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THERMAL DECOMPOSITION OF THE BIGUANIDE COMPLEXES OF THE 3d-TRANSITION METALS

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ABSTRACT

The thermal decomposition (TG, DTG and DTA) of the complexes of biguanide with the following metals was studied: V, Cr, Mn, Co, Ni, Cu and Zn. Structural water, when present, is first eliminated at ~100–150°C; this is followed by a main decomposition stage at ~300–350°C. Pyrolytic residues are analysed and characterised by their x-ray powder diffraction patterns and are found to be the oxides V_2O_5, Cr_2O_3, Mn_3O_4, Co_3O_4, NiO, CuO and ZnO, respectively. The decomposition curves of the free ligand (biguanide) and biguanide sulphate are also given. The decomposition characteristics are discussed.

INTRODUCTION

Considerable work has been carried out on metal biguanide complexes, mainly by Ray and coworkers[1]. This earlier work was mainly concerned with detailed preparative aspects as well as studies of properties such as magnetic susceptibilities, conductance measurements, etc., and structure assignments based on these. Interest in these complexes seems to have somewhat abated after this exhaustive study of the Ray group. Recently, Skabo and Smith[2] have made a brief study of the reflectance spectra and infrared spectra of the biguanide complexes of Cr, Co and Cu, in order to settle the question of the formulation of these complexes.

In the present communication, we wish to report the results of our studies on the thermal decomposition (TG and DTA) of the biguanide complexes of the 3d-transition metals; this aspect of the metal biguanide complexes has not previously been studied, except for a brief mention of a copper biguanide complex[3]. A search through the literature revealed that biguanide complexes of Sc, Ti and Fe do not seem to have been so far prepared, while those of the remaining 3d-transition metals (V, Cr, Mn, Co, Ni, Cu and Zn) have all been prepared and well characterised. The present studies are confined to these known complexes, although attempts are in progress in our laboratories to prepare the biguanide complexes of Sc, Ti and Fe as well as those of the lanthanide elements.

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EXPERIMENTAL

Reagents

Biguanide

Biguanide sulphate was prepared by heating an intimate mixture of dicyandiamide and ammonium chloride, according to Bamberger and Dickmann[4]. Pure biguanide was prepared, when necessary from biguanide sulphate by the procedure of Slotta and Tschesche[5]. The purity of the biguanide sulphate was checked by elemental analysis for nitrogen and by a melting point determination (m.pt. found 233°C; m.pt. from literature 231–232°C).

Complexes

Complexes of biguanide with V, Cr, Mn, Co, Ni, Cu and Zn were prepared by known methods[1]. Conditions were chosen so that the complex bases ($ML_n \cdot xH_2O$) were obtained ($L = C_2N_5H_6$). The compositions were confirmed by elemental analyses for the metal and nitrogen. The formulae of the complexes and their physical characteristics are as follows: $VOL_2 \cdot H_2O$ (green powder, crystalline*); $CrL_3 \cdot H_2O$ (dark-red crystals); $Mn_2L_4(OH)_2 \cdot H_2O$ (dark-chocolate crystals); $CoL_3 \cdot 2H_2O$ (red crystals); $NiL_2 \cdot 2H_2O$ (yellow powder, crystalline*); $CuL_2 \cdot 2H_2O$ (rose-red crystals) and ZnL_2 (white powder, crystalline*)

Thermal decomposition studies

In addition to the studies on the complexes mentioned above, the thermal behaviour of ($LH \cdot H_2SO_4 \cdot H_2O$) and free biguanide (LH) was also studied. TG and DTA studies were carried out in an atmosphere of static air. The instrument used was a Stanton recording thermobalance, model TR-01. The heating rate and other characteristics are given below: heating rate, 4°C per minute; chart speed, 3 inches per hour; crucible (DTA), Pt; reference substance (DTA), alumina.

Pyrolysis

The final decomposition residue in air was examined in each case by separate pyrolysis experiments. For obtaining these pyrolytic residues, samples were taken in silica crucibles and were heated to ~800°C for 2 hours. In a few parallel experiments, samples were taken in porcelain boats and were placed in combustion tubes and were heated to ~800°C in a slow current of pre-dried air.

