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DERIVATOGRAPHIC STUDIES ON DEHYDRATION OF SALT HYDRATES AND THEIR DEUTERIUM OXIDE ANALOGUES. V

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ABSTRACT

Non-isothermal thermal studies of the dehydration of the double salt hydrates of the type $M(I)_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$ and their D_2O analogues were carried out where M(I) = Tl(I) and M(II) = Mg(II), Co(II), Ni(II), Cu(II) or Zn(II). Thermal parameters like activation energy, order of reaction, enthalpy change, etc. were evaluated from the analysis of TG, DTA and DTG curves. These thermal parameters were compared with those of other series, like NH_4(I), K(I), Rb(I) and Cs(I) studied earlier. On deuteration the nature of dehydration altered in the case of $Tl_2Zn(SO_4)_2 \cdot 6H_2O$ only. The thermal stability of the salt hydrates and their D_2O analogues is discussed in relation to the salt hydrates of other series. The role of divalent cation on the thermal properties of dehydration of salt hydrates is also discussed. The order of reaction was always found unity. The values of ΔH were within ~12–~16 kcal mol^{-1}.

INTRODUCTION

Recently, we reported the derivatographic studies on the dehydration of double salt hydrates of the type $M(I)_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$ where M(I) = NH_4(I)[1], K(I)[2], Rb(I)[3] or Cs(I)[4] and M(II) = Mg(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) or Cd(II) and their D_2O analogues. The above studies reveal that the thermal properties of dehydration of double salt hydrates are effected with variation of monovalent cation. In continuation to these works, the present paper deals with the dehydration of similar double salt hydrates of the Tl(I) series and their D_2O analogues. The value of activation energy of the dehydration process evaluated from TG, DTA and DTG curves, the order of reaction from TG, the enthalpy change from DTA peak area and the thermal stability from the first DTG peak temperature are reported in this paper. In addition to the evaluation of these thermal parameters, this paper displays the effect on the thermal properties of dehydration of salt hydrates due to deuteration and also a review of non-isothermal thermal studies of the present series relating the other series of Tutton salts studied by us.

EXPERIMENTAL

Double salt hydrates were prepared according to standard procedures adopted by earlier workers[5] and their D_2O analogues were prepared by dissolving an equimolecular mixture of anhydrous single salts in D_2O and followed by crystallisation. A Paulik–Paulik–Erdey MOM derivatograph had been used for thermal analysis. A platinum crucible was used and the heating rate was 1.5°C min^{-1}. The particle size of the samples was within 150–200 mesh. The volume of the sample in each case was the same.

RESULTS

The double sulphate hydrates of Mg(II) and Ni(II) lose water molecules in a single step, i.e., $Tl_2M(SO_4)_2 \cdot 6H_2O \rightarrow Tl_2M(SO_4)_2$ observed from the respective derivatogram (Fig. 1). Whereas, the derivatogram (Fig. 2) of $Tl_2Co(SO_4)_2 \cdot 6H_2O$ indicates that dehydration takes place in three steps, i.e., $Tl_2Co(SO_4)_2 \cdot 6H_2O \rightarrow Tl_2Co(SO_4)_2 \cdot 1.5H_2O \rightarrow Tl_2Co(SO_4)_2 \cdot 0.25H_2O \rightarrow Tl_2Co(SO_4)_2$. The first step of dehydration shows well-resolved DTA and DTG curves and for the second step of dehydration both DTA and DTG curves are slightly overlapped indicating the existence of an intermediate salt hydrate. Whereas, for the third step, although DTA and DTG curves are not overlapped, attempts to evaluate the activation energy of this step are not successful even by performing the experiment using maximum sensitivity, due to small peak areas of the DTA and DTG curves. The intermediate salt hydrates are thermally unstable. The dehydration of the corresponding salt hydrate of Cu(II) takes place in three steps (Fig. 2) like the corresponding Co(II) salt hydrate but its nature of dehydration is quite different, i.e., $Tl_2Cu(SO_4)_2 \cdot 6H_2O \rightarrow Tl_2Cu(SO_4)_2 \cdot 2H_2O \rightarrow Tl_2Cu(SO_4)_2 \cdot 0.5H_2O \rightarrow Tl_2Cu(SO_4)_2$. Here, also the intermediate salt hydrates are thermally unstable. As a result DTA curves are overlapped with each other to a great extent, whereas, the corresponding DTG curves are not so much overlapped. The DTA peak area of the third step of dehydration is very small to be calculated for thermal parameters. All the above salt hydrates do not show any noticeable effect in thermal properties on deuteration. The double salt hydrate of Zn(II) of the present series loses water molecules in three steps (Fig. 3) like Co(II) and Cu(II) but in a different fashion as follows, $Tl_2Zn(SO_4)_2 \cdot 6H_2O \rightarrow Tl_2Zn(SO_4)_2 \cdot 1.5H_2O \rightarrow Tl_2Zn(SO_4)_2 \cdot 0.5H_2O \rightarrow Tl_2Zn(SO_4)_2$. The last step of dehydration is complicated. Thereby, DTA for this step shows three overlapped endotherms and the respective DTG curve is broad in nature. DTA and DTG curves for the first and second step of dehydration are overlapped. None of the intermediate salt hydrates are thermally stable. Whereas, its D_2O analogue loses D_2O molecules in two steps, i.e., $Tl_2Zn(SO_4)_2 \cdot 6D_2O \rightarrow Tl_2Zn(SO_4)_2 \cdot D_2O \rightarrow Tl_2Zn(SO_4)_2$ observed from the respective derivatogram (Fig. 3). Here like the third step of dehydration of its H_2O analogue, the second step of dehydration is complicated. DTA shows three overlapping endotherms and the DTG is broad. Whereas, both DTA and DTG for the first step of dehydration do not show any sign of overlapping. The DTG peak

