Thermochimica Acta, 101 (1986) 185–194
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMOANALYSIS OF Ca AND Al ACETYLACETONATES: CATALYTIC STUDY OF THEIR BINARY SYSTEMS WITH $Ba(ClO_4)_2 \cdot 3H_2O$

INSAF HAMID and FADHIL JASIM *

Department of Chemistry, College of Sciences, Baghdad University, Jadiriya, Baghdad (Iraq)

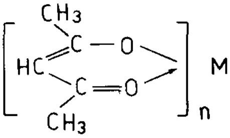
(Received 4 October 1985)

ABSTRACT

The thermoanalytical behaviour of Ca and Al acetylacetonates has been investigated alone and in binary systems with $Ba(ClO_4)_2 \cdot 3H_2O$. Calcium acetylacetonate starts pyrolysis in distinct steps at 205°C forming acetone, acetylacetone and eventually $CaCO_3$ and CaO under static air atmosphere; in N_2 gas a trace of C is also found. Al acetylacetonate suddenly begins melting, vaporisation and partial decomposition at 150°C in rather overlapped steps. Both acetylacetonates catalyse the dehydration of $Ba(ClO_4)_2 \cdot 3H_2O$ as well as the decomposition of the anhydrous $Ba(ClO_4)_2$. The presence of Ba Al_2O_4 has been identified in the final product by X-ray diffractometry which is consistent with the ASTM cards. *n* and *E* for the decomposition of $CaCO_3$ formed are calculated alone and in the presence of $BaCl_2$.

INTRODUCTION

More than 60 metal acetyl acetonates, $(acac)_n^- M^{n+}$ were prepared and their structures investigated and found to be:



$VO(acac)_2$ and $UO_2(acac)_2$ were exceptions. They were used as a source for the preparation of pure metals or oxides which are useful in the electronic manufacturing industry [1]; as a catalyst for oxidative processes and in polymerisation of simple olefins [2], such as polymerisation of ethylene to polyethylene; for coating plastic surfaces for scratch resistance; as colouring agents; as a source for the preparation of some metal acetyl acetonates and

---

* To whom correspondence should be addressed.

heat resistance resins such as those used in the electric insulator industry; as a catalyst, for instance VO(acac)$_2$ was used to increase the production of epoxide in the reaction of allyl alcohol with cumene; as a catalyst in cyclotrimerisation; as a decorator, etc. Alkaline earth acetylacetonates, for instance those of Ca, Mg and Sr, start thermolysis above 150°C, their final residues usually containing their simple oxides. Thermal decomposition data of Al acetylacetonates and congeners are scanty.

25 years ago, careful attention was given to the study of physical and chemical properties of peroxosalts, such as perchlorates and persulfates, since they were considered as an O_2 source and are therefore useful in the preparation of explosives, solid propellants and catalysts. Bansagt and Solymosi and others [3] mentioned that $Ba(ClO_4)_2 \cdot 3H_2O$ loses three H_2O molecules between 60 and 200°C. The anhydrous salt changes its phases at 282 and 357°C respectively and eventually liberates O_2 and $BaCl_2$ through a mechanism suggested in refs. 3 and 4.

The purpose of this and the forthcoming series of papers is (i) to investigate the thermal behaviour of Ca and Al acetylacetonates, alone and in binary mixtures with $Ba(ClO_4)_2 \cdot 3H_2O$ under static air and dynamic nitrogen atmospheres; (ii) to suggest a mechanism for the catalysed reactions; (iii) to calculate some kinetic parameters for the thermal decomposition reactions; (iv) to differentiate qualitatively between the various acetyl acetonates of metals; (v) most of the experimental results are correlated with the thermogravimetric data obtained.

EXPERIMENTAL

All chemicals were of analytical grade. $Ba(ClO_4)_2 \cdot 3H_2O$ was from Hopkin and Williams. All metal acetylacetonates (purum) were from Fluka AG Buchs, α-Al_2O_3 (BDH) was sintered at 1200°C and used as an inert reference material. Sample size was 100 mg and ceramic MOM type crucibles were used for heating. Ultrapure N_2 at a flow rate of 17 ml min^{-1} was used.

The apparatus and procedures employed were as described elsewhere [4].