X-ray powder diffraction patterns

The x-ray powder patterns of the pyrolytic residues were taken using a Philips Debye–Scherrer Powder Camera with a diameter 57.3 mm. Cu Kα radiation was employed. The *d* spacings computed from the patterns were compared with standard

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*As revealed from x-ray powder diffraction patterns.

values taken from the data file of ASTM[6]. Comparisons were made by calculating the *d* spacings for the three most intense lines in the spectrum[7].

RESULTS

Thermal decomposition

Instrumental DTA curves were drawn as such, whereas in the case of TG, the usual TG curves (mass vs. time) as well as the differential (DTG) curves (rate of loss of mass vs. time) were drawn. The positions of the peaks in DTA and the inflections in TG (or peaks in DTG) as well as the plateaus (stability ranges) in TG are listed in Table 1. Results of separate pyrolytic experiments are given in Table 2. Typical curves are given in Fig. 1. The data from the x-ray powder patterns of two typical pyrolytic residues (Ni and Zn oxides) and comparison with standard data are given in Table 3.

TABLE 1

PEAKS AND PLATEAUS IN TG, DTG AND DTA CURVES

Substance	*Peaks in DTA*[a] (°C)	*Peaks in DTG*[a] (°C)	*Stability range in TG* (°C)
Vanadyl biguanide	160 endo w	170 s	upto 125
	190 endo w	210 w	after 450
	245 exo w	250 s	
	340 endo m	350 s	
	395 exo vs	395 s	
Chromium biguanide	100 endo w	100 w	upto 50
	290 endo w	285 w	400 onwards
	350 exo s	335 s	
	420 exo w		
Manganese biguanide	85 endo w	90 w	upto 75
	250 endo s	310 (sh) m	400 onwards
	315 endo w	330 s	
	440 endo vs		
Cobalt biguanide	170 endo w	160 w	upto 85
	290 endo m	280 vs	after 475
	370 exo s	365 s	
	450 exo vs	400 s	
Nickel biguanide	125 endo w	120 (m)	upto 100
	175 exo w	295 vs	400 onwards
	295 endo m (broad)		
	405 exo w		
	480 endo s		
Copper biguanide	125 endo w	100 w	upto 105
	190 exo w	210 vs	400 onwards
	250 endo w (sh)	300 vs	
	325 endo s		
	340 endo m (sh)		
	500 endo vs		

(Continued on p. 274)

TABLE 1 *(continued)*

Substance	*Peaks in DTA*[a] (°C)	*Peaks in DTG*[a] (°C)	*Stability range in TG* (°C)
Zinc biguanide	260 endo s	270 (sh) m	upto 225
	320 endo w	290 s	590 onwards
	375 endo m	355 w	
	340 exo m	445 w	
	395 exo s	550 vs	
	520 exo vs		
Big·SO_4	135 endo m	120 m	upto 100
($LH \cdot H_2SO_4 \cdot H_2O$)	235 endo s (narrow)		140–200
	280 endo w	270 s	
	350 endo m	310 s	
Biguanide	177 endo s	190 s	stable upto 50
(free base)	355 endo w	340 m	275–325
(LH)	400 exo w		
	470 exo w (broad)		
	520 exo w		

[a] Abbreviations: exo = exothermic; endo = endothermic; w = weak; s = strong; m = medium; vs = very strong; sh = shoulder.

TABLE 2

PYROLYSIS DATA

Substance	*% loss of mass* at first stage (from TG data)	*% loss of mass* at first stage (calculated)	*% loss of mass* on heating in air to 800°C	*% loss of mass* at final stage (from TG data)	*probable pyrolytic residue*	*% loss of mass*[a] (theoretical)	*% deviation (cf. cols. 4 and 7)*
(1)	*(2)*	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*
Vanadyl biguanide	3.2	6.3	69.0	68.7	V_2O_5	68.1	+1.3
Chromium biguanide	10.0	4.9	80.5	77.1	Cr_2O_3	79.5	+1.3
Manganese biguanide	3.1	3.2	74.8	74.7	Mn_3O_4	73.0	+2.4
Cobalt biguanide	6.4	10.0	77.6	76.7	Co_3O_4	79.7	−2.6
Nickel biguanide	12.2	12.2	75.3	75.4	NiO	74.7	+0.8
Copper biguanide	4.0	13.7	70.3	71.1	CuO	73.4	−3.9
Zinc biguanide	—	—	70.1	68.6	ZnO	69.3	+1.2

[a] Calculated on the assumption that the final pyrolytic residues are the same as those given in column No. 6.

