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Grivel, J.-C.

Published in:
Journal of Analytical and Applied Pyrolysis

Link to article, DOI:
[10.1016/j.jaap.2018.10.023](https://doi.org/10.1016/j.jaap.2018.10.023)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Grivel, J.-C. (2018). New insights into the thermal behavior and decomposition of sodium propionate. *Journal of Analytical and Applied Pyrolysis*, 136, 62-68. <https://doi.org/10.1016/j.jaap.2018.10.023>

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New insights into the thermal behavior and decomposition of sodium propionate

J.-C. Grivel

Department of Energy Conversion and Storage, Technical University of Denmark,
Frederiksborgvej 399, DK-4000 Roskilde, Denmark

Abstract

Na-propionate ($\text{NaC}_2\text{H}_5\text{CO}_2$) was synthesized from Na_2CO_3 dissolved in propionic acid. Its thermal behavior was studied in argon and in air. In both atmospheres, two solid-solid phase transitions occur below 250°C and are followed by melting near 290°C . Thermal decomposition begins with release of CO_2 attributed to the decomposition of a limited amount of propionyl radicals. Elemental carbon results from this process. This initial reaction is followed by a faster conversion reaction into Na_2CO_3 with evolution of 3-pentanone, CO_2 , CO , CH_4 and C_2H_4 as found during pyrolysis in argon. In air, oxidative decomposition takes place with CO_2 and H_2O as main released gases. The stability of Na-propionate is reduced in air compared to argon atmosphere. The reaction paths are discussed and compared with previously published results on Na-propionate and other propionate metalorganic compounds. The potential of using the low temperature phase transitions of Na-propionate for thermal energy storage ($\Delta H \approx 245 \text{ J/g}$) was evaluated by submitting samples to 25 heating/cooling cycles.

Keywords: Sodium; propionate; decomposition; energy storage

***Corresponding author:** jean@dtu.dk

1. Introduction

Na-propionate is a widely used food preservative, which is listed under number 281 in the *Codex Alimentarius*. Besides this antimicrobial activity, its effects as dietary additive are the topic of intense investigations [1-4] and recent research also found that it plays a role in blood cells differentiation [5]. Considering the variety and importance of the uses of sodium propionate, surprisingly little is known about the thermal decomposition of this key compound. In an early study, Duruz et al. [6] restricted their investigations in the liquid state up to 410°C. The proposed main decomposition reaction should result in the release of 3-pentanone only, but does not match with the observed simultaneous evolution of H₂O and CO as well as minor amounts of C₂H₄, CO₂ and 2-butanone. The side reaction:

was tentatively suggested as an intermediate step leading to other products following reactions between various free radicals such as CH₃· and C₂H₅· formed by primary ion-catalysed cracking in the melt. A very important conclusion of that work however, is that impurities such as NaOH and Cu or Fe ions can have a drastic effect on the decomposition kinetics and products.

More recently, Masłowska and Więdłocha [7] published a succinct study on the thermal decomposition of Na-propionate as part of an investigation of the thermal behavior of various sodium-based food preservatives in static air. Based on the TG and DTA traces, the following decomposition reaction was proposed:

Besides the fact that this reaction is not balanced, the evolved gas were not analysed so that the formation of CO rather than CO₂ as a final reaction product in air may be questioned.

In sharp contrast, the thermal behavior of Na-propionate below its decomposition temperature is well documented (e.g. Mirnaya et al. [8] and references therein). Two solid-solid transitions take place at 197°C and 221°C preceding melting to an isotropic ionic liquid at 289°C.

The aim of the present work was to provide a clearer picture of the thermal decomposition behavior of Na-propionate in oxidizing (air) and inert (argon) conditions. Additionally, the reversibility of the low temperature transitions upon temperature cycling were studied to evaluate the potential of Na-propionate in view of possible exploitation in thermal energy storage applications.

2. Experimental details

The samples were synthesized by dissolving 200 mg of anhydrous Na₂CO₃ (Alfa Aesar, 99.997% purity) into 4 ml propionic acid (Alfa Aesar, 99%). After slow evaporation on a hot plate set to 50°C, the resulting white mass was crushed into a powder that was used without further purification.