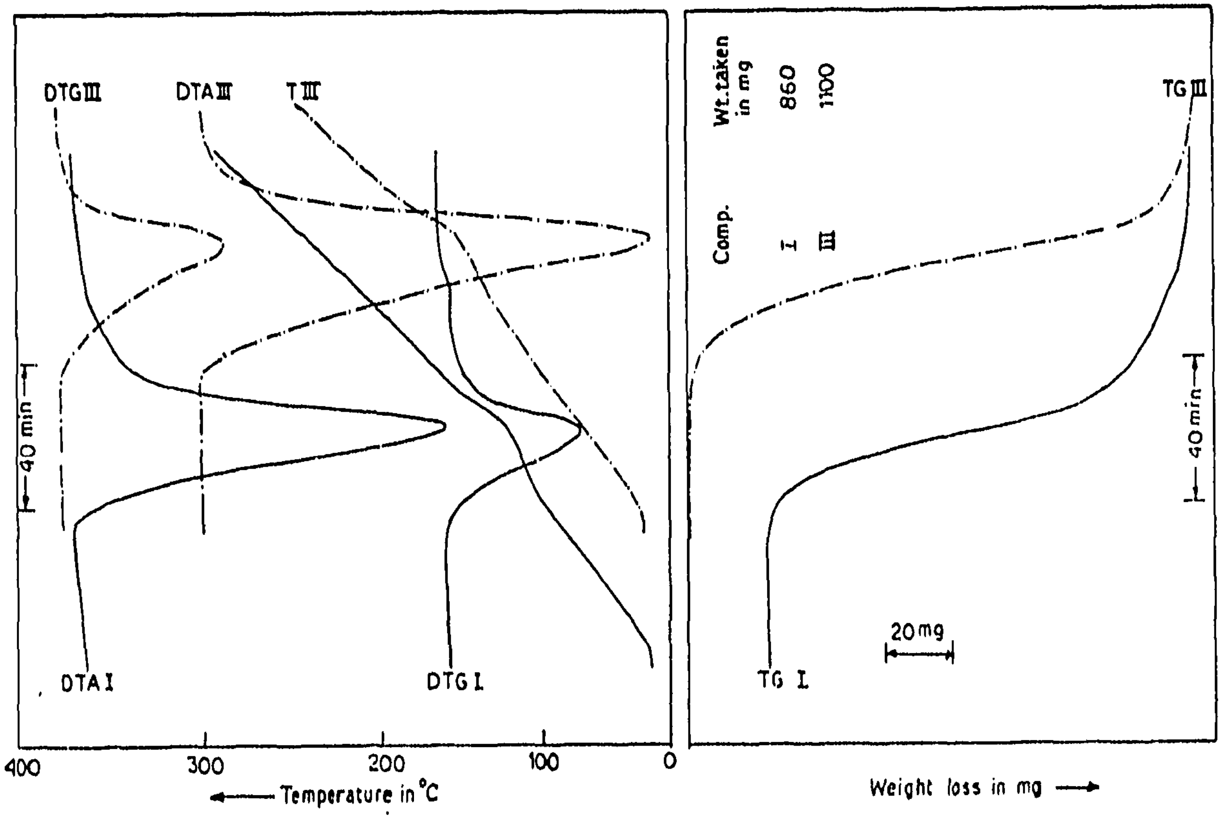

Fig. 1. Derivatograms for the dehydration of $Tl_2SO_4 \cdot MgSO_4 \cdot 6H_2O$(I) and $Tl_2SO_4 \cdot NiSO_4 \cdot 6H_2O$(III).

