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# STUDY OF THE THERMAL BEHAVIOURS OF SOME METAL ACRYLATES

W. BALCEROWIAK, J. HETPER, J. BEREŠ and J. OLKOWSKA

*Blachownia Institute of Heavy Organic Synthesis, Kędzierzyn-Koźle, Poland*

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The thermal behaviours of Na, Ca, Mg and Zn acrylates were investigated by TG and DTA. It was found that the anhydrous acrylates were subject to thermal polymerization processes, which preceded the main decomposition. The presence of oxygen influences the decomposition of the organic part of the molecule very strongly, but it does not markedly affect the extent of polymerization or the type of the resulting solid products. Metal carbonates or oxides make up the major proportion of the residue obtained after the decomposition of the metal acrylates, similarly as in the case of other low molecular monocarboxylic acid salts.

Metal salts of low molecular carboxylic acids behave as both organic and inorganic compounds during thermal decomposition. The decomposition of the "organic" part of the molecule is a complex process. It proceeds over a wide temperature range and is highly dependent on the experimental conditions. The composition of the atmosphere in the heated zone is a very important factor. However, dehydration and the final steps of decomposition of these salts proceed in a typical way as do the similar processes of pure inorganic compounds, although the decomposition of acrylates can be hindered by the presence of crack carbon.

Oxalates [1—5], formates [1, 6, 7] and acetates [8] of various metals have often been the subject of thermal analysis. A variety of thermal curves can be found in Liptay's tables [9]. Concise data on the thermal decomposition patterns of these salts have been collected in Duval's monograph [10].

According to Meisel et al. [6], the main decomposition reactions of alkali metal formates are:

$$\begin{array}{l} 2HCOOM \rightarrow M_2CO_3 + CO + H_2 \\ \phantom{2HCOOM} \searrow M_2C_2O_4 + H_2 \end{array}$$

The above reactions are followed by the decomposition the oxalates and carbonates to the metal oxides.

It has been found that the decompositions of Zn, Ni and Co formates give the respective metal oxides directly [10]. Decomposition of the oxalates is accompanied by carbon monoxide and carbon dioxide liberation. The decomposition pattern of the oxalate is highly dependent on the atmosphere in the heated zone [1, 5].

The following reactions can be used to explain the thermal decompositions of acetates, propionates and butyrates [8, 11] in an inert atmosphere:

$$\begin{aligned}
&2\,\mathrm{R-COOM} \rightarrow \mathrm{R-CO-R} + \mathrm{M_2CO_3}\\
&\mathrm{M_2CO_3} \rightarrow \mathrm{M_2O} + \mathrm{CO_2}\\
&2\,\mathrm{R-COOM} \rightarrow \mathrm{M_2CO_3} + \text{saturated and}\\
&\qquad\qquad \text{unsaturated hydrocarbons}\\
&\qquad\qquad \mathrm{H_2,\ CO,\ CO_2,\ C.}
\end{aligned}$$

Endothermic processes are observed over the temperature range 350 – 500° [9]. However, in the presence of oxygen exothermic processes are dominant.

In the present paper the thermal analysis of Na, Mg, Ca and Zn acrylates is described. The thermal behaviours of these compounds and/or of their hydrates are presented, and the influence of the carbon-carbon double bond on the decomposition pattern is discussed.

## Experimental

### *Preparation of acrylates*

Sodium acrylate was prepared by the following method. Concentrated aq. NaOH solution and a 50% aq. solution of acrylic acid were mixed and maintained at 30° for 1 h. A stoichiometric mixture of aq. NaOH and concentrated acrylic acid was then added to the reactor. The precipitate formed was washed with acetone and dried at room temperature.

Calcium, magnesium and zinc acrylates were prepared by the reaction of a 30% aq. solution of acrylic acid with the respective metal oxide. The reaction mixture was heated at 60° to evaporate the excess water. The precipitated salt was washed and dried as above.

### *Preparation of sodium polyacrylate*

Polymerization of sodium acrylate was carried out in a 30% aq. solution in the presence of some redoxytype chain initiator at 30°. The obtained gel was dried and ground.

### *Thermal analysis*

All experiments were carried out using a Mettler TA – 2 instrument, which is able to record TG, DTG and DTA curves simultaneously. 15 mg of the powdered sample was heated in a 0.1 $\mathrm{cm^3}$ Pt crucible over the temperature range 25 to 1000° at a constant heating rate of 6° per min. Controlled dynamic atmospheres of air or argon were used in the furnace.