Simultaneous Thermogravimetry and Differential Thermal analysis (TG-DTA) measurements were performed in a model STA 449C from Netzsch at a heating rate of 5 °C/min up to 1000°C under argon flow (0.5 ppm residual O₂) or technical air (20.9 % O₂, rest N₂) both provided by AGA A/S, with a flow rate of 40 ml/min at normal pressure. The crucibles (6 mm diameter and 3 mm depth, i.e. 85 µl) consisted of alumina. Buoyancy corrections were applied based on data recorded on empty crucibles but otherwise similar experimental conditions. For the measurements, the sample mass was of 11.5 ± 0.3 mg. The powders were not compacted. α-Al₂O₃ powder (48 mg) was used as reference. Reproducibility was assessed by performing 3 measurements in each atmosphere and it was found that the standard deviation on mass loss amounts to about 0.2%.

A Bruker Tensor 27 spectrometer coupled to the exhaust line of the TG-DTA device by a transfer line heated to 200°C was used for recording Fourier transform infra-red (FTIR) spectra of the evolved gases. FTIR spectra were also recorded on the solid residues of samples heated in the TG-DTA at a rate of 5 °C/min and air quenched by opening the furnace in order to examine the evolution of the decomposition products. The enthalpy of the low temperature phase transitions was estimated from the DTA peaks (endothermic and exothermic upon heating and cooling respectively) calibration was performed using standard powders consisting of KNO₃, RbNO₃ and KClO₄. X-ray diffraction (XRD) patterns were collected in a Bruker D8 X-ray diffractometer with CuK_α radiation on samples heated to various temperatures at a heating rate of 5°C/min under Ar or air flow in the TG-DTA and cooled at a rate of 50°C/min. The room temperature XRD pattern of the as-prepared Na-propionate powder was recorded in the same instrument. The evolution of microstructural features was observed at low magnification (50x) by hot-stage optical microscopy up to 700°C under Ar flow in a HCP901 chamber from INSTEC Ltd calibrated by observing the melting of metal standards (In, Sn, Bi, Zn and Al).

3. Results and discussion

The XRD pattern of the synthesized powder is plotted in Fig.1. Besides a reflection originating from the sample holder, it exhibits all peaks corresponding to Na-propionate [9]. The FTIR spectrum of the powder obtained after drying the precursor solution is shown in the inset of Fig.1. It corresponds to that of anhydrous sodium propionate [10]. These data confirm that the compound prepared as described in the previous section consist of Na-propionate. Furthermore, the absence of a broad absorption band around 3400 cm⁻¹ in the FTIR spectrum shows that the compound is anhydrous. The separation between the asymmetric and symmetric CO₂ stretching

bands, $\Delta\nu = 136.5 \text{ cm}^{-1}$, is very close to that measured by Kakihana and Nagumo ($\Delta\nu = 134.6 \text{ cm}^{-1}$).

Figs.2a and 2b show respectively the TG and DTA traces recorded under argon or air flow on two Na-propionate powder samples from the same batch. The compound appears more stable in argon atmosphere as the main mass loss, which occurs between 420°C and 530°C, is shifted to lower temperature when the powder is heated in air. While the low temperature behavior of the DTA trace (i.e. up to 340°C) is similar in both atmospheres, a strong exothermic peak is registered in air near 500°C, in contrast to the measurement conducted in argon atmosphere, which results in an endothermic peak in the same temperature range (IV in Fig.2b).

The three endothermic peaks appearing at $195\pm 2^\circ\text{C}$, $216\pm 2^\circ\text{C}$ and $284\pm 3^\circ\text{C}$ respectively (I, II and III in Fig. 2b) have been characterized in previous reports [6,8,11]. They are due to two successive solid-solid transitions followed by melting. The observed transition temperatures in the DTA traces recorded in air and argon correspond well with previously reported values [6,8,11]. Hot-stage microscopy pictures of two Na-propionate powder samples heated under argon and air flow respectively are shown in Fig.3. No morphological differences can be seen between the pictures recorded at 190°C and 210°C, i.e. over the first endothermic reaction. In contrast, shrinking occurs during the second solid-solid transition as can be seen by comparing the pictures recorded at 210°C and 250°C. Finally, melting is evident in relation with the third endothermic reaction (pictures recorded at 290°C). The fact that only little change takes place in the morphology of the powder particles during the first and second solid-state transitions is not surprising, because the room temperature phase and the two high temperature modifications all crystallize in the monoclinic system with very close lattice parameters [9].