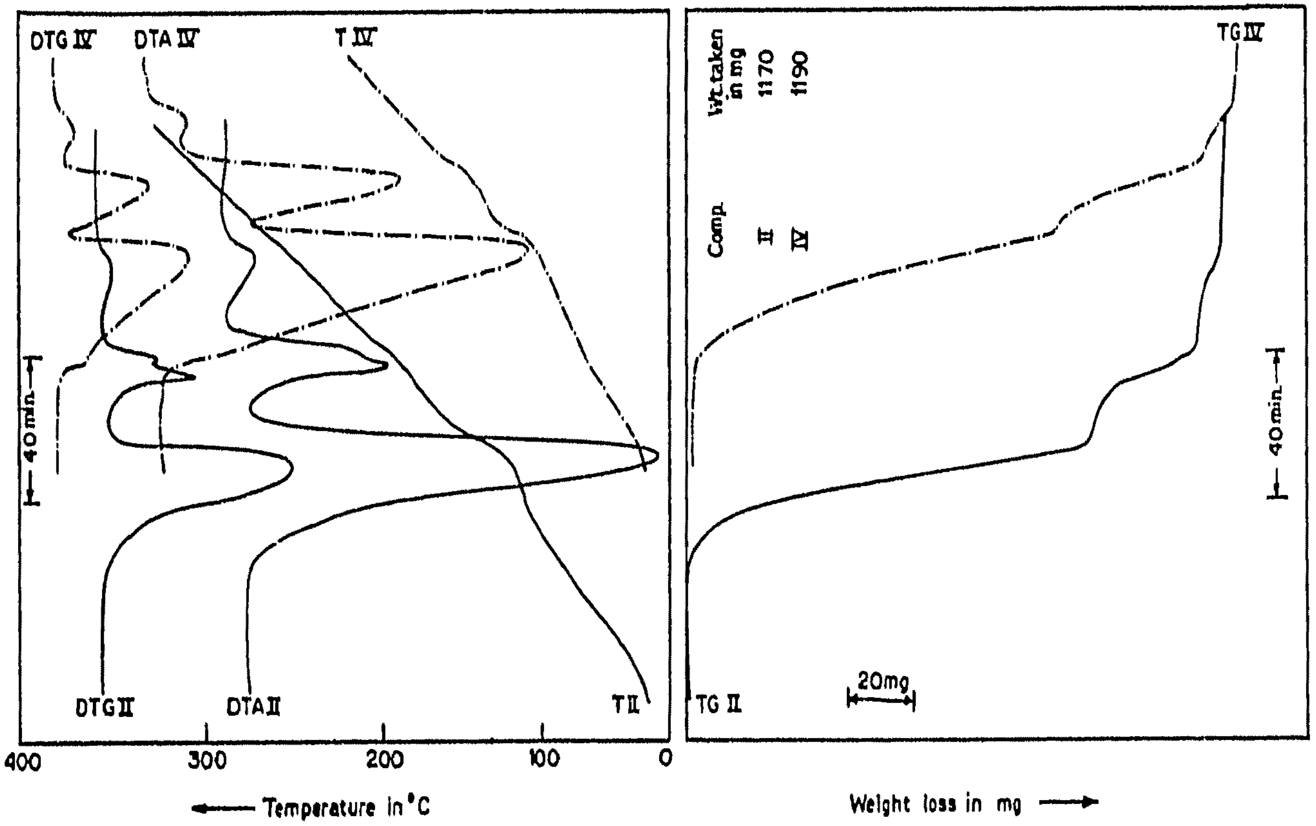

Fig. 2. Derivatograms for the dehydration of $Tl_2SO_4 \cdot CoSO_4 \cdot 6H_2O$(II) and $Tl_2SO_4 \cdot CuSO_4 \cdot 6H_2O$(IV).

