Metal–Fluorocarbon Pyrolants: VII.†
Crackling Effect Based on $Mg/KClO_4/(C_2F_4)_n$

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Abstract: *A mixture of magnesium, potassium perchlorate, $KClO_4$, and polytetrafluoroethylene, $(\text{-}C_2F_4\text{-})_n$, displays an audible crackling effect with nice sparks.*

Keywords: *crackling effect, magnesium, potassium perchlorate, polytetrafluoroethylene, Teflon™*

In fireworks crackling effects are used in small hand-thrown devices like "dragon eggs" or as the payload for firework shells. The crackling effect is based on the thermitic reaction of magnalium (MgAl-alloy), and sometimes aluminum, with lead tetroxide (Pb_3O_4) and copper oxides.[1] Some time ago Jennings-White introduced bismuth oxide (Bi_2O_3) as a non-toxic substitute for lead oxides.[2]

So far it has seemed that the presence of magnalium is a necessary prerequisite for the intermittent reaction explained on the basis of the consecutive combustion of both Mg and Al with different oxidizing entities. In addition, aside from a few reports of potassium nitrate as co-oxidizer, only metal oxides have been reported as main oxidizers.

The present communication reports on a composition free of aluminum, magnalium and metal oxides that gives a crackling sound when ignited.

In the course of pyrolant screening the author tested a composition based on equimolar amounts of magnesium, potassium perchlorate ($KClO_4$) and polytetrafluoroethylene (Teflon™, PTFE, $(C_2F_4)_n$) (Table 1).

The corresponding mixtures were prepared on a 1 g batch size from magnesium powder (non-ferrum Metallpulver, A-5111 St. Georgen, ECKA Mg-Pulver LNR-61, mean particle radius: 20 µm), potassium perchlorate (Aldrich, D-82018 Taufkirchen, #46,049-4, mean particle radius: 25 µm), polytetrafluoroethylene (Dyneon, D-84504 Burgkirchen, TF-9205, mean particle radius: 2 µm) by sieving the ingredients into an agate mortar and homogenizing them with some acetone. The homogenized mixtures were transferred to an oven and dried at 60 °C for 1 hour at ambient pressure.

The mixtures were consolidated by compression in a cylindrical 13 mm diameter die. For the differential scanning calorimetry (DSC) measurements, to achieve greater homogeneity, fragments of the pellets were used.

The overall reaction can be formulated as

$$n\,KClO_{4(s)} + n\,Mg_{(s)} + (C_2F_4)_n \rightarrow n\,KF_{(s)} + n\,MgF_{2(s)} + 2n\,CO_2 + n\,ClF \qquad (1)$$

$\Delta_R H$: −1292 kJ mol^{-1} {That is −4.91 kJ g^{-1} or −11.38 kJ cm^{-3}.}

Ignition of a pressed pellet (13 × 5 mm) of the material ($\rho_{20\,°C}$: 2.23 g cm^{-3}, that is 96% TMD) with a butane flame yields a pink-violet flame and a distinct audible crackling effect. Figures 1 and 2 show the effect and traces of sparks. Figure 1

† For Part VI see ref. 12.

Table 1. *Composition details.*

Component	Density/ g cm^{-3} [a]	Molar mass/ g mol^{-1}	Heat of formation/ kJ mol^{-1}	Moles	Volume (%)	Weight (%)
Magnesium	1.74	24.305	0	1	12.32	9.25
Potassium perchlorate	2.52	138.55	−432	1	48.48	52.71
Polytetrafluoroethylene	2.25[b]	100.016	−809	1	39.20	38.05

[a] The theoretical maximum density (TMD) for such a composition is 2.32 g cm^{-3}. [b] Ref. 3.

shows combustion of the pelletized material. Figure 2 shows combustion of unconsolidated bulk material.

The color of the spark streaks, changing from orange after ejection to dazzling white upon explosion, calls for a delayed combustion not typical for pure magnesium.[4] The crackling of this composition – occurring more loudly if the loose powder is ignited – is a series of intermittent small explosions, clearly distinguished from the general fizzing sound of the pyrolant combustion flames such as $Mg/KClO_4$ and Mg/PTFE.

In order to elucidate the reaction mechanism a series of DSC and DTG experiments with the original composition and the corresponding binary mixtures were conducted. The DSC experiments were conducted with ~5 mg samples in a Mettler DSC 30 at 10 K min^{-1} heating rate under air in open 40 µl aluminum pans. The DTG experiments were carried out with a Mettler TG 50 at 10 K min^{-1} under air in 40 µl open alumina (Al_2O_3) crucibles.