However, above 300°C, the behavior of Na-propionate is strongly dependent on the atmosphere. The nearly 100°C lower temperature for the onset of mass loss under air flow suggests a significantly higher stability under reducing atmosphere. In argon, the main mass loss, occurring between 400°C and 530°C, appears to take place in a single step. At 530°C, the overall mass loss amounts to 43.7 ± 0.1 %, which is a little less than the 44.8% that are theoretically expected for a decomposition from Na-propionate to Na-carbonate (Na_2CO_3). In contrast, when heated in air, the sample mass starts decreasing significantly already from 320°C. After an accelerating stage up to about 450°C, the mass loss slope first decreases prior to accelerating again. The total mass loss at 510°C, at which temperature a plateau has been reached in the TG trace, is equal to 44.6 ± 0.1 %, i.e. very close to the theoretical 44.8% mentioned above. That the TG plateau around 550°C corresponds to the formation of Na_2CO_3 can indeed be verified in the FTIR spectra recorded on the solid residues left in this temperature range in both air and argon, as well as with the XRD patterns recorded on the same samples (Fig.4).

According to the FTIR evolved gas analysis, the gas species released during the decomposition leading to the formation of Na_2CO_3 in argon consist of $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$ (3-pentanone), CO_2 , CH_4 and C_2H_4 (ethylene) as evidenced in Fig. 5. There is no compelling evidence for the presence of H_2O , a significant difference with the data reported for decomposition in the liquid phase at 360°C [6], according to which the most abundant evolving gas species are H_2O , $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$, CO , C_2H_4 , CO_2 and $\text{CH}_3\text{COC}_2\text{H}_5$ in decreasing abundance. The formation of 3-pentanone is a standard characteristic of the thermal decomposition of propionate salts [12-20], although in some cases 2-pentanone [21] or a mixture of CO_2 , CO or H_2O along with traces of $\text{CH}_3\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CH}_2\text{OH}$ or $\text{CH}_3\text{CH}_2\text{CO}_2$ [22,23] were reported for Y and La/Ni/Ca propionates respectively.

The reaction leading to the appearance of the symmetrical ketone can be described as:

And can result from the free-radical mechanism proposed by Hites and Biemann [24]. On the other hand, the presence of CH_4 , C_2H_4 , CO_2 and CO among the evolved gases suggests that the ligands themselves are prone to fragmentation into smaller molecular units. The exact mechanism for this process is however difficult to determine. It is striking that CH_4 and C_2H_4 were not observed during the thermal decomposition of previously studied metal propionate salts [12-23]. This particular situation may be related to the more ionic character of liquid Na-propionate and/or to the relatively higher decomposition temperature of Na-propionate. Studies on other alkaline element propionates are limited. For Li-propionate and K-propionate, Bui and de Klerk [25,26] assumed the evolution of 3-pentanone without direct analysis. A more recent study by Yoon et al. [27] suggests that CO_2 and C_2H_4 are released alongside 3-pentanone during the decomposition of Li-propionate in N_2 . The analysis in that case is however complicated by the fact that Li-propionate only appears as an intermediate decomposition product of Li-ethylene dicarbonate, which itself also releases CO_2 and C_2H_4 when transforming into Li-propionate. The thermal decomposition of Rb and Cs propionates seems to have only been studied as mixed salts with Fe in view of ferrite compounds manufacture and the evolved gaseous products were not analyzed [28,29].

