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THERMAL STUDIES ON ALKALINE EARTH MONOMETHYL VIOLURATES

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ABSTRACT

Some alkaline earth monomethyl violurate hexahydrates were prepared in aqueous medium, and characterized on the basis of elemental analysis and IR spectral data. The thermal behaviour of these salts was studied with the aid of TG, DTG and DSC techniques. Heats of dehydration were calculated from DSC curves.

INTRODUCTION

Violuric and 1,3-dimethyl violuric acid have been used for the spectrophotometric determination of alkaline and alkaline earth metals. A thermogravimetric study of these acids and salts has been reported by Taylor and co-workers [1], who indicate the degree of hydration as well as the stability range of the anhydrous compounds. We have recently shown [2] that monomethyl violuric acid (HAMV) forms highly coloured salts with alkaline metals; these salts have been studied with the aid of TG, DTG and DSC techniques [2]. We report here the results of the thermal behaviour of some alkaline earth monomethyl violurates.

EXPERIMENTAL

Monomethyl violuric acid (2,4-dioxo-6-hydroxy-1-methyl-5-nitroso-1,2,3,4-tetrahydro-pyrimidine) was synthesized using the method described

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TABLE 1

Analytical and reflectance spectra data for some alkaline earth monomethyl violurates

Compound	Colour	Analysis (%)						Reflectance bands (cm^{-1})	
		Found			Calcd.				
		C	H	N	C	H	N		
$Mg(AMV)_2 \cdot 6\ H_2O$	Pink	25.64	3.96	18.10	25.40	4.23	17.78	19.050	30.675
$Ca(AMV)_2 \cdot 6\ H_2O$	Red	24.44	3.57	17.23	24.59	4.10	17.21	18.868	31.250
$Sr(AMV)_2 \cdot 6\ H_2O$	Pink	22.03	3.24	15.49	22.40	3.73	15.68	19.120	30.864
$Ba(AMV)_2 \cdot 6\ H_2O$	Violet-red	20.31	3.57	14.02	20.50	3.42	14.35	18.182	30.300

previously [3]. Alkaline earth monomethyl violurates were prepared by mixing an aqueous solution of alkaline earth acetate with an aqueous solution of HAMV. Solutions were heated to 50°C with constant agitation for 2 h and left to crystallize. Twenty-four hours later, the precipitates were filtered, washed with ethanol and dried. The monomethyl violurates prepared, along with their elemental analysis and reflectance spectra data, are presented in Table 1.

Infrared spectra of these salts were recorded in KBr medium in the region 4000–200 cm^{-1} using a Perkin-Elmer 4250 spectrophotometer; reflectance spectra were recorded in $BaSO_4$ medium in the region 800–200 nm using a Beckman Acta C III spectrophotometer.

TG studies were made in air on a Mettler thermobalance model TG 50 at a heating rate of 10°C min^{-1}; whereas the DSC runs were carried out on a Mettler differential scanning calorimeter model DSC 20 at a heating rate of 5°C min^{-1}. The thermolytic reactions were run with samples varying in weight from 4.530 to 13.484 mg.

RESULTS AND DISCUSSION

The methods used for the preparation and characterization of alkaline earth monomethyl violurates yield materials of high purity, as can be judged by satisfactory elemental analysis, IR spectra and thermoanalytical data. All the compounds are obtained in crystalline form; they are soluble in water and insoluble in common organic solvents, e.g., ethanol, ether, acetone, etc.

The most significant IR bands for isolated salts are collected in Table 2. These assignments have been realized on the basis of the empirical band assignments for the free monomethyl violuric acid [4].

Figures 1 and 2 present the TG and DSC plots of some alkaline earth monomethyl violurates in a static air atmosphere. In all cases, the thermal behaviour of these salts consists of two principal processes: dehydration and decomposition of anhydrous salts to the respective alkaline earth carbonate or oxide.