Behaviour of $Ba(ClO_4)_2 \cdot 3H_2O$

The derivatographic TG, DTG and DTA curves of $Ba(ClO_4)_2 \cdot 3H_2O$ ($= BP \cdot 3H_2O$) are shown in Fig. 1. Calculation from the TG curve indicates that one H_2O molecule is liberated at 100°C [3]. The other two are lost consecutively in overlapping steps ending at 200°C where anhydrous $Ba(ClO_4)_2$ forms, which starts decomposition at 460°C. The XRD pattern (Table 1) confirms the presence of $BaCl_2$ residue at 545°C onward. The

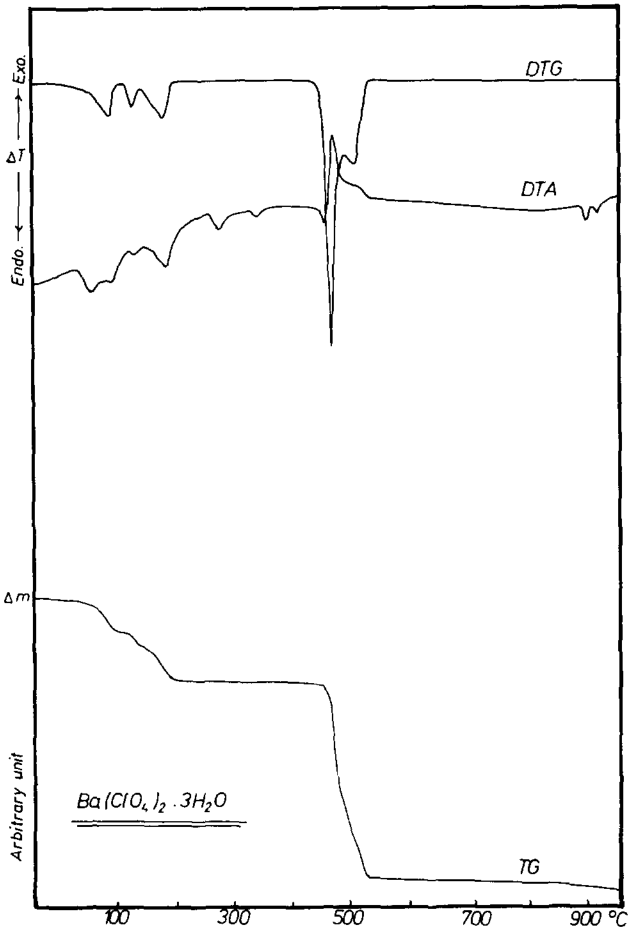


Fig. 1. TG, DTA and DTG curves of barium perchlorate trihydrate.

DTA curve exhibits the typical phase changes for anhydrous $Ba(ClO_4)_2$ at 280 and 350°C. At 915 and 940°C a crystalline phase change and fusion endotherms of $BaCl_2$ are observed which are similar to previous findings [3].

TABLE 1

d-lines for the thermal decomposition residues of barium perchlorate trihydrate heated to 650°C

d (Å)	I/I_0	*d* (Å)	I/I_0	*d* (Å)	I/I_0
5.430	65	2.900	35	2.219	55
4.855	25	2.860	100	2.219	20
4.15	25	2.616	60	2.070	30
4.190	30	2.470	30	1.664	25
4.019	40	2.402	40	1.640	25
3.699	60	2.285	25		

Behaviour of Ca(acac)$_2$

Figure 2 displays the TG and DTA curves of calcium acetylacetonate, Ca(acac)$_2$, in air and N_2 atmospheres. A careful scrutiny of the TG curve infers a slow mass loss of 2 mg due to expulsion of moisture and volatile impurities. Between 205 and 292°C, a further mass loss of 22 mg, which is equivalent to evolution of one mole of acetone is determined. Thereafter one mole of acetylacetone is expelled. The residue left in the crucible at 585°C, as confirmed by chemical analysis and X-ray patterns, is found to be $CaCO_3$. Note that the plateau of $CaCO_3$ is formed in N_2 at earlier temperatures than in air, and it is longer. No explanation could be offered for this. $CaCO_3$ begins decomposition at 670°C. At 810°C CaO and a trace of amorphous charcoal are identified in the crucible. The rather sharp exothermic peak on the DTA curve is attributed to the air oxidation (secondary reaction) or $CO \rightarrow CO_2$ formed by partial combustion of the evolved acetone. The next broad flat peak is due to the prompt combustion of the evolved acetylacetone. In N_2 gas, the two exothermic peaks disappear