The fact that the thermal decomposition process of Na-propionate is more intricate than that of e.g. rare-earth or alkaline earth element propionates is further evidenced by a careful inspection of the DTA trace (Fig. 2b), which shows that in Ar a diffuse exothermic effect sets in at 350°C , at which point the DTA trace goes back to about 0 mW. The endothermic peak (IV in Fig. 2b) corresponding to the main mass loss, is superimposed on this exothermic background. The onset

of the exothermic reaction is correlated to the appearance of dark particles in the liquid and a dark rim all around liquid areas as shown in Fig. 6 (368°C and 400°C) as well as to the detection of CO₂ as the only evolving gas up to about 430°C (Fig. 7). According to Kerr and Lloyd [30], the propionyl radical C₂H₅CO· tends to decompose into CO and an ethyl radical (CH₃CH₂·). Assuming that two CO molecules combine in such a way as to result in CO₂ + C, it could be possible to account for the detection of CO₂. The dark particles observed in the liquid and/or at its surface, would then consist of carbon. Interestingly, the CO₂ gas evolution trace (Fig. 7) presents a minimum at 470°C prior to increasing again in parallel with the accelerating stage of the main mass loss. This suggests that the propionyl radical decomposition process becomes slower or even comes to an end, whereas another decomposition mechanism becomes predominant. A careful look at the number of black particles in hot-stage micrographs (Supplementary material, Fig. S1) reveals that the initial process stops between 440°C and 460°C, short before gas bubbles start to appear (463°C in Fig. S1). It may be speculated that the residual oxygen (0.5 ppm) present in the Ar gas could play a role in this initial process as it is exothermic and CO₂ is released. However, if such was the case, one would expect a similar effect with significantly higher intensity in air and this is clearly not the case. Indeed, the formation of CO₂ does not necessitate an external input of oxygen, because the carbonyl radicals already contain 2 oxygen atoms. The exothermic nature of the reaction might simply be related to the instability of the carbonyl radicals, which spontaneously decompose in this temperature range.

The combination of evolving gasses observed during the main mass loss probably results from several reactions taking place simultaneously. These include reaction (3) associated to the endothermic peak IV between 460°C and 560°C. A recent study by Li et al. [31] showed that n-

butane, which can be considered as resulting from the association of two ethyl radicals, decomposes into a variety of hydrocarbon compounds, the most abundant being C_2H_4 and CH_4 . The ethyl radicals formed during the early stages of Na-propionate pyrolysis may undergo a related decomposition path, although with an onset temperature lower than that of n-butane. However, since the mass loss at $460^\circ C$ is limited to about 2 %, the relatively strong signals of C_2H_4 and CH_4 (Fig. 7), certainly also include contributions from other reactions, the most plausible being the pyrolysis of parts of the produced 3-pentanone itself, which was shown to result in the formation of CO and propionyl radicals that would then in turn result in more C_2H_4 and CH_4 [32]. As shown by the hot-stage micrographs ($485^\circ C$ in Fig. 6), intense gas bubbles formation occurs during the main mass loss. This process is finished when the mass plateau has been reached (image captured at $536^\circ C$ in Fig. 6). At higher temperature, the black surface layer of the remaining sample is slowly disappearing, most probably as a result of slow oxidation of carbon left from the decomposition process by the residual oxygen present in the carrier Ar gas. This oxidation process may be the main contribution for the broad exothermic effect taking place after the decomposition of Na-propionate into Na_2CO_3 ($550^\circ C$ to about $800^\circ C$ in Fig.2b).

In air, the situation is rather different. Although an exothermic contribution to the DTA trace sets in at $350^\circ C$ like in the case of Ar atmosphere (Fig.2b) and is also accompanied by the evolution of CO_2 (Fig.8), its intensity is significantly lower. As shown in Fig. 6 ($360^\circ C$), the sample or at least its surface rapidly solidifies, which must prevent the efficient removal of newly formed gas species. A little exothermic DTA peak appears between $430^\circ C$ and $450^\circ C$ (Fig. 2b). It is related to a surge of CO_2 evolution (Fig.8) and the whitening of the sample surface ($450^\circ C$ in Fig.6). These features are characteristic for the oxidation of the residual carbon that formed during the initial stage of decomposition following a process that may be similar to that

discussed for the case of Ar atmosphere. It can be noted that this exothermic event also matches with the transient accelerating stage of mass loss around 450°C in the TG trace (Fig.2a). At this point, the mass loss has reached about 10%. At higher temperature, an oxidative decomposition process takes place, which is characterized by a strong exothermic effect with a maximum at 510°C in the DTA trace (Fig.2b) and detection of mostly CO₂ and H₂O among the evolved gases. It is not clear whether the oxidative decomposition takes place directly or is preceded by pyrolysis processes similar to those identified in the case of Ar atmosphere, followed by combustion of the decomposition products after release. The presence of some C₂H₄ (Figs. 8 and 9) tends to speak in favor of the second version.