The ternary composition ($Mg/KClO_4/(C_2F_4)_n$) displays two endothermic signals at 306 and 329 °C (Figure 3) which can be assigned to the phase transition of $KClO_4$ and fusion of PTFE respectively (lit: $pt_{(rh–c)}$ ($KClO_4$): 299 °C, $mp_{(PTFE)}$: 328 °C). The onset for the main reaction is at 490 °C and it has a sharp maximum at 545 °C. A second broad exothermic event has its peak at 560 °C.

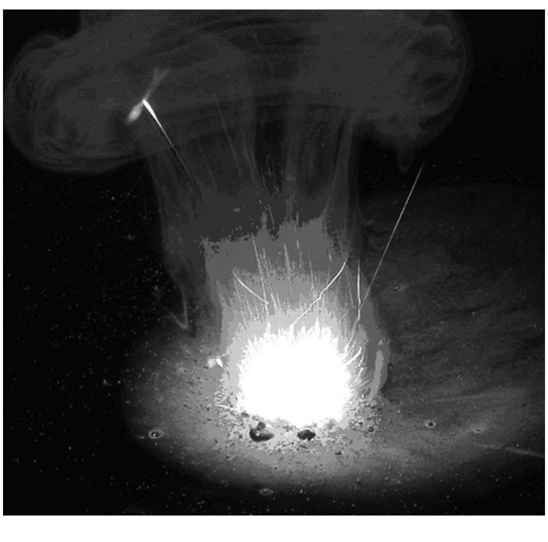

Figure 1. *Combustion of pelletized material.*

Figure 2. *Combustion of bulk pyrolant.*

Investigation of Mg/PTFE reveals an endotherm at 328 °C, a broad exothermic signal with onset at 480 °C, several shoulders and a mean peak at ~560 °C (Figure 4). This is the pre-ignition reaction of the Mg/PTFE system followed by oxidative decomposition of PTFE as has been shown by both Griffiths[5] and Koch.[6]

The binary potassium perchlorate and polytetrafluoroethylene system again shows two known endotherms at 308 and 329 °C. Now there are two clearly separated exothermic peaks, a doublet-like one at 573 °C and a sharp one at 582 °C (Figure 5). A reaction in accordance with equation 4 calling for evolution of chlorine fluoride, ClF, is very likely since the DSC pan was heavily corroded, as is depicted in Figure 6. The left pan is a new one, the middle pan is from the original composition and the pan to the right is from $PTFE/KClO_4$. The DTG diagram shows stepwise evolution of gaseous reaction products at both 582 and 608 °C (Figure 7).

The DSC of $Mg/KClO_4$ now shows, besides the phase transition of $KClO_4$ at 308 °C, onset of a first exothermic reaction at 489 °C with a peak at 511 °C followed by a steep decline in temperature which is obviously due to melting of $KClO_4$ and an adjacent exothermal event still in progress at 600 °C (Figure 8). This is in good accord with investigations carried out by Freeman.[7]

Whereas $PTFE/KClO_4$ (1 : 1) does not ignite, $Mg/KClO_4$ in the given molar proportions (1 : 1) gives a white erratic burning flame, and finally Mg/