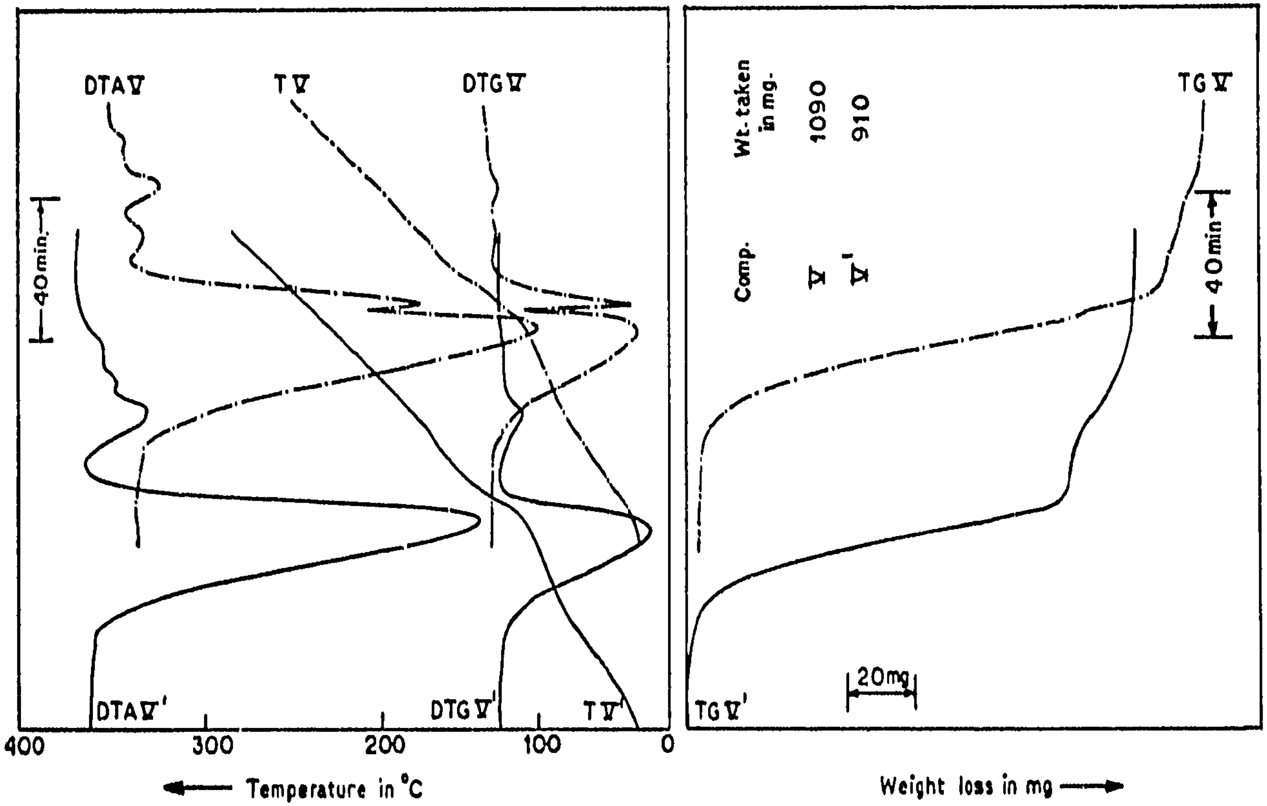

Fig. 3. Deriavtograms for the dehydration of $Tl_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$(V) and $Tl_2SO_4 \cdot ZnSO_4 \cdot 6D_2O$(V').