### *Nuclear magnetic resonance analysis*

A Hitachi Perkin Elmer Instrument (model R 24A) was used for NMR analysis. The samples were dissolved in trifluoroacetic acid and analyzed over the $\delta$ range 0 – 10 ppm.

### *Viscosity measurements*

Viscosities of aqueous solutions of both sodium acrylate and the product of its thermal reaction were measured with the Ubbelohde capillary viscosimeter (Schott, Jena).

## Results and discussion

DTA, TG and DTG curves obtained during the heating of Na, Ca, Mg and Zn acrylates in air are shown in Figs 1–4. The following main thermal processes can be distinguished: (a) dehydration (in the case of hydrates), (b) thermal polymerization, (c) oxidative decomposition and (d) final decomposition of an inorganic residue. These processes will be discussed in sequence.

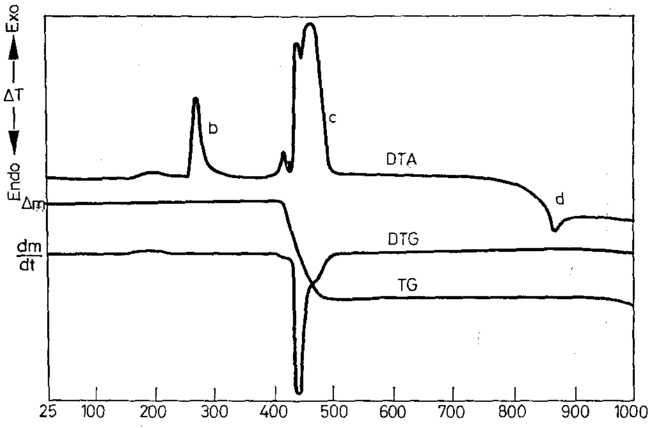

Fig. 1. TG and DTA of sodium acrylate in air

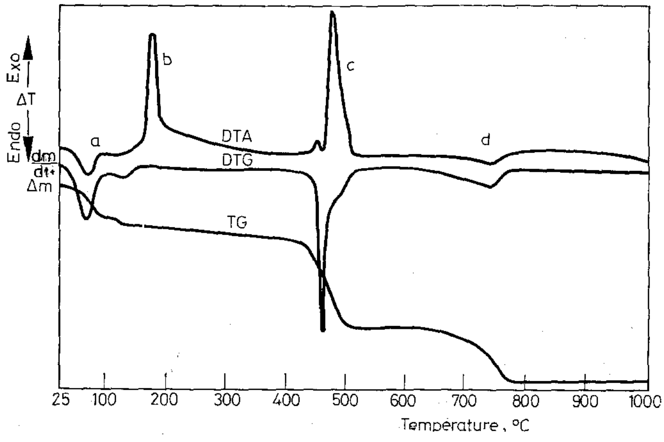

Fig. 2. TG and DTA of calcium acrylate in air

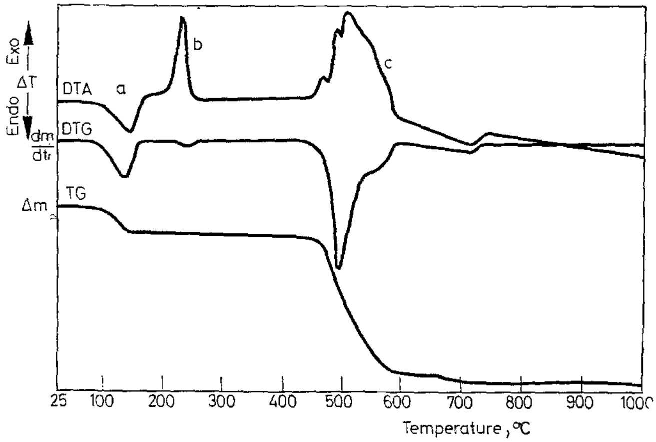

Fig. 3. TG and DTA of magnesium acrylate in air

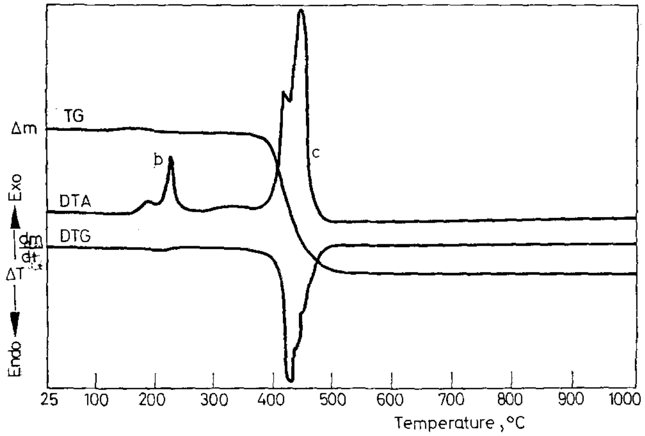

Fig. 4. TG and DTA of zinc acrylate in air

(a) Dehydration

Sodium and zinc acrylates were obtained in anhydrous form, magnesium acrylate in the form of a monohydrate, and calcium acrylate in the form of dihydrate. It is seen in Fig. 3 that a water molecule is liberated from a molecule of magnesium acrylate monohydrate in one-step process at 100–150°. In the case of calcium acrylate dihydrate (Fig. 2), two dehydration steps are observed. In the first step, below 100°, 1.5 moles, and in the second step, above 100°, 0.5 moles of water are liberated.