TABLE 3
X-RAY POWDER DIFFRACTION DATA

Pyrolytic residue	*Diffraction angles observed*	*Intensity order*		*d spacings (Å)*	
		observed	*from ASTM data file*	*calculated from observed values*	*from ASTM data file*
NiO	18°30′	2	2	2.43	2.41
	21°22′	1	1	2.11	2.09
	31°22′	3	3	1.48	1.48
ZnO	16°0′	2	2	2.80	2.82
	17°7′	3	3	2.62	2.60
	18°0′	1	1	2.50	2.48

DISCUSSION

A search through the literature showed that the only biguanide complex whose thermal behaviour had been earlier studied seems to be a copper biguanide sulphate, $(CuL_2)\cdot H_2SO_4\cdot 3H_2O$; but here only the TG (and not DTA) was studied[3]. It is reported that this compound begins to lose water at 40 °C and that the anhydrous salt is stable between 94 and 146 °C. A complicated mechanism, involving the intermediate formation of CuS and ultimate conversion to CuO (from 833 °C onwards) was postulated. The present studies on the related complex $CuL_2\cdot 2H_2O$ show that structural water is eliminated at 100–125 °C; this is followed by endothermic decomposition stages at 190–210 °C and at 250–300 °C and the attainment of steady mass conditions at 400 °C onwards, corresponding to the formation of CuO.

It may be seen from Table 1 that all the complexes except that of Zn begin to decompose at ~100 °C; the Zn complex begins to decompose only at ~225 °C. This could be attributed to the fact that only the Zn biguanide complex is anhydrous, whereas the other complexes are all hydrated; the decompositions at ~100 °C correspond to loss of water. It is interesting to note that while the other complexes begin to show the final TG plateaus at ~400–450 °C, Zn biguanide complex shows this plateau only at ~600 °C.

It has been noted that while the TG curve is most useful for quantitative correlations, comparative studies are best made using the differential curves DTG and DTA, which have higher resolution compared to TG[8]. In the present case, it may be seen from Table 1 that there is a close correspondence between the DTG and DTA peaks in most cases. This clearly shows that in these decompositions, most of the processes which involve change in enthalpy are also processes accompanied by loss of mass. The first endothermic peaks at ~100–150 °C could correspond to loss of structural water; the fact that this peak is absent in both the DTA and DTG curves of Zn complex which does not contain structural water, lends further credence to this view.

Another striking characteristic shown by all the complexes studied is an endothermic DTA peak at ~300–350°C, which has a close parallel peak in DTG. These peak temperatures for DTA and DTG, respectively, are 340 and 350°C for V, 290 and 285°C for Cr, 315 and 335°C for Mn, 290 and 280°C for Co, 295 and 295°C

