is possible to measure VOC sublimation or deposition on the crystal surface by changing the PCM temperature: the mass variation during the sublimation process will give the amount of the volatile component, while the composition can be inferred by the sublimation temperature. A compound can be characterized more precisely by retrieving its enthalpy of sublimation: this is possible by measuring the sample deposition rates on the PCM at different temperatures (see Sect. 5).

Piezoelectric crystal microbalances (PCM) have been recently used in space applications and technology environments, as in industrial and biomedical fields (Palomba et al., 2002; Wood et al., 1998; Freedman et al., 2008; Effiong et al., 2011; Lutfi Yola et al., 2014).

The TG-Lab laboratory located in IAPS-INAF is a dedicated facility to study feasibility, development and calibration of TGA sensors optimised for space measurements. One of the TG-Lab projects concerns VISTA (Volatile In Situ Thermogravimeter Analyser), a sensor developed for the Marco Polo R mission (Palomba et al., 2013; Barucci et al., 2011) and studied for other ESA Cosmic Vision missions, addressed to Venus atmosphere (Wilson et al., 2011), Titan low atmosphere (Longobardo et al., 2013) and sub-surface of Europa (Gowen et al., 2011).

In this work, PCM is cooled down to $-72\,^{\circ}$C by means of a cold sink whereas the sample is positioned in an effusion cell and heated up to sublimation. The setup is placed in vacuum in order to avoid water vapour condensation and to facilitate the sublimation process (occurring between 25 and $80\,^{\circ}$C), whereas the cooled crystal works as mass attractor for VOC's molecules. This configuration allowed to measure the deposition rate of the VOC samples on the PCM at different temperatures and to infer the corresponding enthalpy of sublimation. First attempts to measure enthalpy of sublimation by means of PCM were performed by Dirri et al. (2012) and were focusing on upgrading the thermal contact between PCM and the cold sink, by increasing the difference between sensor effusion cell temperature and the PCM, improving the efficiency of the PCM as mass attractor. This made it possible to measure deposition fluxes even at two close temperatures (e.g. $\Delta T = 5\,^{\circ}$C). However, in the Dirri et al. (2012) experiment a very small frequency variation (3 kHz) was observed, due to the low deposition of acid molecules (Adipic acid), and the retrieved enthalpies of sublimation were different from literature prediction of 20 % (Chattopadhyay, 2007). In this work our accuracy has been improved as described in Sect. 3.

Section 2 describes the theoretical background and the thermodynamic relation considered for data analysis. Setup and measurement procedure are explained in Sects. 3 and 4 respectively, whereas Sect. 5 describes the obtained results. Finally, Sect. 6 is devoted to conclusions.

2 Theoretical approach and thermodynamic relation

Succinic and Adipic acids are formed in SOA from reactions between O_3 and cyclo-hexene and alkenes, the latter emitted from the biosphere (Hatakeyama et al., 1985). Oxalic acid, produced from the fossil fuel combustion and biomass burning, is the most abundant Dicarboxylic acid in tropospheric aerosol (Sorooshian et al., 2006). In order to best characterize and trace the evolution of atmospheric organic aerosol, informa-tion on the thermochemical processes involving these compounds (part of SOA) are required.

At a temperature of 25 °C and low pressure (10^{-6} mbar) it is possible to observe the acid sublimation, due to the their high volatility. The enthalpy of sublimation, i.e. the energy difference between reactants and products, can be seen as the sum between the internal energy of the system and the product between pressure (p) and volume (V) of the system.

The Clausius–Clapeyron relation characterizes a phase transition, since allows us to infer the vapor pressure at each temperature T and the enthalpy variation from vapor pressure at two different temperatures:

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{\Delta H}{T \Delta V} \tag{1}$$

being ΔH the specific latent heat of the process (sublimation, vaporization, or fusion), p the vapor pressure and ΔV the difference between volumes of gaseous and solid/liquid (sublimation/vaporization) phase, respectively. If the products are in gaseous phase and at temperatures much smaller than their critical one, they can be approximated as ideal gases, i.e. $\Delta V \sim V_{gas} = RT/p$. Replacing in the Eq. (1), we have the differential form:

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \tag{2}$$

Dicarboxylic acids with low vapour pressure play an important role on physical-chemical reactions involving aerosol particles, that may be gathered in agglomerates

(sub-micron sized), constituting condensation nuclei for clouds formation. Therefore, it is possible to use thermogravimetry to determine the vapor pressure, by recurring at Langmuir equation for free kinetic sublimation/evaporation in vacuum (Langmuir, 1913):

$$p = \frac{\sqrt{2\pi R}}{\alpha} \times \frac{\mathrm{d}m}{\mathrm{d}t} \times \sqrt{\frac{T}{M}} \qquad (3)$$

where p is the vapor pressure of the gas, $\mathrm{d}m/\mathrm{d}t$ (mass loss rate per unit area) is the deposition rate experimentally measured, M the molecular weight, R the gas constant, T the absolute temperature and α the vaporization coefficient, assumed to be 1 in vacuum environment (Price, 2001). Replacing Eq. (3) in Eq. (2), it is possible to obtain the enthalpy of sublimation (multiplied for a constant) as slope of the curve $\ln(\mathrm{d}m/\mathrm{d}t)T^{1/2}$ vs. T^{-1}

$$\ln \frac{\mathrm{d}m}{\mathrm{d}t}T^{1/2} = \ln C - \frac{\Delta H}{RT} \qquad (4)$$

The enthalpy of sublimation/evaporation can be also obtained by means of the Van't Hoff relation (Benson, 1968), i.e. by measuring at two different temperature T_1 and T_2 the respective rate constants k_1 and k_2 (the deposition rates on the PCM or $\mathrm{d}m/\mathrm{d}t$ per unit area):

$$\Delta H = R \left[\left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \left(\frac{k_1 \sqrt{T_1}}{k_2 \sqrt{T_2}} \right) \right] \qquad (5)$$

Then, the Van't Hoff relation (Eq. 5) is used to monitor the enthalpy variation step by step in the considered temperature interval in order to monitor the state functions (e.g. Enthalpy, Gibbs energy, and Entropy) in a transition phase. According to this relation, for an endothermic process (i.e. $T_1 > T_2$ and $\Delta H > 0$), as those considered in this work, we have $k_1 > k_2$, i.e. temperature increase is related to a rate constant increase.