## (b) Thermal polymerization

In the curves of all the investigated acrylates, a pronounced exothermic peak is observed. Its maximum is located at about 270° for Na acrylate, 230° for Mg and Zn acrylates and 180° for Ca acrylate. The extent of this effect does not exceed 8 kcal/mole. Some additional experiments were made to explain this process. It was established that: (1) the process was not reversible, and (2) the amount of heat emitted was the same in air as in an inert gas atmosphere (Fig. 5). The above observation can only be due to the thermal polymerization of the acrylates.

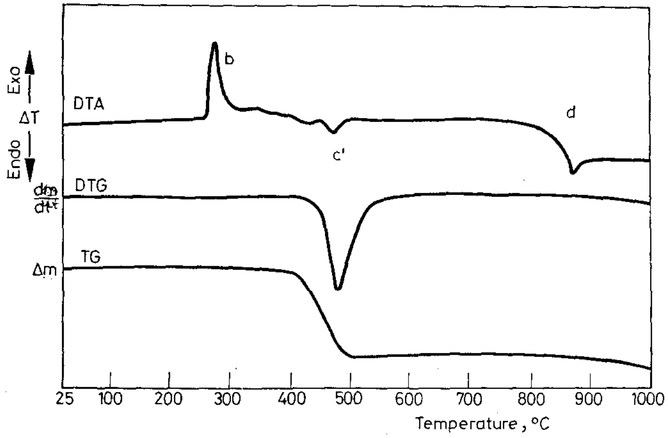

Fig. 5. TG and DTA of sodium acrylate in pure argon

To verify this, a product obtained by heating sodium acrylate at 280° was investigated by using viscosity measurements and NMR. The viscosity level of a 0.5 % aq. solution of this product proved higher by 0.12 cSt than that of a similar solution of freshly prepared acrylate.

The spectrum of the heated acrylate sample showed additional signals at $\delta =$ $= 1-2.7$ ppm, characteristic of a saturated hydrocarbon chain, whereas the spectrum of the parent salt sample showed signals at $\delta = 5.5-6.5$ ppm only (ensuing from the protons of the $CH_2=CH-$ groups).

The ratio of the intensity of the $-CH_2-CH$ signals and the $CH_2=CH-$ signals for a spectrum of heated acrylate was as low as 2.7, indicating that the sample is a short-chain oligomer of sodium acrylate.

The low amount of heat emitted in the effect, and the viscosity levels too are in agreement with this conclusion.

## (c) Oxidative decomposition

The main decomposition tendency of the investigated acrylates on heating in air, is a strong exothermic and complex process at 400–550°. Carbonates or oxides of the metals are essentially the solid decomposition products, although a small amount of crack-carbon is observed too. In an inert atmosphere, e.g. argon, the main decomposition direction is an endothermic one-step process (Fig. 5).