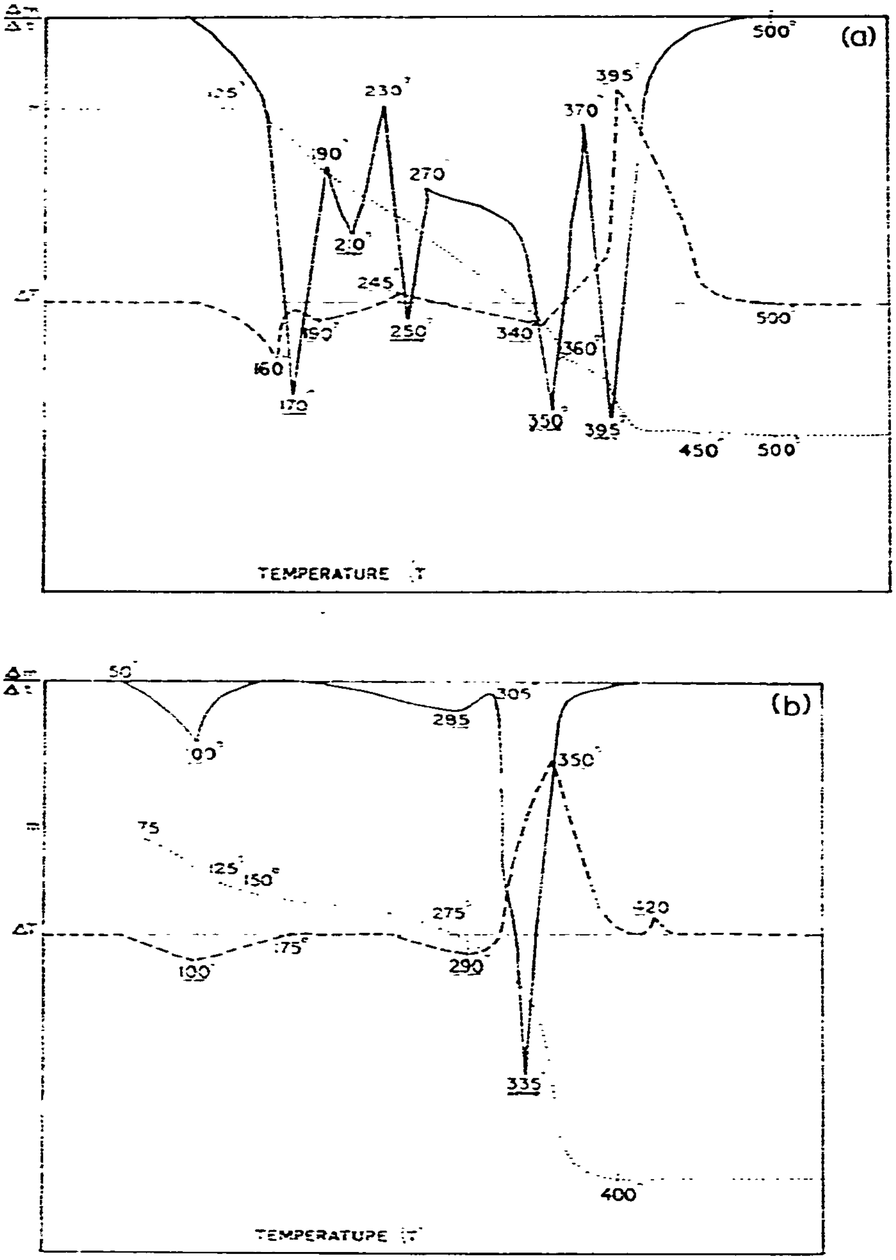


Fig. 1. Thermal decomposition of (a) $VOL_2 \cdot H_2O$ ($L = C_2N_5H_6$ —; LH = biguanide, $C_2N_5H_7$), (b) $CrL_3 \cdot H_2O$, (c) $Mn_2L_4(OH)_2 \cdot H_2O$, (d) $CoL_3 \cdot 2H_2O$, (e) $NiL_2 \cdot 2H_2O$, (f) $CuL_2 \cdot 2H_2O$, (g) ZnL_2, (h) $LH \cdot H_2SO_4 \cdot H_2O$, and (i) LH. (——) DTG curve, (— —) DTA curve, and (····) TG curve.

for Ni, 325 and 300°C for Cu and 375 and 355°C for Zn. These temperatures could correspond to a major stage in decomposition.

It is interesting to note that corresponding endothermic peaks are observed also in the curves for biguanide sulphate and free biguanide. The peak temperatures for DTA and DTG, respectively, are 350 and 310°C for biguanide sulphate and 355 and 340°C for free biguanide. The occurrence of these peak temperatures for the