3 Set-up operation and composition

3.1 PCM and effusion cell

A Piezoelectric Crystal Microbalance (resonance frequency of 10 MHz) has been used to monitor the transition phase (solid → gas) of some Dicarboxylic acids in a controlled environment in order to obtain their enthalpy of sublimation.

The microbalance is composed of a quartz crystal having a diameter of 14 mm and a thickness of 0.2 mm. The electrode, the sensible area of the crystal, is located in the central area and has a diameter of 4 mm (Fig. 1). The microbalance is connected to its proximity electronic (PE), including a frequency counter and an oscillation circuit, powered by USB-PC input.

In order to use the microbalance as an efficient mass attractor, the quartz crystal should be cooled with respect to the surrounding environment and in addition the VOC molecular flux should be focused onto the crystal. The PCM cooling is performed by means of a conductive connection to a copper plate in thermal contact with a coil containing liquid nitrogen. Finally, the PCM is enclosed in a metal case, acting as thermal shield and avoiding the PCM heating by irradiation of internal wall of the vacuum chamber, which are at ambient temperature (see Fig. 2).

In order to maximize the VOC flux, the microbalance has been placed in front of the effusion cell. This configuration strongly improves the flux collimation, increasing the amount of the collected molecules. The metal case has a temperature similar or even slightly smaller of the crystal and if the effusion cell is too far away from the PCM, the molecular flux could condense preferably on the metal case rather than the crystal, lowering the deposition rate too much (Fig. 2, left). It has been experimentally determined by means of preliminary calibrations that the distance between PCM and effusion cell allowing the larger flux onto the PCM crystal is 2 cm. Moreover, reaching lower PCM temperature (i.e. −72 instead of −25 °C of the first attempt) by improving the thermal contact with PCM and cold sink, we were able to increase the incident

molecules flow on the microbalance (avoiding molecules dispersion in the surrounding environment).

Then PCM and effusion cell are placed in a *sublimation micro-chamber*, i.e. a controlled environment of cylindrical form (located inside the vacuum chamber) made of insulating material (Teflon), which further minimises thermal dispersion and avoids VOC's loss into the microbalance surrounding area (Fig. 2, right). The effusion cell is inserted in a hole in the cylinder's base.

In this experiment the PCM is cooled down to −72 °C while the acid sample is placed in a small cylinder case (effusion cell) wide 6 mm and deep 10 mm.

This configuration allows to monitor the VOC's deposition rates from about 10^{-13} up to 10^{-10} mol cm^{-2} s^{-1}, two orders of magnitude better than the first setup version discussed in Dirri et al. (2012). The sample is heated from room temperature (i.e. 25–30 °C) up to its sublimation point (i.e. 75–80 °C) by means a heater of 20 Ω (resistance) in thermal contact with the effusion cell. In Fig. 3 a schematic representation of the set-up is shown.

3.2 Vacuum system and data acquisition system

The whole set-up is placed in a vacuum chamber in order to facilitate the transition phase, to avoid the simultaneous condensation on the PCM of other molecules present in the atmosphere at ambient pressure (mainly H_2O) and to avoid convective heat exchange with the atmosphere which would affect PCM and effusion cell temperature. The Vacuum System (Fig. 4) is composed by a Rotative pump (CF29PR-Alcatel Society), Turbo Pump (1 602 450-Elettrorava Society) and a chamber (90 L), all of them assembled by the Vacuum Centre Representative (CRV S.r.l., Rome, Italy). Rotative Pump can drive the system down to 10^{-2} mbar whereas the Turbo Pump can lower the pressure down to 10^{-6}–10^{-7} mbar. Pressure is measured using the TC1 sensor (Varian) up to 10^{-2} mbar and the IG sensor (Varian) or Ionization Gauge up to 10^{-6}–10^{-7} mbar. During data acquisition the pressure of the system is maintained constant during each experiment (fixed values between 3.5×10^{-6} mbar and 8×10^{-7} mbar).

The temperatures of copper plate, metal case, resistance and effusion cell, have been continuously monitored with platinum sensors (PT100, dimensions of 7.6 mm × 7.6 mm × 0.7 mm), whose resistance changes linearly with temperature. Temperature controls of the effusion cell (heating system from 25 to 110 °C) and of the copper plate (cooling system, set to −90 °C and stable within 0.2 °C) have been driven by a Proportional-Integral-Derivative system (PID), which allows a temperature stability of typically ±1 °C and managed by means the LabView (2010) software (PC1). The frequencies' has been acquired by means of the Eureka electronic box powered by a USB of PC2, controlled by the software provided by Bioelectronics and Advanced Genomic Engineering (BioAge S.r.l., Lamezia Terme, Italy).

4 Experimental activity

4.1 Selection of dicarboxylic acids

The Dicarboxylic acid chemical formula is $HOOC(CH_2)_{n-2}COOH$ where n is the number of carbon atoms. The considered samples are acids in small grains in white crystalline form (odorless solid) with a purity degree of 99 %. Considering the sublimation point of these acids and the temperature range available by our setup (from 25 to 80 °C), the studies were focused on acids with n between 2 and 9 carbon number: Oxalic ($n = 2$), Succinic ($n = 4$), Adipic ($n = 6$) and Azelaic ($n = 9$) acids. Adipic acid was provided by Sigma Aldrich S.r.l., Succinic acid by Institute of Translational Pharmacology (ITF-CNR, Rome, Italy) while Azelaic and Oxalic were kindly provided by University of Rome, La Sapienza (Department of Chemistry).

Adipic acid is related to N_2O emission, a greenhouse gas that causes stratospheric ozone depletion (US EPA, 2013), whereas Azelaic acid is considered a photon-induced oxidation's product, deriving from biogenic unsaturated fatty acid, presenting one or more double bond in their chain (Kawamura and Keplan, 1983). Succinic and Oxalic acid had been proven to be part of the organic materials that contribute to form con-

densation nuclei of atmospheric clouds (Kerminen et al., 2000). Succinic acid origins probably from biogenic sources, and is an important compound in biochemistry due to its role in the citric acid cycle (Krebs cycle), whereas Oxalic acid is one of the most quantitatively represented waste-products of fossil fuel combustion in tropospheric atmosphere (Kawamura and Keplan, 1983). It has been suggested that the ratio between Oxalic and Succinic acid, both deriving from photochemical reactions (Succinic acid may also be a precursor of the Oxalic acid), is a good marker of the atmospheric aerosol oxidation state. On the other hand, Adipic–Azelaic ratio could be an indicator of anthropogenic sources, considering that Adipic acid derives from cycle-hexane's oxidation (Kawamura and Ikushima, 1993). Some structural and thermodynamic characteristics of the acids utilized in this work are shown in Table 1.