Dehydration occurs in the temperature range 50–175°C. The observed weight losses in this temperature range are indicative of the hexahydrate nature of these salts. Under the experimental conditions used in this work, the dehydration process occurs in one step for $Mg(AMV)_2 \cdot 6\ H_2O$ and $Ba(AMV)_2 \cdot 6\ H_2O$, whereas for $Ca(AMV)_2 \cdot 6\ H_2O$ and $Sr(AMV)_2 \cdot 6\ H_2O$ this dehydration occurs in two steps. The expected endothermic behaviour for the dehydration process associated with these compounds has been observed from DSC curves in almost the same temperature ranges. The dehydration temperatures, observed weight losses, calculated weight losses and dehydration enthalpies calculated from the DSC curves of Fig. 2 are shown in Table 3. Values of dehydration enthalpies show a direct relation with the radii of alkaline earth ions; this suggests that six molecules of water are directly linked to the metallic cation.

TABLE 2

Principal IR bands (cm^{-1}) of some alkaline earth monomethyl violurates

Compound	ν(O–H)	ν_{as}(N–H)	ν_s(N–H)	ν(C=O)	ν(C–N)	ν(C–O)
$Mg(AMV)_2 \cdot 6\ H_2O$	3525s 3450s	3160w	3050w	1728s 1680s	1302s	1017m
$Ca(AMV)_2 \cdot 6\ H_2O$	3515m 3450s	3180w	3025w	1715s 1695	1322m	1050m
$Sr(AMV)_2 \cdot 6\ H_2O$	3530s 3460b	3220w		1725s 1700	1330m	1022m
$Ba(AMV)_2 \cdot 6\ H_2O$	3520s 3430s	3240w		1720s 1670s	1330m	1025m

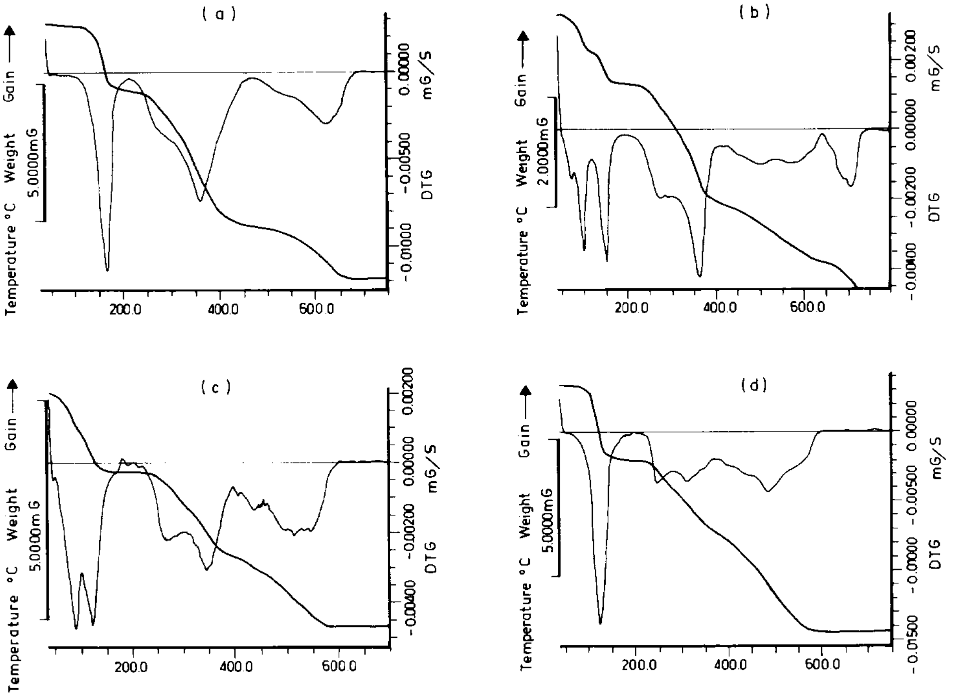

Fig. 1. TG and DTG plots of (a) $Mg(AMV)_2 \cdot 6\ H_2O$, (b) $Ca(AMV)_2 \cdot 6\ H_2O$, (c) $Sr(AMV)_2 \cdot 6\ H_2O$ and (d) $Ba(AMV)_2 \cdot 6\ H_2O$.