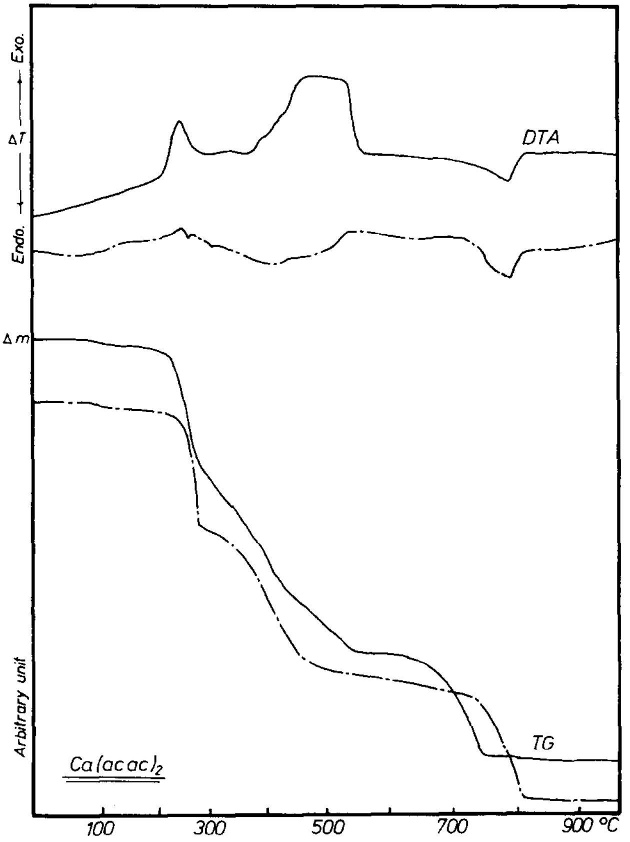


Fig. 2. TG and DTA curves of calcium(II) acetylacetonate: (———) in air; (- — -) in N_2.

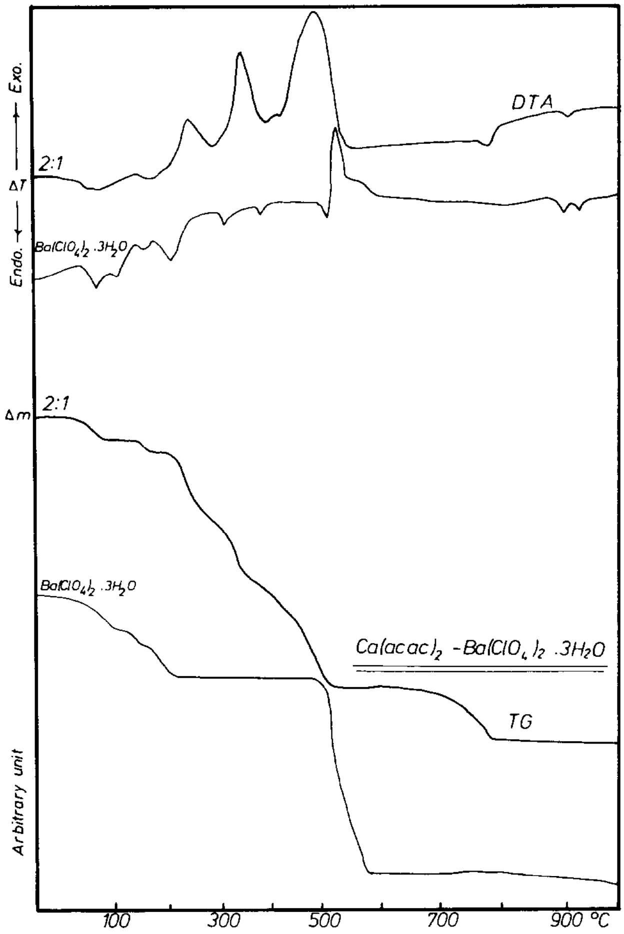


Fig. 3. TG and DTA curves of calcium(II) acetylacetonate–barium perchlorate trihydrate mixture.

indicating that no air oxidation of the organic, carbon and hydrogen gaseous products takes place. Computation shows that the weight of CaO is about 5 wt.% less than the actual weight indicated by running the instrument under air. This extra weight is found to be due to the accumulation of free carbon inside the ceramic crucible. The broad endotherm at 810°C is attributed to the slow decomposition of $CaCO_3$ formed under either atmosphere.