4.2 Measurement procedure

In order to measure the enthalpy of sublimation, PCM has been used as mass attractor for the volatile molecules inside the teflon micro-chamber. Firstly, the crystal in thermal contact with a copper plate has been cooled down to $-72\,°C$ (constant temperature during the heating cycles).

Then, each sample (13–20 mg) has been placed in effusion cell and at a later stage has been heated by a resistance in a range of temperature from 25–30 to 75–80 °C. The stabilization of VOC's molecular flow at each temperatures has been obtained by keeping the temperature constant for 30 min, while a good distinction between two successive flows at two different temperatures has been possible by adopting temperature steps of 5 °C. During each heating, the PCM frequency and temperature have been measured every two seconds. Then, deposition rates have been measured at each temperature set point in $mol\,cm^{-2}\,s^{-1}$.

Finally, the enthalpy variation between two different temperatures T_1 and T_2 have been inferred by applying the Van't Hoff relation (Eq. 5) at the two respective rate constants k_1 and k_2, measured in $Hz\,s^{-1}$. The parameters of heating cycles of different

acids, i.e. initial mass, pressure, expected enthalpy of sublimation, temperature range, stabilization time at each temperature, are listed in Table 2.

Considering this measurement procedure and temperature stability of $\pm 1\,°C$ (temperature control on effusion cell), an uncertainty of 10 % on the retrieved enthalpy of sublimation could be sufficient to provide a good accuracy for our measurements.

Since Succinic and Oxalic acids have smaller sublimation temperature than Adipic and Azelaic acids, we considered for these acids a narrower temperature range (see Table 3). In fact the retrieval of the enthalpy of sublimation can be considered reliable as long as T_2 is quite distinct ($\geq 5\,°C$) from the sublimation point. Indeed, it was avoided to choose $T_2 \sim T_c$, where a slope change of deposition curve is expected due to the phase transition.

5 Data analysis and results

Deposition rates df/dt in $Hz\,s^{-1}$ have been measured with a sampling rate of 10 s. A PCM frequency decrease has been observed at increasing temperature due to the larger VOC deposition.

The rates in $Hz\,s^{-1}$ have been multiplied for the PCM sensitivity ($4.4\,ng\,cm^{-2}\,Hz^{-1}$) and converted in $g\,cm^{-2}\,s^{-1}$. Then, they have been divided by the substance molecular weight and converted in $mol\,cm^{-2}\,s^{-1}$ (Table 3). Finally, the enthalpy of sublimation and its error have been expressed in $kJ\,mol^{-1}$ (Table 3). The uncertainty on temperatures and deposition rates have been calculated as standard deviation of the mean, due to the Gaussian distribution of measured values.

Thus, in order to monitor enthalpy variation over the whole temperature range considered, a good choice for T_2 could be a temperature far away from the sublimation point (i.e. from 55 to 75 °C for Adipic–Azelaic acid and from 45 to 55 °C for Succinic acid).

5.1 Oxalic acid (C$_2$)

A total frequency variation of 13 kHz has been observed for the Oxalic acid from 25 to 60 °C, corresponding to a mass deposition of 28.6 µg. This compound (with short carbon chain, C$_2$) showed a high volatility even at low temperature confirmed by the moderately high deposition rate measured already at 25 °C. The deposition rate curve shows a continuous increase up to 60 °C, with a constant slope (Fig. 5, blue curve).

The Oxalic acid presents in its molecular structure two water molecules (dihydrate, monocline structure) which loses at about 100 °C and 1 bar. In this dehydration reaction, its molecular structure changes from monocline to rhombic crystals and becomes anhydrous (Bahl, 2007). In our experiment, we considered a monocline dehydrate Oxalic acid and the obtained enthalpy results (Table 4) differ than previous works, relative to the anhydrous form (Booth et al., 2009). On the contrary, our results agree within ±8 % with values, relative to dehydrate Oxalic acid (De Wit et al., 1983; Granovskaya, 1948), as it should be. Moreover, choosing T_1 quite lower than T_2 value a best agreement is obtained, whereas when T_1 approaches T_2 the agreement is worse ($\geq$ 15 %). Indeed, as verified by de Wit at al. (1983), a difference for the sublimation enthalpy values between the two anhydrous forms (beta and alpha, obtained by means vacuum sublimation) and the dehydrate state (this work) happens, due to the two water molecules desorption from Oxalic acid structure.

5.2 Succinic acid (C$_4$)

In the Succinic acid case, the frequency decreases of 11 kHz from 30 to 75 °C, corresponding to 24.2 µg. The measured deposition rates are shown in Fig. 5 (orange curve).

Succinic acid (with short carbon chain, C$_4$) shows a smaller deposition rates than the Oxalic acid, even if it strongly sublimates already at 25 °C. Deposition rate curve shows an increase up to 60 °C and a slope change beyond this temperature. The Succinic acid tends to lose easily one water molecule, becoming succinic anhydride. A good

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temperature range to monitor enthalpy variation is 30–60 °C, far away from the point where Succinic acid changes its structure ($\sim$ 137 °C) (Vanderzee and Westrum, 1970). In this range, the average enthalpy of sublimation measured is $113.3 \pm 1.3 \, \text{kJ mol}^{-1}$, in agreement with previous works within 5 % (Chattopadhyay and Ziemann, 2007; Davies and Thomas, 1960; Table 4). Considering an upper temperature larger than 60 °C, the retrieved enthalpy are instead not reliable due to a possible beginning of transformation of Succinic acid crystalline form (monocline/triclinic prisms) into cyclic anhydride, a ring structure (pyramidal crystal) losing one water molecule. Above this temperature (> 60 °C), the deposition rate oscillates around a medium value (Fig. 5, orange curve).

