Thermochimica Acta, 92 (1985) 505-508
Elsevier Science Publishers B.V., Amstedam

STUDY OF THERMAL PROPERTIES OF NEW COMPOUNDS CONTAINING FORMATES OF ALKALI AND RARE EARTH ELEMENTS

S.M.Portnova, E.V.Petrova, I.B.Kudinov, N.K.Semendyaeva, V.F.Ryurikov
Kurnakov's Institute of General and Inorganic Chemistry
Academy of Sciences, Moscow, USSR

ABSTRACT

DTA, DTG and DSC defined phase transformation temperatures and heats of following compounds: $LiHCOO \cdot (1-2)NaHCOO \cdot nH_2O$; $LiHCOO \cdot KHCOO$; $LiHCOO \cdot RbHCOO \cdot 0,5H_2O$; $LiHCOO \cdot CsHCOO$; $NaHCOO \cdot 2,5KHCOO$ $Na[Y(HCOO)_4 H_2O]H_2O$; $K[Y(HCOO)_4 H_2O]$; $K_5[Y(HCOO)_8]$. We established correlation between thermal properties (T_m and ΔH) and the nature of structure of compounds.

INTRODUCTION

Nowadays there exists extensive literature on study of thermal properties of simple formates. We have studied thermal properties of a number of complex formates of the following formula: $LiHCOO \cdot (1-2)NaHCOO \cdot nH_2O$; $LiHCOO \cdot KHCOO$; $LiHCOO \cdot RbHCOO \cdot 0,5H_2O$; $LiHCOO \cdot CsHCOO$; $NaHCOO \cdot 2,5KHCOO$; $Na[Y(HCOO)_4 H_2O]H_2O$; $K[Y(HCOO)_4 H_2O]$; $K_5[Y(HCOO)_8]$. We obtained these phases in the course of investigation of corresponding water-salt systems [1-7]. The abovementioned compounds were identified by means of IR spectroscopy, X-ray difraction and crystal-optic method. Structures were defined for complex compounds on the basis of Yttrium formate [8].

EXPERIMENTAL

The study of thermal stability of compounds was carried out by the methods: DTA - on PRT-1000M; DTG by Paulik-Erdey derivatograph with temperature programator LP-980 and Q-derivatograph MOM (the heating rate - 5^{o}/min, mass of sample approximately 1g). The heats of dehydration, melting and thermal decomposition were defined by differential scanning calorimeters of the Du Pont - 990 and Mettler TA - 2000 type. Scanning rate

is 2-10°/min, mass of sample from 2 to 20 mg, reference- Al_2O_3. The experiment was made in the air as well as in inert gases. The enthalpy was defined according to the programme " Peak Integration" on Mettler TA - 2000. The enthalpy on Du Pont- 990 was calculated by formula:

$$\Delta H = \frac{A}{m}(60 \cdot E \cdot \Delta q_s \cdot \beta) M ,$$

where A - area of the peak (sm^2),
m - mass of sample,
β - reverse value from rate of paper-strip movement,
Δq_s - sensitivity (mv/sm),
M - molecular mass.

RESULTS AND DISCUSSION

All data obtained are shown in tables 1-3.

Alkali metals double formates as well as the corresponding simple formates melt without decomposition. Melting temperatures and heats of compounds $LiM(HCOO)_2$, where M= Na, K, Rb, Cs are reduced: Na → Rb → K → Cs (Table 1).

Table 1.

Data of calorimetric study of melting.

Compound	Melting temperature	Melting heat kJ/mole	Atmosphere
$LiHCOO \cdot (1-2)NaHCOO \cdot nH_2O$	455	*151 ± 7	nitrogen
$LiHCOO \cdot KHCOO$	428	14,8± 0,7	nitrogen
$LiHCOO \cdot RbHCOO \cdot 0,5H_2O$	441	19,8 ± 0,2	nitrogen
$LiHCOO \cdot CsHCOO$	410	** 2-3	nitrogen
$NaHCOO \cdot 2,5KHCOO$	453	16,6 ± 1,6	nitrogen

* melting heat in J/G
** due to little effect a major error is possible in calculating melting heat.