TABLE 1

THERMAL PARAMETERS OF DEHYDRATION OF SALT HYDRATES AND THEIR DEUTERIUM OXIDE ANALOGUES

Decomposition reaction		*Temp. range (°C)*	*DTG peak temp. (°C)*	*Activation energy (kcal mol⁻¹)*			*Enthalpy change (kcal mol⁻¹)*
				TG	*DTG*	*DTA*	
(I)	$Tl_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot MgSO_4$	75–250	120	30.6	32.8	36.8	12.3
(I′)	$Tl_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot MgSO_4$	74–249	117	35.8	35.8	35.8	13.3
(IIa)	$Tl_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 1.5H_2O$	80–135	120	26.8	31.7	31.7	12.1
(IIb)	$Tl_2SO_4 \cdot CoSO_4 \cdot 1.5H_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 0.25H_2O$	135–215	185	92.0	—	88.0	11.4[a]
(IIc)	$Tl_2SO_4 \cdot CoSO_4 \cdot 0.25H_2O \rightarrow Tl_2SO_4 \cdot CoSO_4$	217–270	250	—	—	—	—[b]
(II′a)	$Tl_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 1.5D_2O$	84–140	121	28.7	36.8	34.5	14.1
(II′b)	$Tl_2SO_4 \cdot CoSO_4 \cdot 1.5D_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 0.25D_2O$	142–210	185	88.0	—	88.0	12.7[a]
(II′c)	$Tl_2SO_4 \cdot CoSO_4 \cdot 0.25D_2O \rightarrow Tl_2SO_4 \cdot CoSO_4$	213–275	255	—	—	—	—[b]
(III)	$Tl_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot NiSO_4$	95–225	150	23.0	26.3	26.3	13.1
(III′)	$Tl_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot NiSO_4$	100–230	151	23.0	25.5	25.5	12.8
(IVa)	$Tl_2SO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 2H_2O$	55–107	100	27.0	27.0	—	14.7[a]
(IVb)	$Tl_2SO_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 0.5H_2O$	110–147	142	46.0	46.0	—	—
(IVc)	$Tl_2SO_4 \cdot CuSO_4 \cdot 0.5H_2O \rightarrow Tl_2SO_4 \cdot CuSO_4$	147–200	180	—	—	—	—[b]
(IV′a)	$Tl_2SO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 2D_2O$	57–110	100	27.6	27.6	—	15.8[a]
(IV′b)	$Tl_2SO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 0.5D_2O$	112–149	142	57.5	57.5	—	—[b]
(IV′c)	$Tl_2SO_4 \cdot CuSO_4 \cdot 0.5D_2O \rightarrow Tl_2SO_4 \cdot CuSO_4$	149–202	180	—	—	—	—[b]
(Va)	$Tl_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot ZnSO_4 \cdot 1.5H_2O$	75–120	110	24.5	—	—	12.4[a]
(Vb)	$Tl_2SO_4 \cdot ZnSO_4 \cdot 1.5H_2O \rightarrow Tl_2SO_4 \cdot ZnSO_4 \cdot 0.5H_2O$	120–155	130	—	—	—	—[b]
(Vc)	$Tl_2SO_4 \cdot ZnSO_4 \cdot 0.5H_2O \rightarrow Tl_2SO_4 \cdot ZnSO_4$	155–210	200	—	—	—	—[b]
(V′a)	$Tl_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot ZnSO_4 \cdot 1D_2O$	75–125	107	28.7	28.7	28.7	15.4
(V′b)	$Tl_2SO_4 \cdot ZnSO_4 \cdot D_2O \rightarrow Tl_2SO_4 \cdot ZnSO_4$	130–210	185	—	—	—	—[b]

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[a] These indicate the overall enthalpy changes where DTA curves overlap too much. [b] The calculation of thermal parameters is not done due to very poor resolution of the curve.

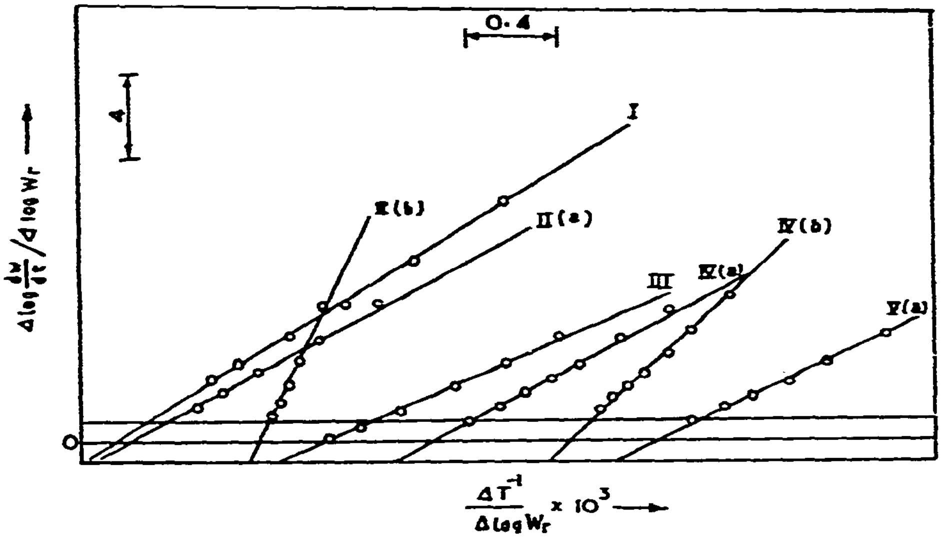

Fig. 4. Plots of $\Delta \log \frac{dw}{dt} / \Delta \log W_r$ vs. $\Delta T^{-1}/\Delta \log W_r \times 10^3$, from the TG curves for the dehydration of $Tl_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot MgSO_4$(I), $Tl_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 1.5H_2O$(IIa), $Tl_2SO_4 \cdot CoSO_4 \cdot 1.5H_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 0.25H_2O$(IIb), $Tl_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot NiSO_4$(III), $Tl_2SO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 2H_2O$(IVa), $Tl_2SO_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 0.5H_2O$(IVb) and $Tl_2SO_4 \cdot ZnSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot ZnSO_4 \cdot 1.5H_2O$(Va).