5.3 Adipic acid (C$_6$)

Adipic acid (long carbon chain, C$_6$) shows a total frequency decrease of 27 kHz from 30 to 75 °C (Fig. 6, black curve) corresponding to a 59.4 µg. A considerable frequency variation is observed above 50 °C, due to the high volatility of the acid at these temperatures. This acid sublimates at low pressure without a decomposition and only at 230–250 °C changes its molecular structure becoming cyclopentanone plus H_2O and CO_2. As a matter of fact, at temperatures smaller than 50 °C, the variation of deposition rates of Adipic acids are only 1.5 and 27 % of that measured for Oxalic and Succinic acid, respectively: this is due to the better stability of its carbon chain at these temperatures. Results, listed in Table 3, show that when T_2 is close to the sublimation point, the enthalpies of sublimation obtained are in disagreement with literature.

5.4 Azelaic acid (C$_9$)

Azelaic acid shows a larger frequency variation than Succinic and Oxalic acid, with a total frequency decrease of 21 kHz up to 80 °C (Fig. 6, red curve) corresponding to 42.4 µg. Azelaic acid presents a very slow sublimation up to 35 °C and reaches the maximum deposition rate at 75 °C (whereas at 80 °C deposition rate begins to decrease).

This compound starts to decay at 360 °C (at atmospheric pressure) but in our experiment the deposition curve shows a slope variation at 80 °C. The reasons for that should be studied in more detail and the temperature range should be increased in order to monitor enthalpy variation at larger temperatures. Probably, monitoring a wider temperature range for the two other acids (Oxalic and Adipic) we could observe the same trend.

5.5 Discussion and comparison of obtained results

As listed in Table 3, when the temperature oscillations are larger than ±0.5 °C, the errors on the enthalpy of sublimation are larger than 10 kJ mol^{-1} (Adipic, Succinic and Azelaic acid). Thus, in order to understand better our results, enthalpy of sublimation has been compared with data obtained from different techniques (Table 4): TDMA (Bilde et al., 2003), Knudsen mass loss (Silva et al., 1999), KEMS (Booth et al., 2009), TDPB (Chattopadhyay and Ziemann, 2007), effusion method, EM (Davies and Thomas, 1960; Granovskaya, 1948).

The values of enthalpy of sublimation obtained in our experiments for Succinic, Adipic and Azelaic acids are slightly smaller than the enthalpies values reported by Chattopadhyay and Ziemann (2007), who measured vapour pressure and evaporation rates of submicron particles in vacuum, and quite lower than those measured by Bilde et al. (2003), who measured vapor pressure of organic particles at ambient temperature. Booth et al. (2009) directly measured steady state vapour pressure using KEMS method with solid sample, obtaining smaller enthalpies than those obtained in this work for Adipic and Succinic acid, and larger one for the Oxalic acid, even if the working pressure and heating method of the sample were similar to ours (temperature step of 5 °C with 10 min stabilization time). However their measurements are affected by a large uncertainty, which makes their results (at least for Adipic and Succinic acid) consistent with ours. Regarding the Oxalic acid, as discussed above, these authors measured the value of the anhydrous form and a difference from our results is expected. This difference is evident in de Wit et al. (1983) results, where the analysis of dehydrate

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and anhydrous form (prepared by a prolonged evacuation of the hydrate substance and vacuum sublimation) of the Oxalic acid has been performed. Our results, as stated from the Table 4 are in agreement within 10 % with the results of the hydrate substance. Instead, Da Silva et al. (1999) used a method similar to Booth et al. (Knudsen Mass Loss Effusion) in order to study evaporation rates of aerosol particles of Dicarboxylic acids, and found values larger than ours (in particular for Azelaic acid), whereas Davies and Thomas (1960), who measured heats and entropy of sublimation by means of Effusion Method at 1.013 bar pressure, are in agreement (within 10 %) with our values (for the Adipic and Succinic acid). Chattopadhyay and Ziemann (2007) used a TDPD method shows a good agreement with our results: within 10 % for Azelaic acid and within 5 % for Adipic and Succinic acid.

Main differences observed among the various examined works are probably due to different temperature and pressures considered in the experiments and different forms of the sample (e.g. solid or aerosol), that produced different evaporation rates and different vapour pressures at each monitored temperature. Furthermore, the experiments show different error sources: e.g. the large error in Bilde et al. (2003) measurements is due to the presence of unevaporated water within the aerosol particle. In our procedure the efficiency of deposition process was improved when the difference between PCM surface's and effusion cell's temperature increased, and molecules flux was focused directly on PCM crystal (Dirri et al., 2012). In this way, we were able to discern deposition rate at different temperatures. In Fig. 7 the enthalpy of sublimation of four Dicarboxylic acids analyzed in this work are compared with previous studies. This trend shows as the enthalpy of sublimation increases its value with the carbon chain number of the substance. Indeed, the substances with a short carbon chain (Oxalic and Succinic acid) show a lower enthalpy of sublimation compared with the substances with a higher carbon chain (Adipic and Azelaic acid), which require a higher temperature to reach the complete sublimation (up to 70–80 °C).

6 Conclusions and future perspective

A new experimental set-up has been developed in order to characterize the C_2–C_9 Dicarboxylic acids (i.e. Oxalic, Succinic, Adipic and Azelaic acid), compounds present in atmospheric aerosols, over the temperature range of 25–80 °C. The capability of our instrumental setup to monitor the sublimation process in vacuum condition (10^{-6} mbar) has been tested successfully. The measurement procedure is relatively simple and yields about 6 h for a single experiment (cooling the PCM, heating the sample and follow the process minute by minute). Then, the deposition rates of Dicarboxylic acids have been measured and their sublimation enthalpies have been obtained. The results were compared with the other techniques (KEMS, TDMA, EM, TDPD).

This experimental set-up, based on Piezoelectric Crystal Microbalance technology, provides many advantages over other methods: it is lightweight, with a better accuracy and requires a smaller amount of materials for the analysis.

The values of the enthalpy of sublimation obtained in this study for Succinic and Adipic acid are in agreement within 10 % with previous works (Chattopadhyay and Ziemann, 2007; Davies and Thomas, 1960; Bilde et al., 2003, de Wit et al., 1983). The results for the Oxalic acid are in good agreement with the literature (within 3 %, Granovskaya,1948). The enthalpies calculated for the Azelaic acid are in agreement within 15 %, even if they are systematically lower, with previous studies (i.e. Bilde et al., 2003; Da Silva et al., 1999).