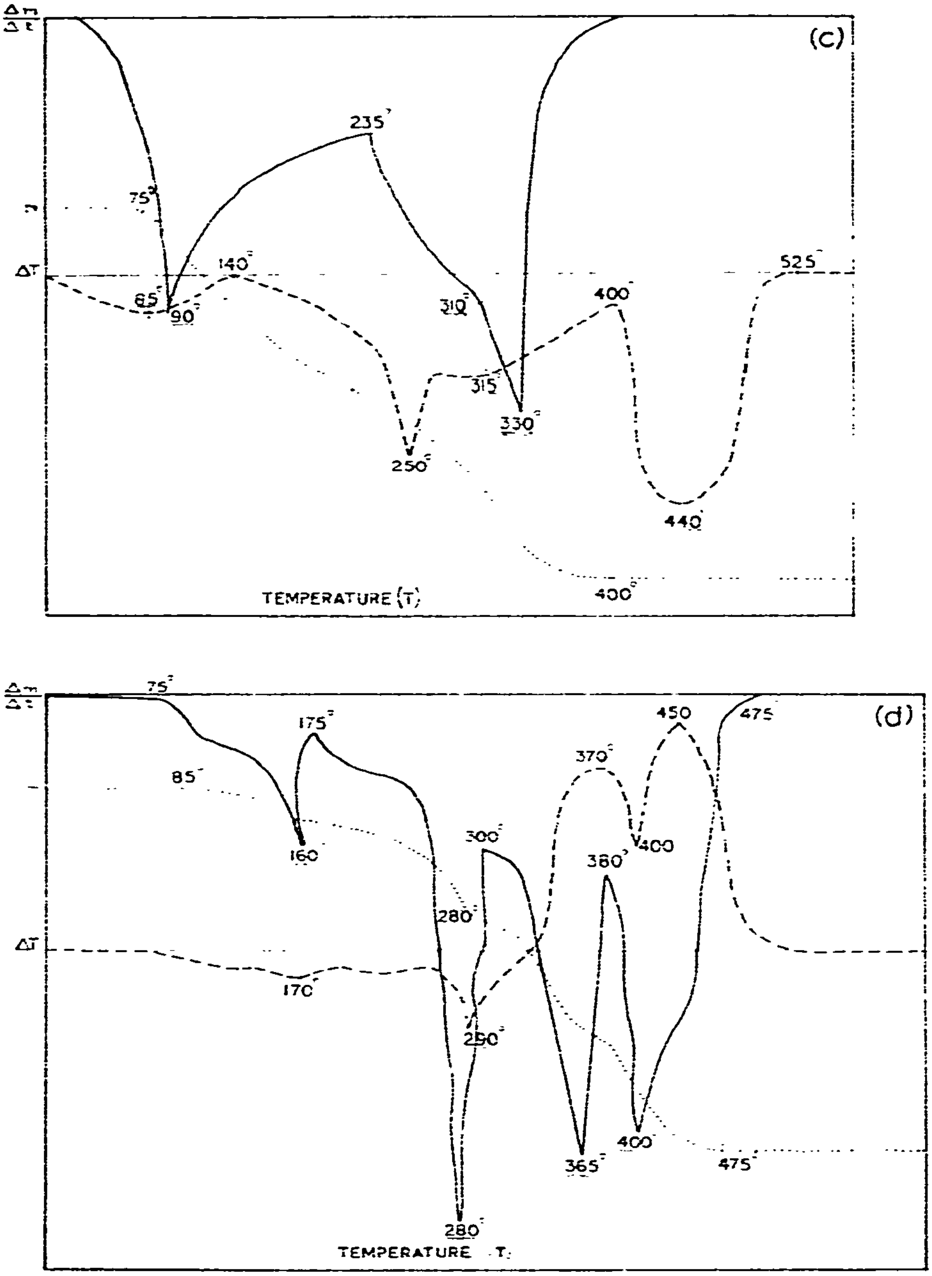