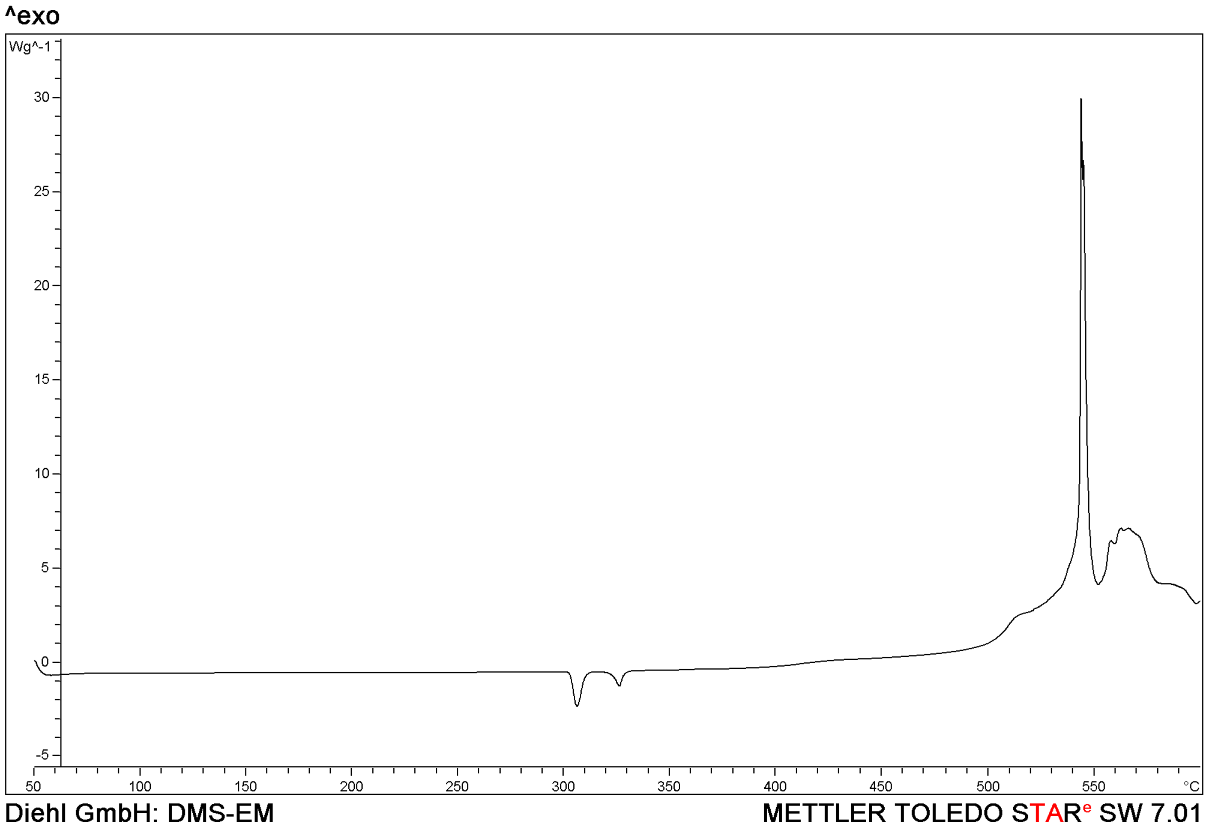

Figure 3. *DSC plot of ternary composition.*

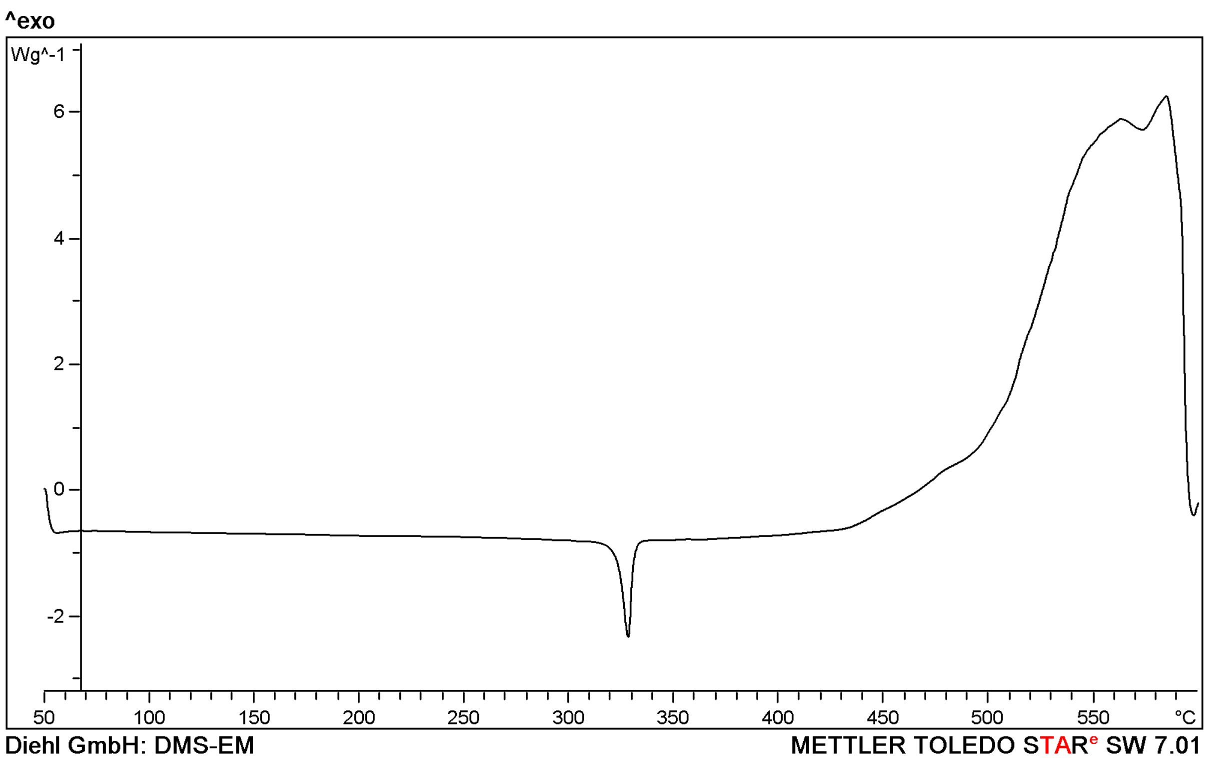

Figure 4. *DSC plot of Mg/PTFE.*

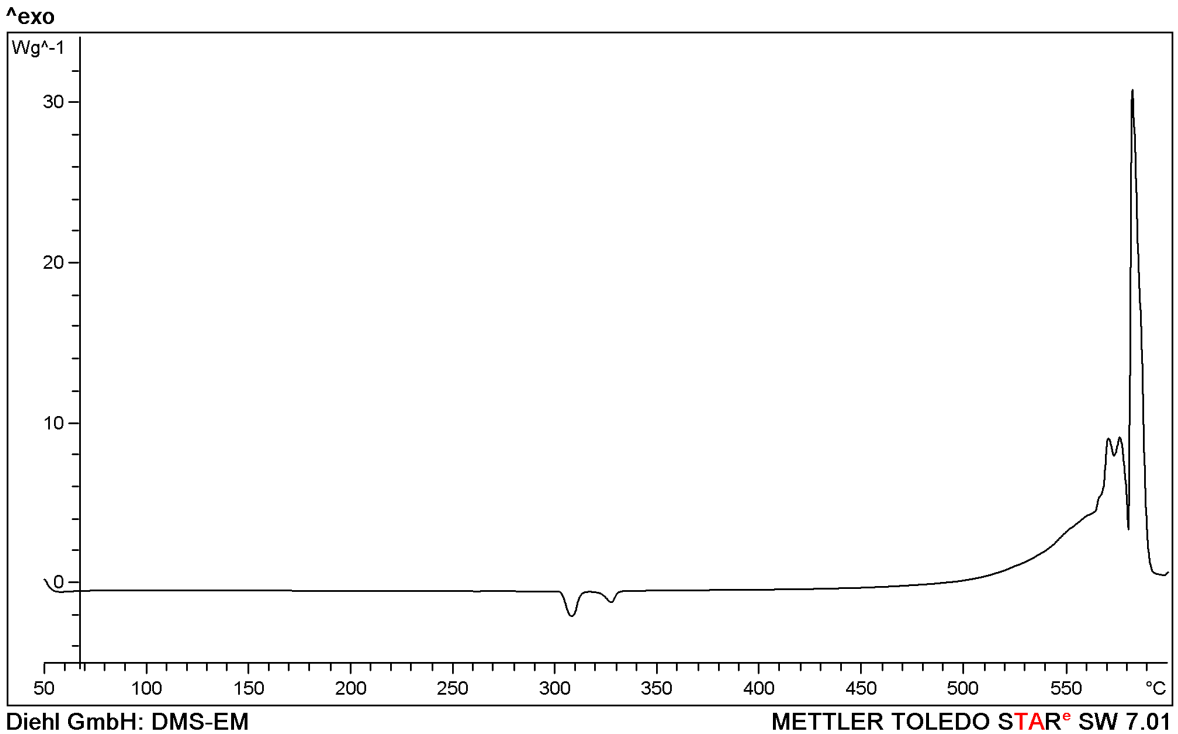

Figure 5. *DSC plot of PTFE/$KClO_4$.*

PTFE (1 : 1) burns also with an erratic flame.

Jennings-White quite recently in his review on strobe chemistry divided oscillating reactions into two stages: one being the flash/audible stage and one being the smolder/dark phase.[8]

In view of this a series of reactions can be tentatively formulated to explain the observed crackling effect of the ternary system Mg/$KClO_4$/$(C_2F_4)_n$.