In addition, our results show a good accuracy (within 4 %) if we consider the values obtained with an accurate temperature control (within ±0.3 °C). Contrarily, the accuracy worsens (and results are less reliable) when T_2 approaches the sublimation temperature, T_c (Adipic and Succinic acid case).

Thus, by means of our measurement procedure and comparing the results with previous works (Bilde et al., 2003; Davies and Thomas, 1960; Ribeiro da Silva et al., 1999) we have been able to obtain a best accuracy on the enthalpy of sublimation results, as listed in Table 4. In particular, the accuracy may be refined by improving

the temperature control system, in order to extend the temperature range. To work at lower temperatures would be useful especially for Oxalic and Azelaic acids and this would allow to monitor solid → gas phase and to obtain more information about other phase transitions (gas ↔ liquid, solid ↔ liquid). On the other hand, the extension at larger temperatures, which can be simply obtained by changing the resistive element, would make it possible to study also less volatile compounds, such as some Carboxylic Acids or Polycyclic Aromatic Hydrocarbons (PAH).

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Table 1. Thermodynamic properties of the compounds used in experiments at ambient pressure. In particular, the Oxalic and Succinic acids have a high solubility in water, and are the most present in submicron terrestrial aerosol.

Name	Oxalic (C$_2$)	Succinic (C$_4$)	Adipic (C$_6$)	Azelaic (C$_9$)
Chemical formula[a]	C$_2$H$_2$O$_4$	C$_4$H$_6$O$_4$	C$_6$H$_{10}$O$_4$	C$_9$H$_{16}$O$_4$
Molecular weight[a]	90.03	118.0880	146.1412	188.2209
Water solubility (mg L^{-1}) at 25 °C	2.2×10^{5}[b]	8.3×10^{4}[b]	3.2×10^{2}[b]	2.28×10^{3}[c]
Vapour Pressure (torr)	3.5×10^{-5}[b]	6.9×10^{-7}[b]	1.5×10^{-7}[b]	2×10^{-6}[c]
ΔH_{sub} (kJ mol^{-1})[a]	93–98	118–123	129,3	156–159
ΔH_{fus} (kJ mol^{-1})[a]	–	32.9	34.8	32.6
T_{fusion} (°C)[a]	189.5	188	152.1	110

[a] Afeedy et al. (1998).
[b] Prenni et al. (2001).
[c] CAS DataBase List – Chemical Book.

Table 2. Parameters of the experiments involving the different Dicarboxylic acids. Pressure is stable in the range of 10^{-6}–10^{-7} mbar. T_c is the sublimation point, i.e. threshold where the sample sublimes in steadily mode. $\Delta H_{\text{literature}}$ is the average between enthalpies of sublimation obtained in literature with different methods (see Table 4).

Name	Oxalic (C_2)	Succinic (C_4)	Adipic (C_6)	Azelaic (C_9)
M_{Start} (mg)	20 ± 0.5	13.0 ± 0.5	13.0 ± 0.5	19 ± 0.5
P_{Work} (mbar)	$3{,}5 \times 10^{-6}$	6.5×10^{-6}	5.5×10^{-6}	8×10^{-7}
T_c (°C)	60	60	80	80
$T_{\text{Monitored}}$ (°C)	25 to 60	30 to 75	30 to 75	25 to 80
$\Delta t_{\text{Stabilization}}$ (min)	30	30	30	20
$\Delta H_{\text{Literature}}$ (kJ mol^{-1})	68.4	122.1	137.2	148.9
$M_{\text{Sublimated}}$ (mg)	3	1	4	3

Table 3. Enthalpy of sublimation calculated from acid deposition rates measured in our experiment. When T_2 approaches T_c, the calculated enthalpy deviates from the previous work values (see enthalpy values highlighted in bold of Adipic and Succinic acid). Temperature oscillation $\geq 0.5\,°C$ produces an error $\geq 8\,kJ\,mol^{-1}$ on the enthalpy of sublimation (italic values). Oxalic and Succinic acids (weak lattice energies at low temperature) sublimate at smaller temperatures, in the range 25–60 °C where the sublimation process was monitored. Otherwise, Adipic and Azelaic acid sublimate at larger temperatures. The temperature range is wide enough to calculate the enthalpy of sublimation but should be extended if the intent is to monitor the complete sublimation process (in particular for Adipic acid, $T \geq 75\,°C$).

Acid	$T_1 \pm \sigma_{T_1}$ (°C)	$T_2 \pm \sigma_{T_2}$ (°C)	k_1 (mol cm^{-2} s^{-1})	k_2 (mol cm^{-2} s^{-1})	$\Delta H_{sub} \pm \sigma_{\Delta H}$ (kJ mol^{-1})
Oxalic	24.772 ± 0.111	44.969 ± 0.002	6.56×10^{-12}	3.01×10^{-11}	60.67 ± 1.31
	29.843 ± 0.105	44.969 ± 0.002	9.15×10^{-12}	3.01×10^{-11}	64.35 ± 0.64
	34.964 ± 0.015	44.969 ± 0.002	1.52×10^{-11}	3.01×10^{-11}	56.85 ± 0.93
	24.772 ± 0.111	49.962 ± 0.075	6.56×10^{-12}	4.59×10^{-11}	63.15 ± 1.34
	29.843 ± 0.105	49.962 ± 0.075	9.15×10^{-12}	4.59×10^{-11}	66.65 ± 0.84
	34.964 ± 0.015	49.962 ± 0.075	1.52×10^{-11}	4.59×10^{-11}	62.40 ± 1.07
	24.772 ± 0.111	54.952 ± 0.059	6.56×10^{-12}	6.04×10^{-11}	61.06 ± 1.07
	29.843 ± 0.105	54.952 ± 0.059	9.15×10^{-12}	6.04×10^{-11}	63.44 ± 0.60
	34.964 ± 0.015	54.952 ± 0.059	1.52×10^{-11}	6.04×10^{-11}	59.32 ± 0.73
Succinic	34.85 ± 0.02	45.42 ± 0.68	1.59×10^{-12}	7.22×10^{-12}	117.93 ± 4.36
	39.90 ± 0.04	45.42 ± 0.68	3.31×10^{-12}	7.22×10^{-12}	*118.45 ± 7.97*
	34.85 ± 0.02	50.22 ± 0.02	1.59×10^{-12}	1.35×10^{-11}	116.61 ± 3.32
	39.90 ± 0.04	50.22 ± 0.02	3.31×10^{-12}	1.35×10^{-11}	116.21 ± 3.41
	29.98 ± 0.02	54.64 ± 0.02	8.01×10^{-13}	2.17×10^{-11}	111.88 ± 4.15
	34.85 ± 0.02	54.64 ± 0.02	1.59×10^{-12}	2.17×10^{-11}	112.17 ± 2.66
	39.90 ± 0.04	54.64 ± 0.02	3.31×10^{-12}	2.17×10^{-11}	110.27 ± 2.47
	45.42 ± 0.68	54.64 ± 0.02	7.22×10^{-12}	2.17×10^{-11}	***105.14 ± 11.75***
	50.22 ± 0.02	54.64 ± 0.02	1.35×10^{-12}	2.17×10^{-11}	**95.73 ± 3.47**