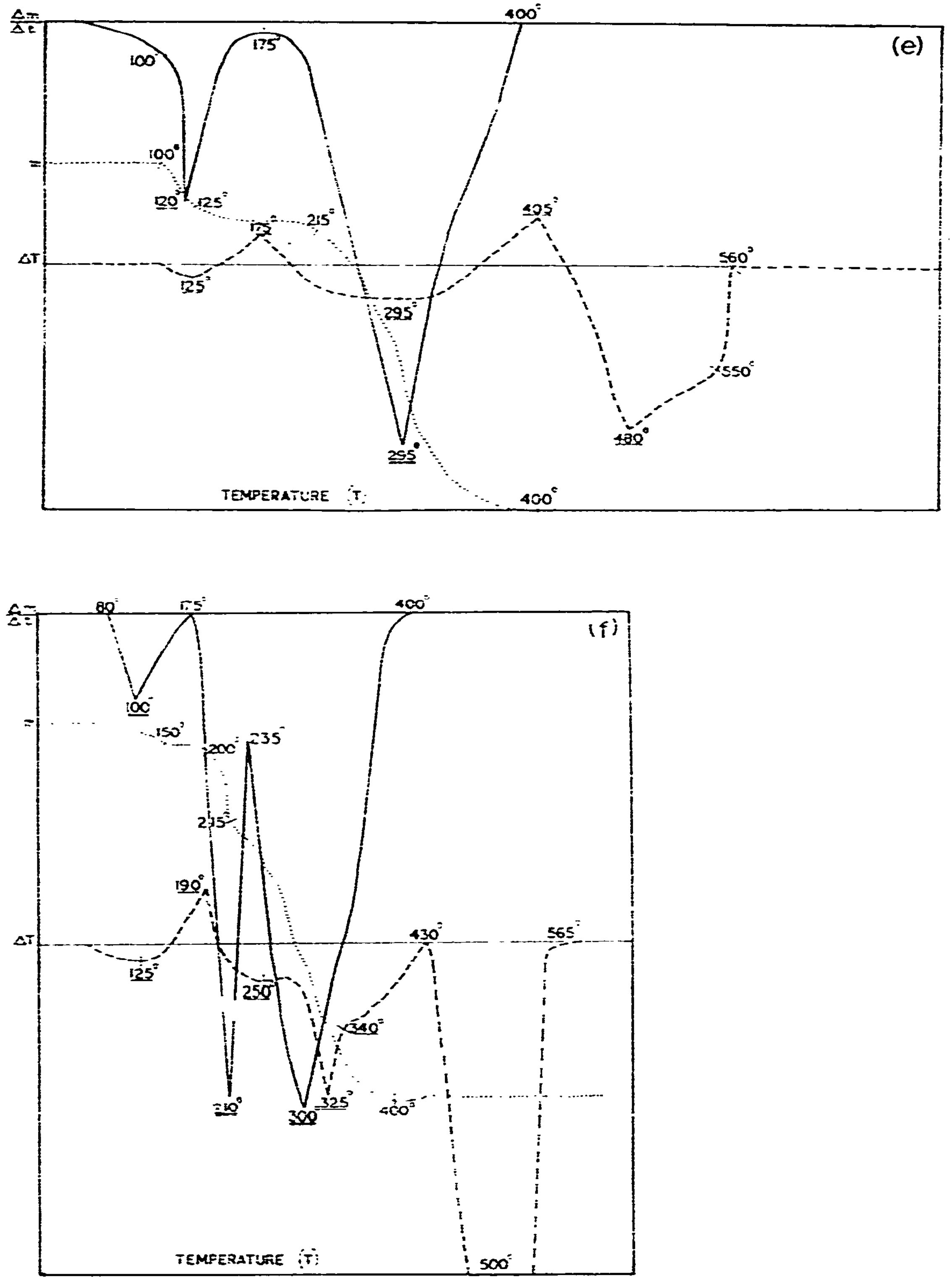