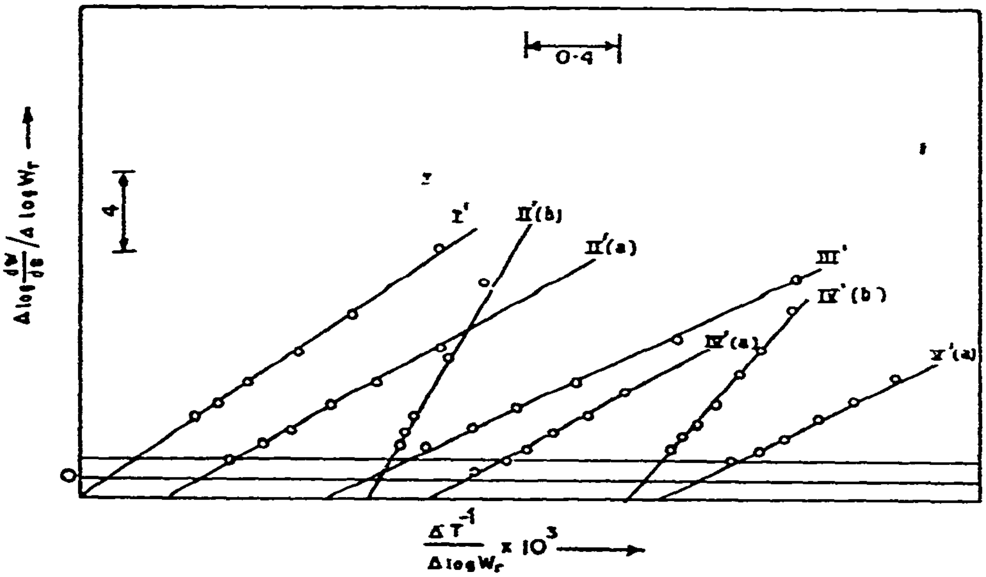

Fig. 5. Plots of $\Delta \log \frac{dw}{dt} / \Delta \log W_r$ vs. $\Delta T^{-1}/\Delta \log W_r \times 10^3$, from the TG curves for the dehydration of $Tl_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot MgSO_4$(I′), $Tl_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 1.5D_2O$(II′a), $Tl_2SO_4 \cdot CoSO_4 \cdot 1.5D_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 0.25D_2O$(II′b), $Tl_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot NiSO_4$(III′), $Tl_2SO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 2D_2O$(IV′a), $Tl_2SO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 0.5D_2O$(IV′b) and $Tl_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot ZnSO_4 \cdot D_2O$(V′a).

temperatures and the temperature ranges of dehydration of the double salt hydrates and their corresponding D_2O analogues are tabulated in Table 1. Enthalpy changes for each step of dehydration are evaluated by the method of Sano[6] using copper sulphate pentahydrate as the standard and the values are tabulated in Table 1. ΔH values are evaluated from the overall area of the DTA curves, where the DTA curves are too much overlapped. Activation energies for each step of dehydration of the salt hydrates and their D_2O analogues are evaluated from the analysis of TG curves using Freeman and Carroll's[7] equation. The results are tabulated in Table 1 and the corresponding curves are shown in Figs. 4 and 5. The activation energies for each step of dehydration were also evaluated from the analysis of DTG curves using the method of Dave and Chopra[8] and the method described in our earlier work[1] and also from the analysis of DTA curves using Brochardt's[9] equation for first order reactions. All these values are tabulated in Table 1 and the corresponding Arrhenius plots are shown in Figs. 6 and 7. The order of reaction for each step of dehydration was found to be unity. The IR spectra of the salt hydrates and their D_2O analogues are taken to ensure that deuteration of the hydrates takes place to the desired extent. The X-ray diffraction pattern shows that the salt hydrates and their corresponding D_2O analogues are isomorphous to each other.