Table 3. Continued.

Acid	$T_1 \pm \sigma_{T_1}$ (°C)	$T_2 \pm \sigma_{T_2}$ (°C)	k_1 (mol cm^{-2} s^{-1})	k_2 (mol cm^{-2} s^{-1})	$\Delta H_{sub} \pm \sigma_{\Delta H}$ (kJ mol^{-1})
Adipic	39.84 ± 0.04	59.65 ± 0.05	1.10×10^{-12}	2.60×10^{-11}	139.58 ± 3.69
	49.82 ± 0.04	59.65 ± 0.05	5.47×10^{-12}	2.60×10^{-11}	142.90 ± 3.06
	39.84 ± 0.04	64.93 ± 0.04	1.10×10^{-12}	5.78×10^{-11}	140.26 ± 1.22
	49.82 ± 0.04	64.93 ± 0.04	5.47×10^{-12}	5.78×10^{-11}	142.95 ± 1.86
	55.01 ± 0.68	64.93 ± 0.04	1.25×10^{-11}	5.78×10^{-11}	*143.54 ± 13.90*
	59.65 ± 0.05	64.93 ± 0.04	2.59×10^{-11}	5.78×10^{-11}	142.99 ± 4.98
	39.84 ± 0.04	70.01 ± 0.03	1.10×10^{-12}	1.20×10^{-10}	140.15 ± 2.29
	49.82 ± 0.04	70.01 ± 0.03	5.47×10^{-12}	1.20×10^{-10}	142.14 ± 1.22
	55.01 ± 0.68	70.01 ± 0.03	1.25×10^{-11}	1.20×10^{-10}	*142.24 ± 9.01*
	59.65 ± 0.05	70.01 ± 0.03	2.59×10^{-11}	1.20×10^{-10}	141.34 ± 2.18
	59.65 ± 0.05	75.30 ± 1.10	2.59×10^{-11}	2.21×10^{-10}	***133.28 ± 13.11***
	64.93 ± 0.04	75.30 ± 1.10	5.77×10^{-11}	2.21×10^{-10}	***128.05 ± 18.79***
Azelaic	34.95 ± 0.22	50.16 ± 0.02	6.94×10^{-13}	6.09×10^{-12}	119.59 ± 6.91
	40.13 ± 0.26	50.16 ± 0.02	1.48×10^{-12}	6.09×10^{-12}	120.24 ± 8.27
	45.26 ± 0.48	50.16 ± 0.02	2.98×10^{-12}	6.09×10^{-12}	*126.42 ± 20.11*
	40.13 ± 0.26	55.14 ± 0.27	1.48×10^{-12}	1.29×10^{-11}	124.70 ± 8.06
	45.26 ± 0.48	55.14 ± 0.27	2.98×10^{-12}	1.29×10^{-11}	*130.25 ± 14.03*
	50.16 ± 0.02	55.14 ± 0.27	6.09×10^{-12}	1.29×10^{-11}	*134.14 ± 11.74*
	45.26 ± 0.48	60.04 ± 0.02	2.99×10^{-12}	2.48×10^{-11}	127.81 ± 6.72
	50.16 ± 0.02	60.04 ± 0.02	6.09×10^{-12}	2.48×10^{-11}	128.53 ± 1.86
	55.14 ± 0.27	60.04 ± 0.02	1.29×10^{-11}	2.48×10^{-11}	*122.65 ± 10.71*

Table 4. Comparison of enthalpy of sublimation of Dicarboxylic acids retrieved by different techniques (1 = Booth et al., 2009, 2 = Granovskaya, 1948, 3 = Chattopadhyay and Ziemann, 2007, 4 = Bilde et al., 2003, 5 = Davies and Thomas, 1960, 6 = Ribeiro da Silva et al., 1999, 7 = de Wit et al., 1983). ΔT are the temperature range monitored in order to calculate the enthalpy of sublimation. The enthalpy values and corresponding errors reported for this work have been calculated as the weighted average. The anhydrous (A) and dehydrate (deh) forms of the Oxalic acid have been treated and the results for the enthalpy of sublimation have been reported.

Compound	P_{work} (mbar)	ΔT (°C)	ΔH_{sub} (kJ mol^{-1})	Reference
Oxalic	10^{-6}	25/60	(deh)62.5 ± 3.1	This work
	10^{-6}	30/60	(A)75.0 ± 19.0	1
	–	20/50	(deh)61.8	2
	–	−22/54	(deh)56.5	7
	–	37/62	(A)98.5	7
Succinic	10^{-6}	30/75	113.3 ± 1.3	This work
	10^{-6}	30/60	93.0 ± 6.0	1
	10^{-8}	7/29	119.5	3
	10^{3}	17/41	138.0 ± 11.0	4
	10^{3}	99/128	117.5 ± 3.3	5
Adipic	10^{-6}	30/75	141.6 ± 0.8	This work
	10^{-6}	30/60	119.0 ± 26.0	1
	10^{-8}	12/34	146.2	3
	10^{3}	17/41	154.4 ± 6.0	4
	10^{3}	86/133	129.2 ± 1.0	5
Azelaic	10^{-7}	25/80	124.2 ± 1.2	This work
	10^{-8}	21/38	138	3
	10^{3}	17/41	153 ± 24	4
	10^{-6}	95/113	155.8 ± 1.6	6