Fig. 1.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295°
550°
295°
480°
TEMPERATURE (T)
400°
Δm/Δt
80°
175°
400°
(f)
100°
π
150°
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Fig. 1.

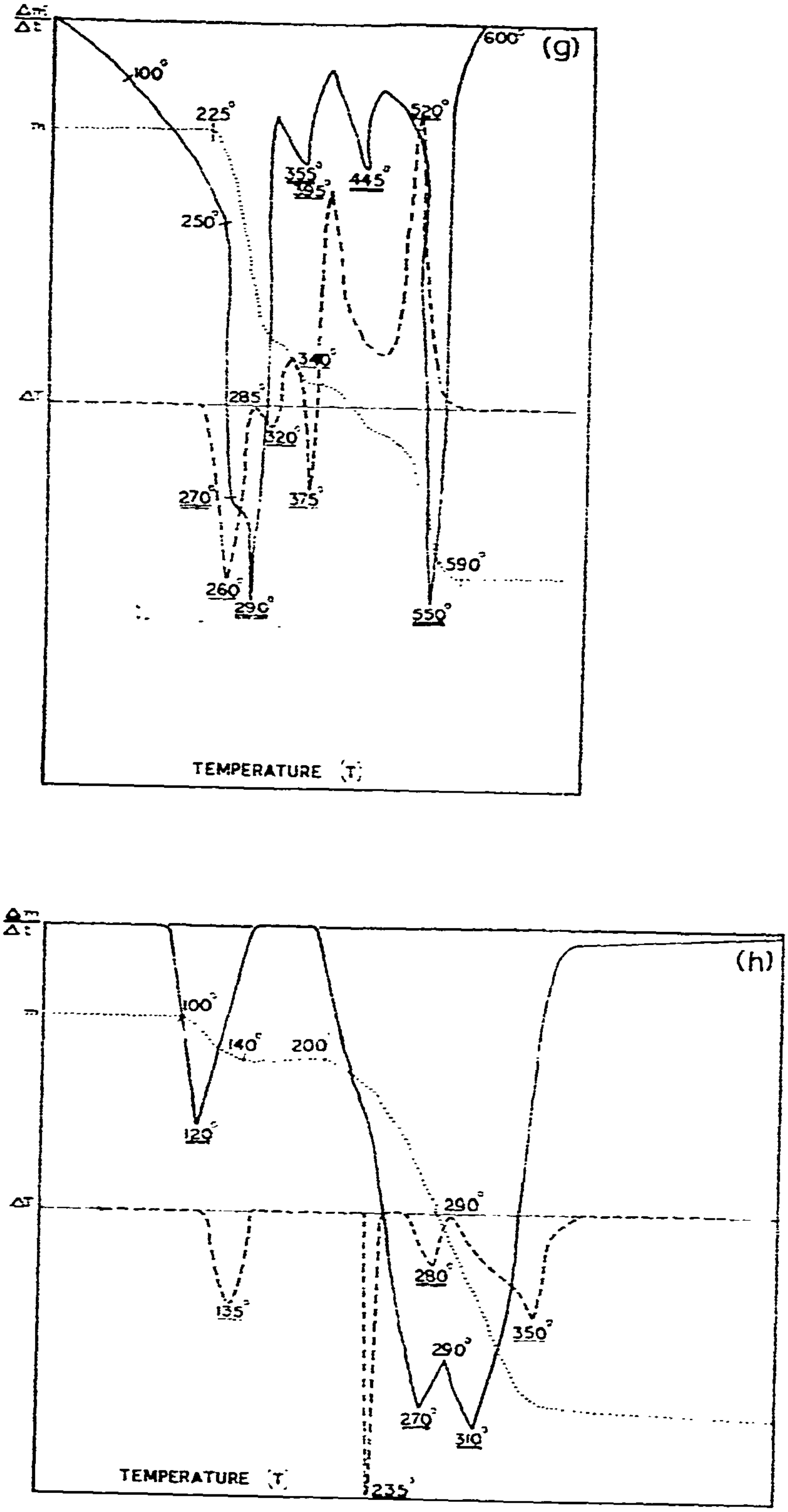
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Fig. 1.

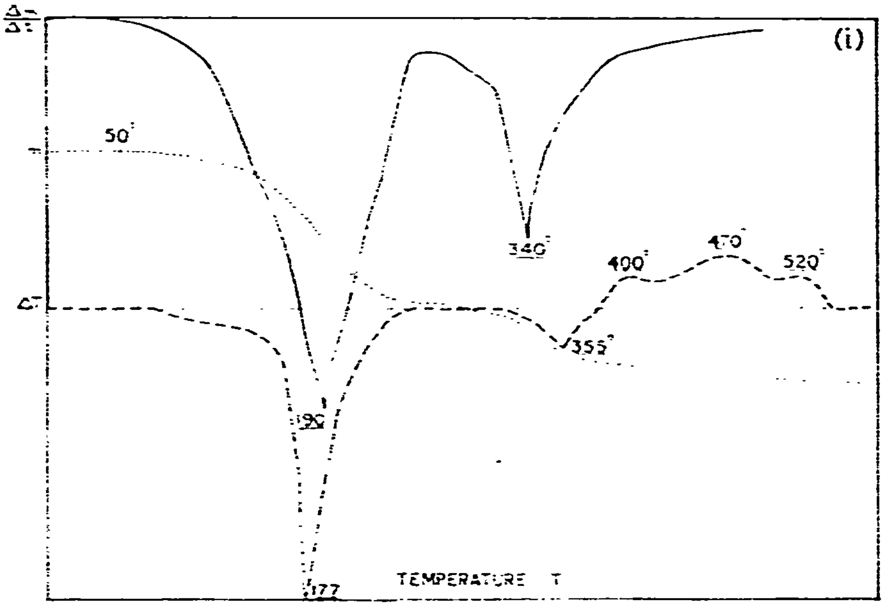

Fig. 1.

complexes as well as for the free ligands indicates that the chief process occurring here is the decomposition of the biguanide molecule.