Behaviour of $Ca(acac)_2$–$Ba(ClO_4)_2 \cdot 3H_2O$ system

Figure 3 depicts TG and DTA curves for 2 : 1 $Ca(acac)_2$: $BP \cdot 3H_2O$ which is the highest mole ratio where it is possible to avoid explosive reactions caused by the catalytic thermal decomposition of the reactants. Computation from TG curves infers that the expulsion temperature for the second H_2O molecule is lowered through the catalytic activity effect of

Ca(acac)$_2$ and it escaped together with the first H_2O molecule between 55 and 87°C. The temperature loss of the second half of the second H_2O molecule is lowered by 58°C. The third H_2O molecule is lost between 145 and 173°C, and therefore the catalytic lowering is determined to be 26°C. Also calculation from the TG curve infers that the T_i of anhydrous BP is catalytically lowered by about 150°C (from 460 to 310°C). The large exotherm on the DTA curve represents a loss of 3(O_2) and the consequent formation of Ba(ClO)$_2$ which decomposes between 380 and 408°C yielding $BaCl_2$ and O_2. The typical phase change endotherm of $BaCl_2$ is shifted to 888°C.

Determination of n *and* E *for $CaCO_3$ decomposition*

The reaction order, n, and activation energy, E, for the decomposition of $CaCO_3$ formed from individual Ca(acac)$_2$ or as a binary system with $BP \cdot 3H_2O$ are calculated from the corresponding TG and DTG curves (Figs. 2 and 3) [5,6]. The decomposition is found to be of the first order (Table 2) and the formation of $BaCl_2$ lowers the E value.

Ca(acac)$_2$ starts decomposition at 207°C as though it was alone in the crucible. It is eventually converted to $CaCO_3$ at 500°C. At 655°C a mass loss of 9.2 wt.% occurs, which is equivalent to the liberation of CO_2. The only exception is the sharpening of the second exothermic peak due to rapid combustion of gaseous organic products which is brought about by excessive amounts of early decomposition of $Ba(ClO_4)_2$. The exothermicity of the reacting binary system is shown by enlargement of the three exotherms appearing in the upper DTA curve of 2 : 1 ratio. The horizontal plateau of $Ba(ClO_4)_2$ between 210 and 460°C as well as the phase change endotherms which have not yet disappeared completely in the presence of Ca(acac)$_2$ due to the catalytic activity of the latter should be noted. Lower molar ratios lead to highly explosive thermal reactions accompanied by huge energetic gaseous products, so one should deal cautiously with experiments to avoid tragic events!

TABLE 2

Values of n and E for the thermal decomposition of $CaCO_3$ by-product alone and in the presence of $BaCl_2$

Parameter	$CaCO_3$		$CaCO_3 + BaCl_2$	
	F–C [a]	C–R [b]	F–C [a]	C–R [b]
n	0.987	1	1.06	1
E (kJ mol^{-1})	275.43	279.15	211.5	236.5

[a] F–C = Freeman–Carroll [6].

[b] C–R = Coats–Redfern [5].

Behaviour of Al(acac)$_3$

Experiments have shown that Al(acac)$_3$ under static air atmosphere is thermally stable up to 150°C, then it volatilises and partially decomposes. The TG curve, which is identical in air or nitrogen (Fig. 4) shows a mass loss of 2 mg (due to moisture and volatile impurity of unknown nature) followed by a sudden and continuous loss of 90 mg between 150 and 292°C. However, the DTA curve reveals a small endotherm whose $T_{\max}$ is 184°C representing the melting of aluminium acetylacetonate, Al(acac)$_3$. Next comes a small decomposition endotherm followed by a broad combustion exotherm due to slow burning of a carbon trace. Nevertheless, under N_2 gas, this combustion exotherm disappears because of the absence of air oxidation. The final product (tiny amount) is a white crystalline powder which is identified to be α-Al_2O_3.