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Figure 1. Piezoelectric Crystal Microbalance: quartz crystal (transparent plate) and gold electrode in the centre. On the right side and left side are presents the contact points for the proximity electronic.
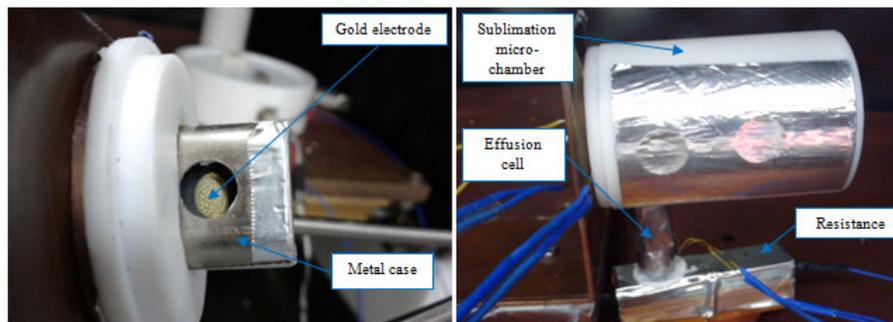
Figure 2. Pictures of the experimental setup. Left: PCM inserted in the metal case. VOC molecules deposited on the PCM's electrode are visible and correspond to the white spots on the crystal area. Right: the sublimation micro-chamber containing the PCM and the out-gassing material. It is made of insulating material (Teflon) in order to limit sublimation and thermal dispersion. The contacts are instead made of grease vacuum.
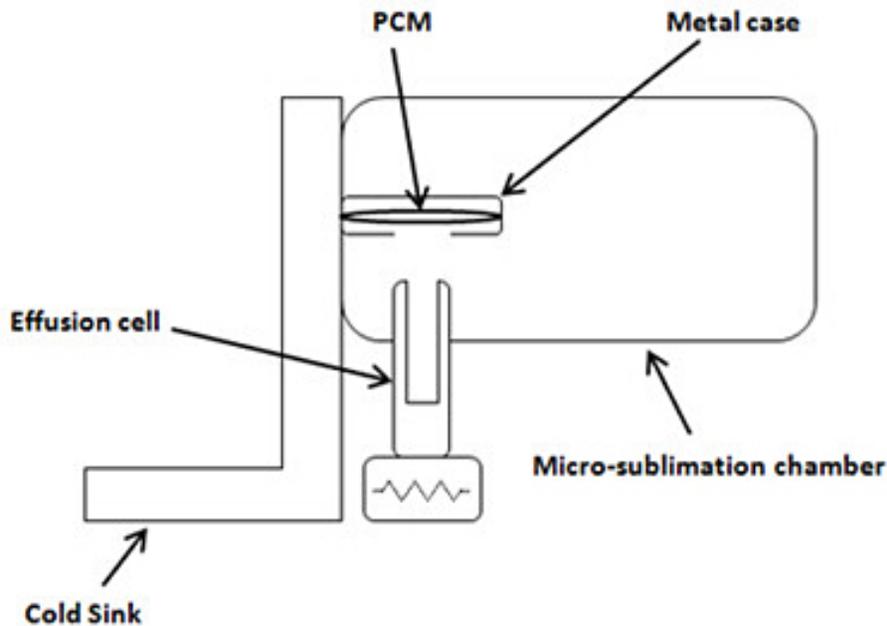
Figure 3. Schematic representation of the experimental setup. The sample is placed in the effusion cell and heated by a resistance. PCM (cooled by a cold sink) is positioned in a metal case perforated in the center to allow the VOC deposition. The deposition rates are monitored by PCM frequency whereas the sample temperature is monitored (5 °C for each step) by a resistance temperature with PT100 sensor (see Sect. 4.2). In order to avoid flux dispersion, PCM and effusion cell are located in an isolated micro-chamber and the whole set-up is placed in a vacuum chamber. The resistance is separated by cold sink in order to obtain a first sublimation step from 25–30 °C.

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Figure 4. The Vacuum System, composed by a Rotative pump, Turbo pump and a Vacuum Chamber. Each pump is managed by an electro-valve: in the initial phase, the first valve (Rotative) is opened whereas the second valve is closed (Turbo); in the next phase (at pressure of 10^{-2} mbar) the first valve is closed whereas the second valve is opened (down to 10^{-6} mbar). The third valve is used to apply the re-entry in air at the end of each experiment.
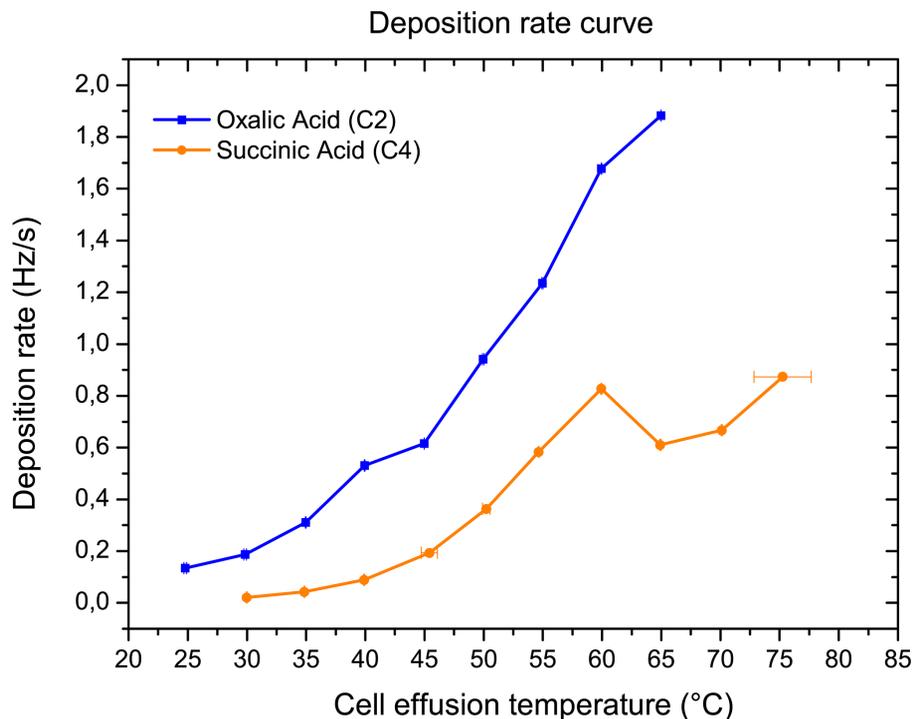
Figure 5. Blue curve: deposition rate curve of Oxalic acid with temperature steps of 5 ˚C, each lasting 30 min. The deposition linearly increases with temperature, up to 60 ˚C. Orange curve: deposition rate curve of Succinic acid. Deposition rate increases with temperature up to 60 ˚C, whereas at larger temperatures tends to oscillate around an average value of $0.75\,\mathrm{Hz\,s^{-1}}$, due to the steadiness of the sublimation flux.