In just a few cases, there are DTA peaks which have no parallel in DTG. These are 420°C (weak, exo) for Cr, 250 (strong, endo), and 440°C (strong, endo) for Mn, 175 (weak, exo), 405 (weak, exo) and 480°C (strong, endo) for Ni, 500°C (very strong, endo) for Cu, 320 (weak, endo) and 395°C (strong, exo) for Zn, 235°C (strong, endo, narrow) for biguanide sulphate and the broad and diffuse exothermic peaks at 400–520°C for free biguanide. Of these, some could be attributed to a possible overlap in DTG, corresponding to which there is a resolution in DTA. Thus the single DTG peak at 355°C for Zn complex could be correlated with its exothermic DTA peak at 340°C and endothermic DTA peaks at 320 and 375°C. Similarly the single DTG peak at 300°C for Cu is correlated with its endothermic DTA peaks at 250, 325 and 340°C. Similar overlap effects may be invoked to explain the apparently anomalous DTA peaks at 250°C for Mn, 175°C for Ni and 320°C for Zn. The DTA peak at 395°C for Zn is correlated with its DTG peak at 440°C. This leaves the following DTA peaks to be explained: 420°C for Cr, 440°C for Mn, 405 and 480°C for Ni, and 500°C for Cu. These DTA peaks, which are found to be reproducible, and which occur well after steady mass conditions are attained, could be explained as due to phase changes[9]. The large and sharp endothermic peak at 235°C for biguanide sulphate clearly represents melting (m.pt. 233°C), while the broad and diffuse exothermic peaks in the DTA curve of biguanide at ~400°C probably represent combustion of the carbonaceous decomposition products.

In the absence of facilities for a thorough examination of the gaseous products of decomposition, only simple qualitative tests could be carried out. These revealed the existence of ammonia and biguanide vapours among the decomposition products.

Part of the biguanide vapours could be obtained as a white sublimate in the cooler parts of the combustion tube.

It may be seen from Table 2 that the final products of pyrolysis in air seem to be oxides. Good agreement (less than 1.5% deviation) between calculated and observed percentage loss in mass is obtained for the biguanide complexes of V, Cr, Ni and Zn, confirming that the pyrolytic residues in these cases, are, respectively, V_2O_5, Cr_2O_3, NiO and ZnO. In the case of Mn, Co and Cu complexes the agreement, while not so good, is still reasonably satisfactory. Here, the possibility of formation of a mixture of oxides has to be considered. Analysis of the pyrolytic residues for the metal, by dissolution in concentrated HCl and estimation of the cations by the usual methods[10], confirmed that the residues are V_2O_5, Cr_2O_3, NiO and ZnO in the case of V, Cr, Ni and Zn respectively; in the other cases the compositions correspond approximately to Mn_3O_4, Co_3O_4 and CuO. It may be mentioned here that an examination of thermogravimetric literature revealed that the final pyrolytic residues on heating in air are the same oxides mentioned above for the majority of complexes of the above metals[11]. Comparison of the observed *d* spacings from the x-ray powder patterns of the pyrolytic residues with standard values (Table 3) confirmed the identity of the products.

Some quantitative correlations, as to the first stage loss of mass during heating, may also be made. The percentage loss in mass at the first DTG peak may be attributed to loss of structural water in the case of complexes other than that of Zn. The observed and theoretical values for this first stage loss in mass may be seen to agree reasonably (Table 2) only in the case of Mn, and Ni. In these cases, it is apparent that dehydration and further decomposition do not overlap, whereas in the other cases these processes probably overlap to varying extents. The fact that temperature programme control is not quite accurate at these lower temperatures may also be a factor contributing to these discrepancies.

An examination of the TGA curve of biguanide sulphate reveals a horizontal portion between 140 and 200°C. The loss of mass, at this stage, from the curve is 8.4%, whereas the calculated loss of mass for the transition from hydrated biguanide sulphate ($LH \cdot H_2SO_4 \cdot H_2O$) to the anhydrous salt ($LH \cdot H_2SO_4$) is 8.3%. From this, it may be seen that the required drying temperature to get anhydrous biguanide sulphate from the hydrated salt should be at least 140°C, a temperature which is somewhat higher than what is recommended (110°C) in the literature[12].

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