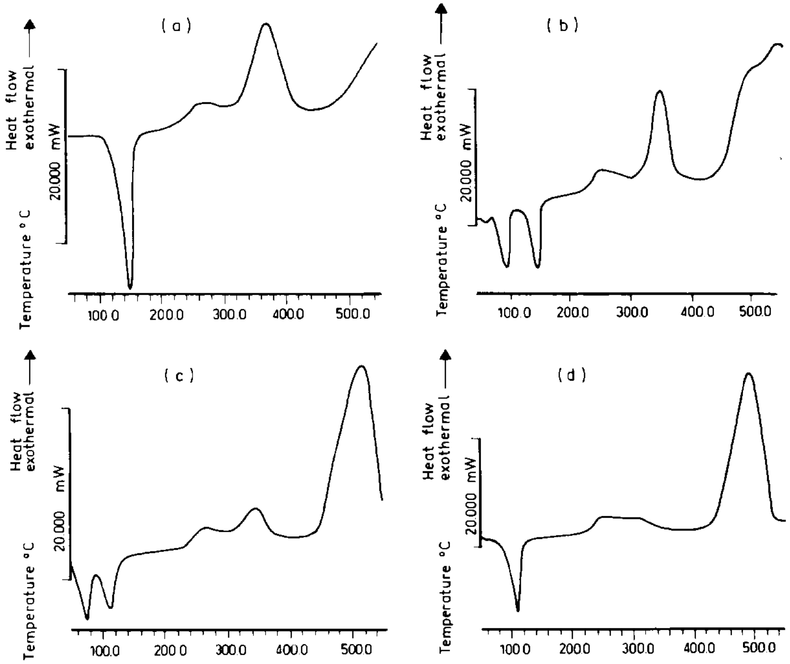

Fig. 2. DSC curves of (a) $Mg(AMV)_2 \cdot 6\ H_2O$, (b) $Ca(AMV)_2 \cdot 6\ H_2O$, (c) $Sr(AMV)_2 \cdot 6\ H_2O$ and (d) $Ba(AMV)_2 \cdot 6\ H_2O$.

TABLE 3

TG and DSC data for the dehydration of some alkaline earth monomethyl violurates

Compound	Water loss (dehydration)	Dehyd. temp. (°C)	wt. loss (%)		$\Delta H_{\text{dehyd.}}$ (kJ mole^{-1} H_2O)
			Found	Calcd.	
$Mg(AMV)_2 \cdot 6\ H_2O$	$-6\ H_2O$	148	22.8	22.86	53.5
$Ca(AMV)_2 \cdot 6\ H_2O$	$-3\ H_2O$	96	11.6	11.06	24.1
	$-3\ H_2O$	146	10.7	11.06	31.6
$Sr(AMV)_2 \cdot 6\ H_2O$	$-3\ H_2O$	73	11.2	10.08	52.3
	$-3\ H_2O$	112	10.9	10.08	
$Ba(AMV)_2 \cdot 6\ H_2O$	$-6\ H_2O$	108	19.4	18.45	51.5

Anhydrous magnesium and calcium monomethyl violurates are stable from 190°C to 240°C. TG curves of these anhydrous salts show a fast decomposition in the temperature range 240–410°C, followed by slow decomposition from 410°C to 750°C; at this point the residual weights are 9.0% and 12.2% of the original weight which correspond narrowly with the theoretical values required for MgO (8.53%) and CaO (11.47%), respectively.

Anhydrous strontium and barium monomethyl violurates are stable in the temperature range 175–225°C; from the last temperature up to the end of the run (800°C) the total pyrolysis of the pyrimidinic ring takes place in two processes that apparently overlap under the experimental conditions; these processes are associated with the exothermic effects in the DSC curves (Fig. 2). At 800°C the percentage weights of the residues are 28.2% and 33.6% of the initial weights, and correspond to $SrCO_3$ (27.56%) and $BaCO_3$ (33.71%), respectively. In all cases, the nature of the residue has been verified by R–X diffraction methods.

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