In N_2 gas the two small endotherms that belong to melting and volatilisation (including partial decomposition) become more distinguished as com-

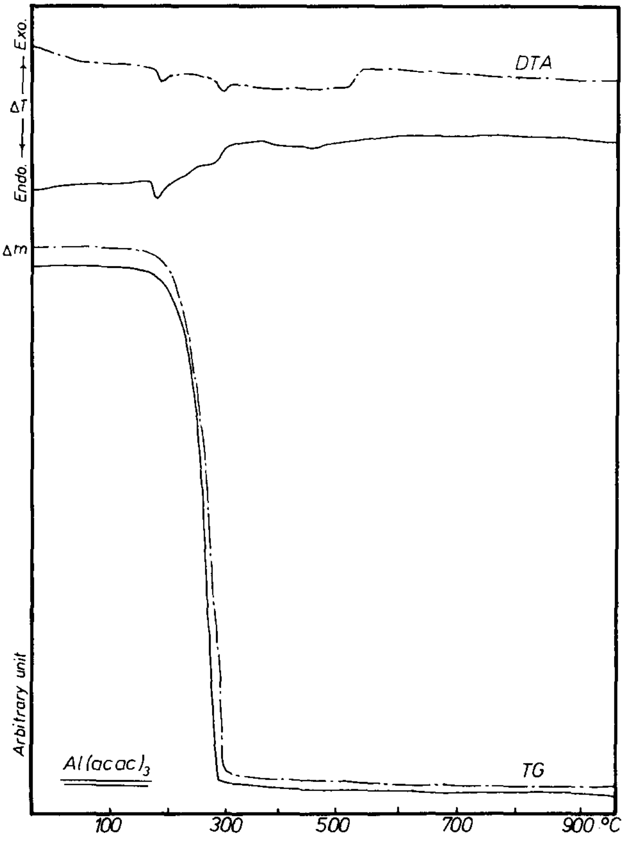
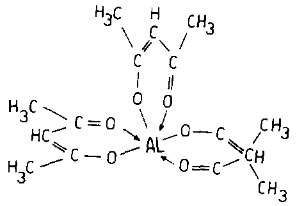


Fig. 4. TG and DTA curves of aluminium(III) acetyl acetonate: (———) in air; (- — -) in N_2.

pared with air, and have inflection peaks at 190 and 298°C, respectively. Comparing the two TG curves, it seems that in N_2 gas the temperatures of volatilisation, melting, etc., are shifted to higher values.

Behaviour of Al(acac)₃–Ba(ClO₄)₂ · 3H₂O system



The TG and DTA curves for the 1 : 1 $Al(acac)_3$: $BP \cdot 3H_2O$ and 2 : 1 $Al(acac)_3$:$BP \cdot 3H_2O$ under air and N_2 are displayed in Fig. 5, from which it appears that $Al(acac)_3$ in 1 : 1 ratio could catalytically lower the temperature of elimination of the second H_2O molecule (together with the first) between 55 and 90°C, that is by a difference of 55°C for the second half of the second H_2O molecule. The third H_2O molecule is lost between 140 and 173°C (a difference of 27°C) resulting in the formation of anhydrous $Ba(ClO_4)$. The onset temperature for the stepwise decomposition of the latter is also lowered catalytically from 460 to 280°C with subsequent formation of $BaCl_2$ as final product. As for the 2 : 1 ratio the first $1\frac{1}{2}$ H_2O are lost between 55 and 80°C (a difference of 65°C) for the second half of the second H_2O. The remaining $1\frac{1}{2}$ H_2O are lost between 140 and 175°C (a difference of 25°C). The $Ba(ClO_4)_2$ thus formed is then decomposed before 280°C. This is because the steps of losing the first O_2 and that of volatilisation of $Al(acac)_3$ overlap. It is worth mentioning that the two typical phase change of $Ba(ClO_4)_2$ in both molar ratios have disappeared; this is attributed to the promoting catalytic effect of $Al(acac)_3$ to lower the activation energy of the anhydrous salt. X-ray diffraction of the final products for both molar ratios confirms the presence of the bright *d*-lines of $BaCl_2$ and also of the mixed oxide, $BaAl_2O_4$. An inference from the latter that around 500°C, part of $BaCl_2$ reacts with α-Al_2O_3 formed according to the solid-state reaction

$$Al_2O_3 + BaCl_2 \rightarrow BaAl_2O_4 + ACl_2$$

Compare ASTM Card Nos. 17–306. The peak at the inflection points of the DTA curve approved the validity of such a reaction. The unreacted (excess) $BaCl_2$ for both ratios is indicated by its typical endotherm at about 900°C. Nevertheless, the XRD lines obtained with the 2 : 1 ratio are brighter than those obtained with the 1 : 1 ratio. In the meantime it is observed that some