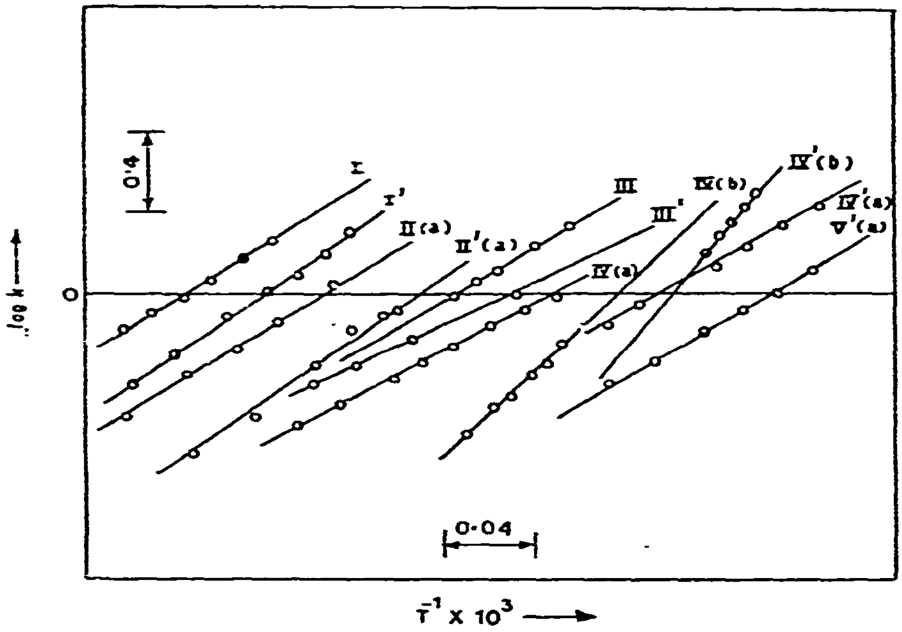

Fig. 6. Arrhenius plots of log k vs. $T^{-1} \times 10^3$ from DTG curves for the dehydration of $Tl_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot MgSO_4$(I), $Tl_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot MgSO_4$(I'), $Tl_2SO_4 \cdot CoSO_4$ $6H_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 1.5H_2O$(IIa), $Tl_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 1.5D_2O$(II'a), $Tl_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot NiSO_4$(III), $Tl_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot NiSO_4$(III'), $Tl_2SO_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 2H_2O$(IVa), $Tl_2SO_4 \cdot CuSO_4 \cdot 2H_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 0.5H_2O$(IVb), $Tl_2SO_4 \cdot CuSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 2D_2O$(IV'a), $Tl_2SO_4 \cdot CuSO_4 \cdot 2D_2O \rightarrow Tl_2SO_4 \cdot CuSO_4 \cdot 0.5D_2O$(IV'b) and $Tl_2SO_4 \cdot ZnSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot ZnSO_4 \cdot D_2O$(V'a).