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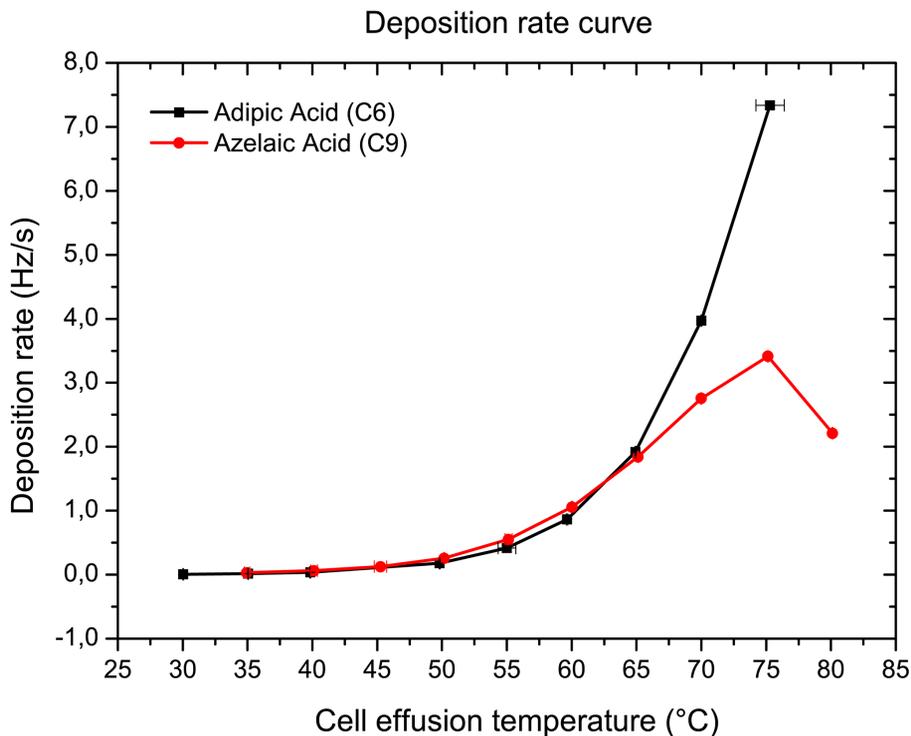
Figure 6. Black curve: deposition rate curve of Adipic acid shows an increase up to 75 °C without decrease at larger temperature (an oscillation around an average value would be observed at even larger temperatures). Red curve: deposition rate curve of Azelaic acid: molecules flux is small at low temperature as for Adipic acid case and contrarily to Oxalic and Succinic acids that show an high sublimation rates at these low temperature, i.e. 25–30 °C (weak intermolecular forces).

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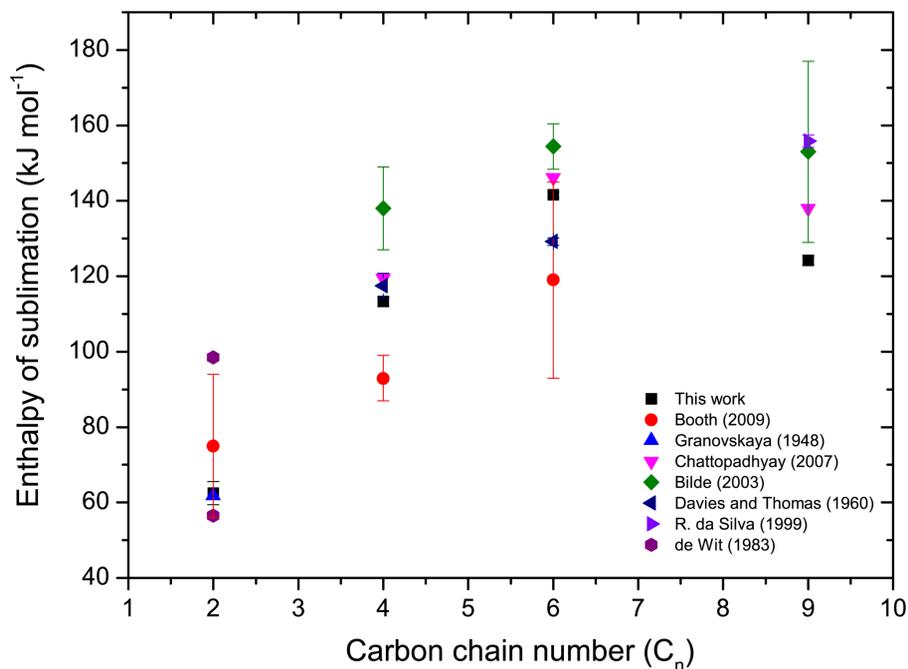
Figure 7. Comparison between the enthalpies of sublimation obtained with various methods and different compounds (C_2, Oxalic acid; C_4, Succinic acid; C_6, Adipic acid and C_9, Azelaic acid, weight average values). Different experiment conditions (temperature monitored and work pressure, Table 4) lead to diverging results: Booth et al. (2009), Chattopadhyay and Ziemann (2007), da Silva et al. (1999) in vacuum environments, Bilde et al. (2003), Davies and Thomas (1960) at atmospheric pressure. For Oxalic acid are plotted the results for anhydrous and dehydrate forms (de Wit et al., 1983; Booth et al., 2009).