The flash reaction is probably the initial step

$$Mg_{(s)} + KClO_{4(s)} \rightarrow MgO_{(s)} + KCl_{(l)} + 1.5\ O_2 + 605\ kJ \qquad (2)$$

yielding both heat and surplus oxygen available for further oxidation reactions

The following reaction probably acts as a delay element in consuming the heat to decompose the PTFE.

$$n\ 176\ kJ + (C_2F_4)_{n(s)} \rightarrow (C_2F_4)_{x(l)} + y\ C_2F_{4(g)} \qquad (3)$$

As PTFE melts at 327 °C it is assumed that this covers all the solid particles present in the mix. Thus it may act as a transient barrier between the reactants thus delaying the Mg/$KClO_4$ reaction. When gasified it reacts with the oxygen provided from both the decomposition of the potassium perchlorate and the ambient air

$$KCl + 1.5\ O_2 + (C_2F_4)_{(g)} + \text{ambient air} \rightarrow COF_2 + CO_2 + KF_{(s)} + \tfrac{1}{2}\ O_2 + ClF + 462\ kJ \qquad (4)$$

Finally Mg might react with liquid PTFE:

$$Mg_{(s)} + (C_2F_4)_{(l)} \rightarrow MgF_{2(s)} + :CF_2 + \{C\} + 510\ kJ \qquad (5)$$

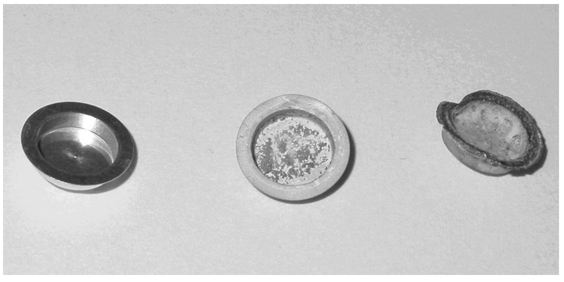

Figure 6. *DSC pans.*

Ladouceur has pointed out that the oxidation kinetics and transport effects of fluorocarbons are much slower as compared to hydrocarbons,[9] thus

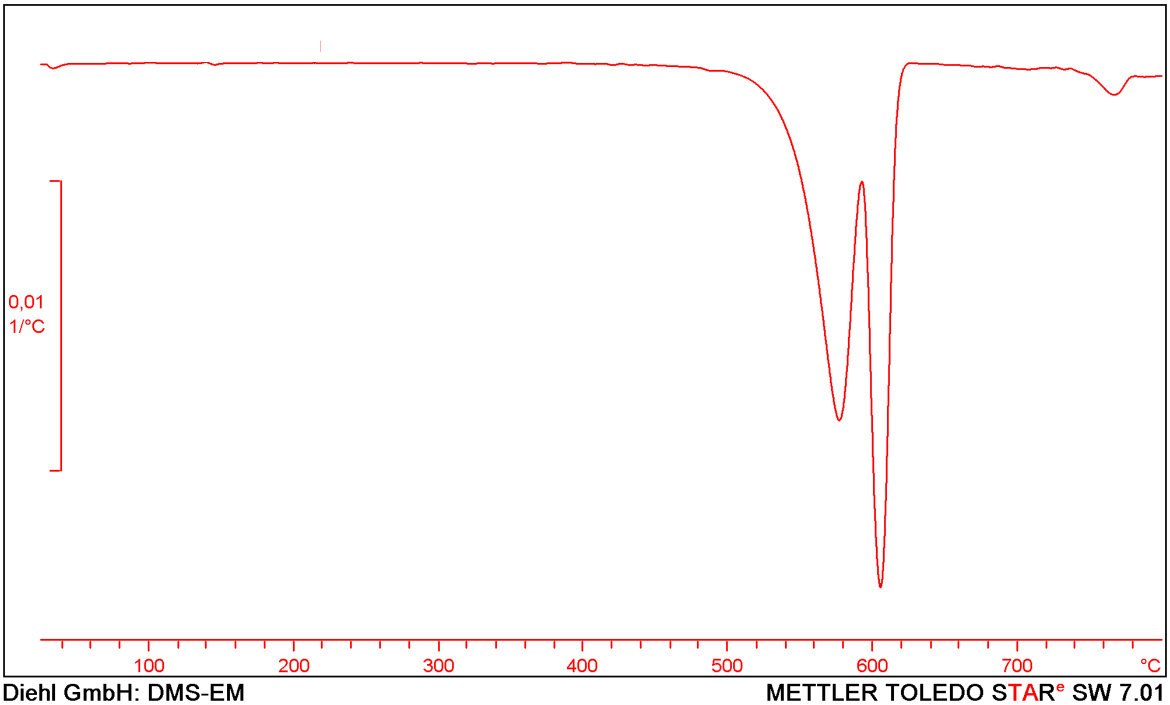

Figure 7: *DTG plot of binary PTFE/KClO4*

the delayed combustion of liquid PTFE can be explained.

