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THERMOANALYSIS AND CATALYTIC STUDY OF TRANSITION METALS ACETYLACETONATES

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ABSTRACT

The T, TG, DTG, and DTA curves of eight transition metals acetylacetonates, namely, those of Cr(II), Co(II), Cu(II), Fe(III), Mn(II), Ni(II), V(III) and VO(III) have been studied under air static and inert dynamic nitrogen or argon gases. Under the letter, their decomposition temperatures were increased by about 30-50 C. Their roles as promoting catalysts for the thermal decomposition of barium perchlorate trihydrate ($BP.3H_2O$) have been investigated as well as the kinetic parameters, such as n, E, and log Z, of the decomposition of them. Evolved gaseous products (methane, acetylacetone, carbon dioxide and water) have been detected by GC. Solid intermediates and final products have been identified by XRD methods. Eight DTG and eight DTA curves (Figures 1 and 2) have been established to characterise each of the above metals acetylacetonates.

INTRODUCTION

More than 60 metal acetylacetonates, $M(acac)_n$, were prepared and their structures carefully determined [1-7]. Their industrial applications are enormous [8]. Thermoanalytical investigations of transition metals acetylacetonates are so far considered scanity, therefore, it is thought worthwhile to study them.

MEASURING METHODS

The eight metals acetylacetonates were from Fluka AG, Buchs. Apparatus, procdures and techniques were as previously described [9]. Analysis of gaseous products was conducted with an automatic laboratory chromatographic analyser.

RESULTS AND DISCUSSION

$VO(acac)_2$: It partially volatilises and disproportionates between 170-288 °C forming acetyl acetone and unknown aldehyde. Between 288-426° the rest of the sample together with the gaseous intermediates were combusted to form CO_2 and H_2O. Under inert gases both acetylacetone and aldehyde formed. The resulting V_2O_5 is subsequently decomposed into VO_2 and O_2. Where as under inert gases acetone and aldehyde formed; and beyond 550°, VO_2, O_2 and amorphous carbon were obtained.

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occurred with the formation of acetylacetone and $VO(acac)_2$. Another acetylacetone was splitted between 313-480°. Afterwards, VO_2 and O_2 were obtained. Under inert atmosphere amorphous carbon in addition to the last two substances was detected.

$\underline{Cr(acac)_3}$: Rapid melting and volatilisation (with minor decomposition) of the substance took place between 180-330°. Between 355-375° combustion occurred for the rest of the non-volatiles $Cr(acac)_3$; in inert gases volatilisation delayed (200°) due to absence of O_2.

$\underline{Mn(acac)_2}$: Between 185-255° melting and disproportionation occurred with the formation of acetone plus unknown species. One acetylacetone was lost between 255-492° followed by the combustion of organic matters and therefore the formation of H_2O, CO_2 and Mn_2O_3. Under inert atmosphere amorphous carbon in addition to the last-named products were detected.

$\underline{Fe(acac)_3}$: CH_4 liberated between 130-170°. One acetylacetone and one acetone were lost between 170-232° and 232-332° respectively. Fe_2O_3 residue was finally identified. Under inert atmospheres stability of $Fe(acac)_3$ was increased by 30°. After melting, T_{max} = = 181°, two acetylacetones and one acetadehyde evolved at 181-335 and 335-755° respectively, which then burnt to form H_2O and CO_2. The free iron eventually formed is reoxidised into Fe_2O_3.

$\underline{Co(acac)_2}$: Partial volatilisation occurred before melting (at 160°) between 55-130°. Then one acetylacetone and one acetone liberated (170-325°). Between 325-440° the rest of $Co(acac)_2$ burntout leaving CO_2, H_2O and Co_3O_4 which decomposes after 870° giving CoO and O_2. In inert gases similar products were identified in addition to free Co and amorphous carbon.

$\underline{Ni(acac)_2}$: One molecule acetone was lost between 220-307°. One acetylacetone and one acetadehyde were expelled between 242-500° with simultaneous combustion and formation of CO_2, H_2O and NiO, which on futher heating was oxidised into Ni_2O_3. Under inert atmosphere acetylacetone was not liberated and partial decomposition of NiO into Ni and O_2 as well as free carbon was observed.