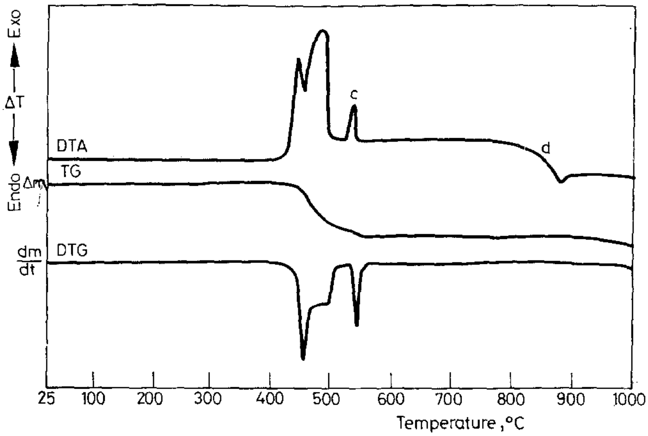

Fig. 6. TG and DTA of sodium polyacrylate in air

Curves of a separately-prepared high molecular sodium polyacrylate (Fig. 6) shows that the decomposition temperature of this polymer is near that observed for the monomer, although the course of this process is slightly different. The absence of the exothermic peak at about 270° in Fig. 6 is noteworthy.

### (d) Final decomposition of the inorganic residue

During the main decomposition step, almost all the organic content of the molecule is liberated in the form of volatile compounds including water and carbon dioxide. At temperatures above 550°, the presence of carbonates in the residue was found in the case of the thermal analysis of Na and Ca acrylates: on the other hand, Mg and Zn oxides were found in the case of the salts of these metals. In the curves of Ca acrylate, the decomposition of $CaCO_3$ was observed as an endothermic process at about 700°. When sodium acrylate was heated the effect of melting of $Na_2CO_3$ was observed. The oxides of Mg and Zn remain unchanged in the range 550–1000°.

## Conclusions

The thermal decompositions of Na, Ca, Mg and Zn acrylates proceed in a similar way as the decompositions of other low molecular monocarboxylic acid salts heated in air or an inert gas atmosphere, in spite of the fact that polymerization processes precede the decompositions of the acrylates.

The main solid products of the thermal reactions of acrylates are either metal carbonates (if stable, e.g. in the case of the Na and Ca salts), or metal oxides (in the case of carbonates which readily decompose, e.g. the Mg or Zn salts). These carbonates are likely to be intermediates in the latter case.

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Résumé — Etude du comportement thermique des acrylates de Na, Ca, Mg et Zn par thermogravimétrie et par analyse thermique différentielle (TG et ATD). On observe que les acrylates anhydres subissent un processus de polymérisation thermique qui précède la décomposition principale. La présence d'oxygène exerce une forte influence sur la décomposition de la partie organique de la molécule mais elle n'affecte pas de manière importante le degré de polymérisation ni la nature des produits solides formés. La majeure partie du produit obtenu après la décomposition des acrylates métalliques est constituée de carbonates et d'oxydes métalliques comme c'est le cas pour les autres sels d'acides monocarboxyliques à faibles poids moléculaires.

Zusammenfassung — Das thermische Verhalten von Na, Ca, Mg und Zn-Akrylaten wurde mittels TG und DTA untersucht. Es wurde festgestellt, daß die wasserfreien Akrylate einen termischen Polymerisierungsprozeß erleiden, der der Hauptzersetzung vorangeht. Die Gegenwart von Sauerstoff wirkt sich sehr stark auf die Zersetzung des organischen Teils des Moleküls aus, beeinflußt jedoch das Ausmaß der Polymerisierung und den Typ der entstandenen festen Produkte nicht besonders. Die bei der Zersetzung von Metallakrylaten erhaltenen Substanzen bestehen größtenteils aus Metallkarbonaten oder -oxiden, analog wie bei anderen Salzen von niedermolekularen Monokarbonsäuren.

Резюме — С помощью TG и ДТА исследовано термическое поведение акрилатов Na, Ca, Mg и Zn. Найдено, что безводные акрилаты подвергаются термической полимеризации, которая предшествует основному разложению. Наличие кислорода оказывает очень сильное влияние на разложение органической части молекулы, но вместе с тем не наблюдалось заметного влияния на степень полимеризации и тип конечных твердых продуктов. Главными составными частями вещества, полученного после разложения акрилатов металлов, являются карбонаты или окислы металлов, подобно тому как это наблюдается в случае других солей низкомолекулярных монокарбоновых кислот.