Thermochemical calculation with NASA CEA code[10] reveals an adiabatic combustion temperature of 2243 K. From the mole fractions of both O_2 and atomic chlorine and fluorine (Table 2) it is obvious that the composition provides a distinct surplus of oxidizing agents, a situation generally found in intermittent combustion systems.

Although the above considerations do not allow for a precise elucidation of the crackling mechanism there are several hints as to what is actually happening:

- $Mg/KClO_4$ reaction triggers ignition of the complete composition and acts as an "energetic sustainer" → (605 kJ).
- PTFE acts as a heat sink to generally delay combustion of $Mg/KClO_4$. PTFE also yields a fluid coating on both Mg and $KClO_4$ thereby also delaying reaction between $Mg/KClO_4$.
- An orange flame of sparks calls for reaction between TFE and oxygen[11] → (462 kJ).
- $Mg/(C_2F_4)_{n(l)}$ particles are ejected from the combustion zone to finally yield dazzling white exploding sparks (MgF_2 formation) → (510 kJ).

UV-VIS Spectroscopic investigations are in progress to reveal the chemical nature of both the sparks and sustaining reaction.

Table 2 *Calculated thermochemical properties of pyrolant applying NASA CEA.*[9]

Species	Molar fraction (%)
CO_2	30.769
$KF_{(g)}$	16.575
$MgF_{2(g)}$	16.447
Cl	13.932
F	11.788
COF_2	2.570
O_2	2.121
CO	1.692
ClF	1.342
$MgF_{2(l)}$	1.038
$KCl_{(g)}$	0.856
Cl_2	0.687

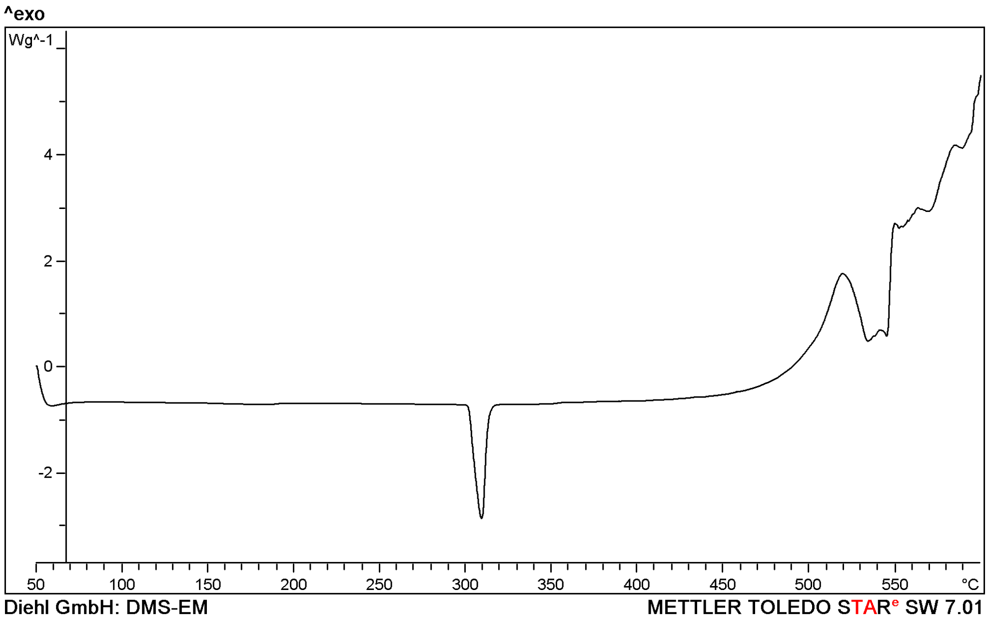

Figure 8. *DSC plot of binary Mg/KClO$_4$.*

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