In contrast to Ar atmosphere, the main decomposition in air occurs in solid form as shown by the in-situ hot stage microscope images captured at 450°C and 520°C (Fig. 6). In spite of these differences, it appears that notwithstanding on the reducing or oxidative nature of the atmosphere, Na-propionate is more stable than other propionates metalorganic salts with a decomposition temperature 100°C to 150°C higher than reported for rare earth propionates [12-16,20-22,33] and about 50°C higher than in the case of alkaline earth propionates [18,19].

Above 700°C, the mass of the samples decreases again, both in air and in Ar, reaching total mass losses of 50.0% and 54.7% respectively at 1000°C. These values are lower than the 67.7% that are theoretically expected for decomposing Na-propionate into Na₂O. Nevertheless, the TG traces have not reached a plateau at 1000°C, indicating that the decomposition process is not finished yet. No evidence for the presence of Na₂O was found in the XRD patterns and FTIR spectra of samples heated to 1000°C. This can be due to several reasons: rapid reformation of Na₂CO₃ upon contact with ambient air, formation of intermediate oxycarbonates or evaporation of Na₂O (as sodium gas and oxygen [34]). The last of these possibilities is the most probable.

Indeed, Motzfeldt [34] demonstrated that elemental Na and O₂ escape molten Na₂CO₃ during the thermal decomposition of the latter and that during the decomposition process, the concentration of Na₂O at steady-state is of the order of magnitude of 1%, which precludes the detection of Na₂O by means of XRD or FTIR techniques. The clear evolution of CO₂ at high temperature (Fig.7), which is also in agreement with the work of Motzfeldt [34] supports the decomposition of Na₂CO₃ into Na(gas) + O₂(gas) + CO₂(gas). It is interesting to note that the mass loss starts at lower temperature and is occurring faster in Ar than in air. This can be related to a carbothermic effect induced by the larger amount of residual carbon in the Na₂CO₃ formed in Ar [35]. In that case, melting, the occurrence of which is revealed by an endothermic peak with onset at 854°C in the DTA traces (Fig. 2b), has an influence on decomposition kinetics that translates into a change of mass loss rate (see TG trace for Ar in Fig. 2a) and a non-monotonic rate of CO₂ evolution above 700°C (Fig.7). An acceleration of the mass loss rate is clearly taking place after melting, whereas it was negligible up to that point, again in agreements with previous reports on the thermal decomposition of Na₂CO₃ [34,36].

The total enthalpy of the three low temperature phase changes amounts to about 245 J/g (85 J/g for the two solid-solid transitions together), values that could be interesting for thermal energy storage applications as they are comparable with the enthalpy reported for neopentyl glycol/pentaerythritol (NPG/PE) systems that also have transitions at temperatures a little higher than 150°C and phase change enthalpies of the order of 200 J/g [37,38]. In order to evaluate the potential of using Na-propionate for such purpose, the stability of the salt and its behavior below the decomposition temperature was tested by subjecting Na-propionate samples to thermal cycling between room temperature and 310°C. The results from 25 cycles (temperature increasing and decreasing at 5 °C/min) are shown in Fig. 8 and some traces are plotted in Fig.

S2. In Ar, the ΔH is constant, but in air a clear degradation takes place. It shall be noted that the sample mass used for ΔH calculations is the sample's original mass. The monotonically decreasing ΔH for thermal cycling in air is primarily due to Na-propionate decomposition and therefore to decrease of the actual Na-propionate mass.