$\underline{Cu(acac)_2}$: Simulataneous melting, volatilisation, and decomposition occurred between 205-294°. About 20 wt. % of sample escaped without pyrolysis. The reaction was violent and difficult to

recognise. Cu_2O was left. Under inert atmosphere free Cu was detected in addition to Cu_2O. It is worth-noting that volatilisation took place with melting of $Cu(acac)_2$.

Catalytic study: Various molar ratios of the binary systems, $M(acac)_n$: BP.$3H_2O$, were prepared. Each of the 8 metals acetylacetonates could catalytically lower the temperatures of decomposition of ($3H_2O$) and of the anhydrous BP thus formed (Table 1). A mechanism is proposed for this catalytic lowering of the (T_i) temperatures based on the fact that the thermally liberatid M_2O and BaO are adsorbed on the surfaces of the acetylacetonates molecules whereby lowering their activation energies causing disruption of their bonds.

Table 1

$M(acac)_n$	Ti lowering, °C	
	$3H_2O$	BP
$VO(acac)_2$	85	290
$V(acac)_3$	57	295
$Cr(acac)_3$	35	265
$Mn(acac)_2$	65	268
$Fe(acac)_3$	65	328
$Co(acac)_2$	65	270
$Ni(acac)_2$	43	270
$Cu(acac)_2$	58	235

Kinetic study: The thermokinetic parameters (n, E_a, and log Z) have been determined from TG and DTG curves for BP decomposition in the presence of $Ni(acac)_2$ and $VO(acac)_2$ using Coats-Redfernand Freemann-Carroll [10-11]. The results are summerised in Tables 2 and 3 which they also show that the E_a for the decomposition of BP has been reduced by about 3 folds.

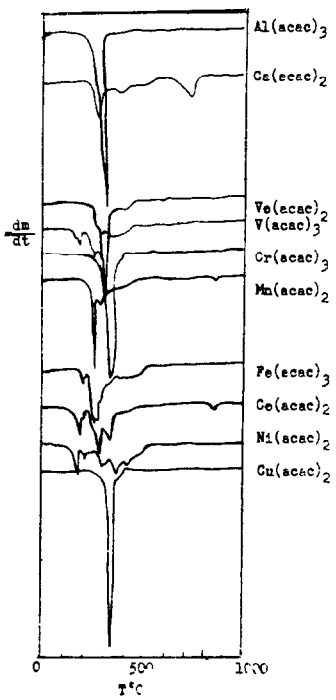

Fig. 1. DTG curves of metal acetylacetonates in air

Table 2

Kinetic parameter	1:1::Ni(acac):BP
Ea, KJ mol^{-1}	93.8
Log Z	3.2
n	1.4

Table 3

Kinetic parameter	1:1::$VO(acac)_2$:BP
Ea, KJ mol^{-1}	89.5
Log Z	2.9
n	1.0

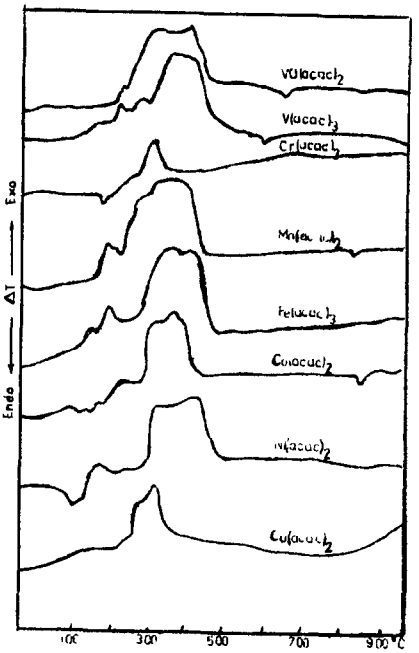

Fig. 2. DTA curved of metals acetylacetonates in air

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