We established that dehydration temperature is reduced in $Y(HCOO)_3 \cdot 2H_2O \rightarrow Na[Y(HCOO)_4 H_2O] H_2O \rightarrow K[Y(HCOO)_4 H_2O]$ (table 2) which corresponds to structure data, because it has been found that the distance $M-O_w$ increases from 2,35Å in dihydrate of Yttrium formate to 2,48Å in $Na[Y(HCOO)_4 H_2O] H_2O$ [8,9].

The specific features of structure of the studied compounds

decrease melting and decomposition temperature in $Y(HCOO)_3 \cdot 2H_2O$ (I) - $Na\left[Y(HCOO)_4 H_2O\right] H_2O$ (II) - $K\left[Y(HCOO)_4 H_2O\right]$ (III) - $K_5\left[Y(HCOO)_8\right]$ (IV).

Table 2.

DTA, DTG and DSC results of dehydration process.

Compound	Melting temperature, K	Melting heat, kJ/mole	Loss of mass, % theor	Loss of mass, % exp	Atmosphere
$LiHCOO \cdot (1-2)NaHCOO \cdot nH_2O$	361-366	*167 ± 3	-	-	nitrogen
$Y(HCOO)_3 \cdot 2H_2O$	383-418	24 ± 2	13,86	4,03	air
	418-431	28 ± 2		9,57 13,60	air
$Na\left[Y(HCOO)_4 H_2O\right] H_2O$	345-356	5,29±0,1			air
	356-358	3,80±0,1	5,52	6,09	nitrogen
$K\left[Y(HCOO)_4 H_2O\right]$	355-366	34,57±0,1			nitrogen
	366-378	13,41±0,1	5,52	5,20	air

* dehydration heat is given in J/G

Table 3.

Melting and decomposition temperatures of compounds on the basis of Yttrium formate.

Compound	Melting temperature, K	Decomposition temperature, K
$Y(HCOO)_3 \cdot 2H_2O$	603	648
$Na\left[Y(HCOO)_4 H_2O\right] H_2O$	583	638
$K\left[Y(HCOO)_4 H_2O\right]$	558	633
$K_5\left[Y(HCOO)_8\right]$	493	

Structures II and III are polymeric, layered with independent formate groups, having different conformation structure and dentate type. However, the character of structures II and III has much in common with structure of $Y(HCOO)_3 \cdot 2H_2O$, whereas structure IV is isolated, ionic. All formate radicals are monodentate. The structure of this compound is an analogue of that of the original Potassium formate, the melting temperature of

wich is 439K, that is, 164K lower than melting temperature of $Y(HCOO)_3 \cdot 2H_2O$. The melting temperature of IV is lower than those of II and III, accordingly.

REFERENCES

1 S.M.Portnova, L.S.Itkina, J.Neorg.Chim. 24 (1979) 213
2 L.S.Itkina, N.M.Chapligina, E.V.Petrova, J.Neorg.Chim. 24 (1979) 788
3 L.S.Itkina, E.V.Petrova, J.Neorg.Chim. 24 (1979) 1103
4 L.S.Itkina, E.V.Petrova, J.Neorg.Chim. 27 (1982) 517
5 E.V.Petrova, S.M.Portnova, L.S.Itkina, V.N.Schurkina, J.Neorg.Chim. 26 (1981) 3121
6 L.S.Itkina, E.V.Petrova, A.S.Antsishkina, J.Neorg.Chim. 26 (1981) 3112
7 S.M.Portnova, E.V.Petrova, A.K.Lyascenko, I.N.Lepeshkov, J.Neorg.Chim. 28 (1983) 2952
8 A.S.Antsishkina, M.A.Poray-Koshits, V.N.Ostrikova, E.V.Petrova, Koord.Chimiya 9 (1983) 986
9 A.S.Antsishkina, M.A.Poray-Koshits, I.V.Arhangelskiy, L.A.Butman, Koord.Chimiya 2 (1976) 565