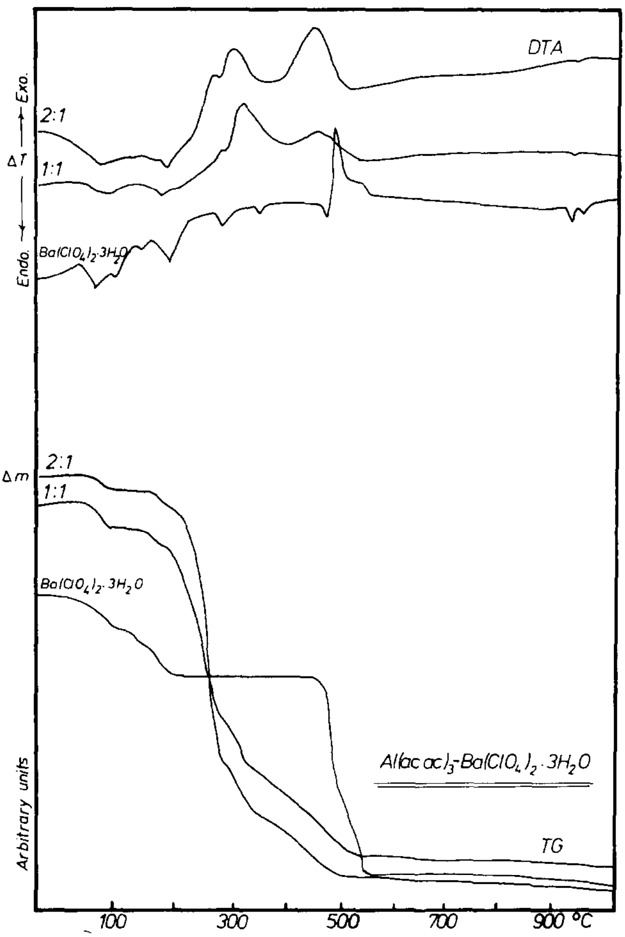


Fig. 5. TG and DTA curves of aluminium(III) acetyl acetonate–barium perchlorate trihydrate mixture.

of the bright lines of $BaCl_2$ have disappeared; this suggests that the 2 : 1 ratio is more stoichiometric than the 1 : 1.

CONCLUSIONS

Comparing the thermoanalytical behaviour of both compounds alone or in binary molar ratios, it seems that factors such as steric hindrance, Van der Waals forces, electron density and number of resonating structures play important roles in their thermal stability. We are of the impression that the Van der Waals forces between the $Al(acac)_3$ are weaker than those between $Ca(acac)_2$ molecules since the former volatilises at lower temperatures and with meagre decomposition. Since the higher the number of resonating structures of a compound the more stable it is, it is to be concluded that $Ca(acac)_2$ has more resonating structures than $Al(acac)_3$.

Therefore not only can acetyl acetonates act as catalysts in solution but also in the solid state high temperatures reactions.

REFERENCES

1 L.M. Legasova and M.M. Pushik, Tr. Mosk. Inst. Inzh. Zheleznodorozhn. Transp., (1979) 652.
2 Chem. Abstr., 94 (1981) 122618u, 156015k, 155970f.
3 T. Bansagt and F. Solymosi, J. Therm. Anal., 16 (1979) 137.
4 R.M. Al-Shukry and F. Jasim, Thermochim. Acta, 37 (1980) 97; K.R. Idan and F. Jasim, Thermochim. Acta, 39 (1980) 277.
5 A.W. Coats and J.P. Redfern, Analyst, 88 (1963) 906; Nature (London), 201 (1964) 68.
6 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.