4. Conclusions

The thermal decomposition of Na-propionate in Ar comprises a first stage resulting in the release of CO_2 and in the formation of carbon particles, which could be due to the decomposition of propionyl radicals. This stage is replaced above about 460°C by the more familiar decomposition process of metal carboxylates resulting in the formation of the symmetrical ketone 3-pentanone as well as residual solid Na_2CO_3 . Side reactions, which can involve partial pyrolysis of 3-pentanone and/or ethyl radicals induce the detection of CH_4 , C_2H_4 , CO and CO_2 . It is worth noting that based on the vibrational spectrum provided in [41] no propionyl radicals were detected by evolved gas analysis, involving that they either decompose on the way between the crucible and the FTIR cell or decompose in the molten sample prior to leaving the crucible. In air, the sample solidifies around 70°C above the melting point of Na-propionate and oxidative decomposition reactions are predominant, resulting in the release of mostly CO_2 and H_2O . Na-propionate might be an interesting candidate for thermal energy storage applications owing to its low temperature phase changes associated to the total ΔH of nearly 250 J/g . However, the salt should be maintained in a non-oxidative atmosphere to avoid progressive decomposition taking place even just a few degrees above its melting temperature.

Acknowledgements

This work was financially supported by the Technical University of Denmark [internal grant 49632].

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Figure captions

Figure 1: XRD pattern of the as-prepared powder: ● Na-propionate [9], ○ sample holder. Inset: FTIR spectrum of the same powder. The assignment of the absorption bands is based on reference [10] and vertical tick marks indicate the position and relative intensities of the reference pattern. NB: the lowest angle peak has been reduced by a factor 4 to improve the visibility of the other tick marks.

Figure 2: (a) TG traces recorded on Na-propionate powders in air or Ar. (b) Simultaneous DTA traces of the samples in Fig.2a. The insets show details of the low temperature region, highlighting the low temperature phase transitions (left) and the onset of the exothermic effects (right). Exothermic effects upwards.

Figure 3: In-situ, hot stage optical microscope images of Na-propionate powders heated either in argon (left column) or in air (right column). The same magnification was used for all images.

Figure 4: FTIR spectra of samples heated to 525°C (in air) or 550°C (in Ar) showing the formation of Na₂CO₃ (●). Inset: XRD patterns of the same samples confirming the presence of Na₂CO₃ (▼).

Figure 5: FTIR spectrum of the gas phase evolved from Na-propionate heated in Ar at 5°C/min. Spectrum recorded at 516°C. ▼: CO₂, ▽: 3-pentanone, ■: CH₄, △: C₂H₄, ◆: CO. The identification of the compounds was based on a comparison with reference patterns [39,40].

Figure 6: In-situ, hot stage optical microscope images of Na-propionate samples heated in argon or in air. The same magnification was used for all images.

Figure 7: Evolution of the intensity of characteristic absorption bands of the detected evolving gas species versus temperature during heating in Ar. The wavenumbers selected for the

respective traces are: C_2H_4 : 946 cm^{-1} , CH_4 : 1306 cm^{-1} , 3-pentanone: 1722 cm^{-1} , CO : 2116 cm^{-1} and CO_2 : 2355 cm^{-1} . The lower curve is the DTG trace.

Figure 8: Evolution of the intensity of characteristic absorption bands of the detected evolving gas species versus temperature during heating in air. The wavenumbers selected for the respective traces are: C_2H_4 : 946 cm^{-1} , CO_2 : 2355 cm^{-1} and H_2O : 1507 cm^{-1} . NB: The intensity of the C_2H_4 signal has been multiplied by a factor 10 for ease of visualization. The lower curve is the DTG trace.

Figure 9: FTIR spectrum of the gas phase evolved from Na-propionate heated in air at $5^\circ\text{C}/\text{min}$. Spectrum recorded at 507°C . $\blacktriangledown$: CO_2 , $\triangle$: C_2H_4 , $\bullet$: H_2O . The wavenumbers selected for the respective traces are: C_2H_4 : 946 cm^{-1} , H_2O : 1558 cm^{-1} and CO_2 : 2355 cm^{-1} .

Figure 10: Total enthalpy for the 3 low temperature phase transitions corresponding to peaks I, II and III in Fig.2b for Na-propionate samples cycled 25 times between 30°C and 310°C in argon or in air. The solid symbols are for heating and the open symbols correspond to cooling.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Supplementary files

Figure S1: In-situ, hot stage optical microscope images (detail) of the Na-propionate sample heated in argon. The same magnification was used for all images.

Figure S2: Selected DTA traces from the cycling experiments in air (left) and in argon (right). Exothermic upwards / Endothermic downwards.