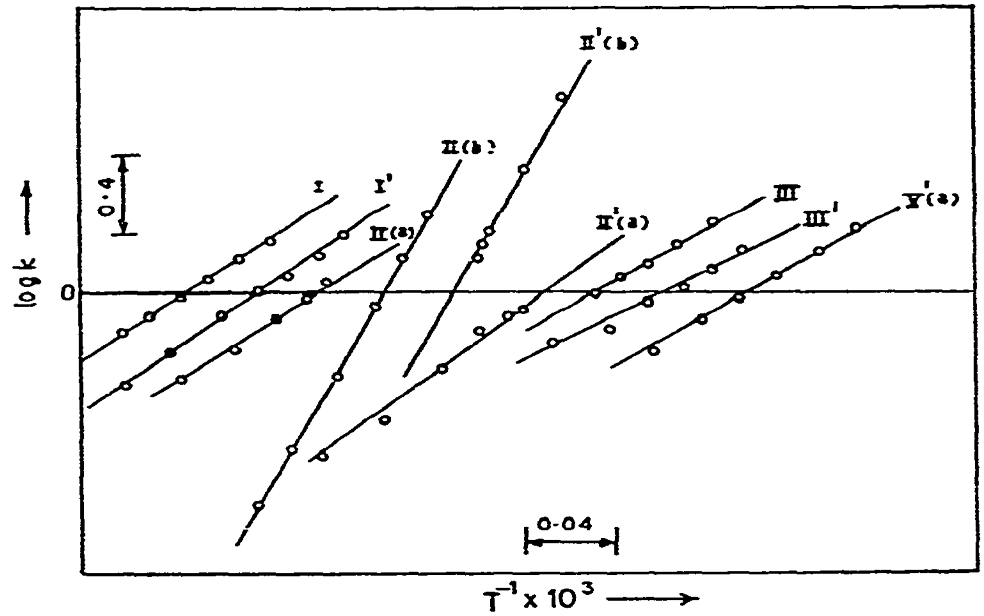

Fig. 7. Arrhenius plots of log *k* vs. $T^{-1} \times 10^3$ from the DTA curves for the dehydration of $Tl_2SO_4 \cdot MgSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot MgSO_4$(I), $Tl_2SO_4 \cdot MgSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot MgSO_4$(I′), $Tl_2SO_4 \cdot CoSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 1.5H_2O$(IIa), $Tl_2SO_4 \cdot COSO_4 \cdot 1.5H_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 0.25H_2O$(IIb), $Tl_2SO_4 \cdot CoSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 1.5D_2O$(II′a), $Tl_2SO_4 \cdot CoSO_4 \cdot 1.5D_2O \rightarrow Tl_2SO_4 \cdot CoSO_4 \cdot 0.25D_2O$(II′b), $Tl_2SO_4 \cdot NiSO_4 \cdot 6H_2O \rightarrow Tl_2SO_4 \cdot NiSO_4$(III), $Tl_2SO_4 \cdot NiSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot NiSO_4$(III′) and $Tl_2SO_4ZnSO_4 \cdot 6D_2O \rightarrow Tl_2SO_4 \cdot ZnSO_4 \cdot D_2O$(V′a).

DISCUSSION

The nature of dehydration of the salt hydrate of Mg(II) of the present series is different from the other Tutton salts of Mg(II). But it is similar to that of the deuterated salt hydrate of the K(I)[2] series, where dehydration took place in a single step instead of in three equal steps for its H_2O analogue. In our earlier works[1–4], two other Tutton salts of Mg(II), i.e., of the K(I) and Rb(I) series showed changes in the nature of dehydration on deuteration, whereas, no such change is observed in the present salt hydrate like in the corresponding NH_4(I) and Cs(I) series. The thermal stability of this salt hydrate with respect to the first DTG peak temperature is close to that of NH_4(I). Similar closeness is also observed between the corresponding salt hydrates of Rb(I) and Cs(I). The order of thermal stability of the present salt hydrate with other Tutton salts of Mg(II) is as follows: $NH_4(I) \geqslant Tl(I) > Cs(I) = Rb(I) > K(I)$. But on deuteration the thermal stability of the present salt hydrate is close to that of other deuterated Tutton salts of Mg(II) except $(NH_4)_2Mg(SO_4)_2 \cdot 6D_2O$. Our earlier works report that the thermal stability increases slightly in the case of the corresponding salt hydrates of NH_4(I), Rb(I) and Cs(I) and increases considerably in the case of the corresponding K(I) series due to deuteration, whereas, a slight decrease in the thermal stability is observed in the case of $Tl_2Mg(SO_4)_2 \cdot 6D_2O$. The noticeable change in the thermal stability in the case of the corresponding salt hydrate of the K(I) series is probably due to the complete change in the nature of dehydration due to deuteration. The value of activation energy* obtained for the dehydration of the present salt hydrate is close to that of Cs(I) and is much higher in comparison to that of NH_4(I) and low with respect to the K(I) series. The value for Rb(I) is slightly high. It is noticed in our earlier work that the value of activation energy of dehydration of the Tutton salts of Mg(II) remains unaltered on deuteration except for the corresponding salt hydrate of the K(I) series where the value decreases to a considerable extent, thereby changing the order as follows: Rb(I)>Tl(I)>Cs(I)>K(I)>NH_4(I). The value of enthalpy change of dehydration of the present salt hydrate is close to those of the other Tutton salts of Mg(II). On deuteration like other series except the corresponding Rb(I) series where the value increases no effect on the value of enthalpy change of dehydration of the Tutton salts of Mg(II) is observed.

The nature of dehydration of the double salt hydrate of Co(II) of the present series is quite different from the corresponding salt hydrates of NH_4(I), K(I), Rb(I) and Cs(I). The corresponding salt hydrates of NH_4(I) and Rb(I) series lose water molecules in a single step, whereas, the corresponding salt hydrates of K(I) and Cs(I) show dehydration in two steps. The first step corresponds to four molecules of water and the second step corresponds to the rest. The intermediate products, i.e., $Tl_2Co(SO_4)_2 \cdot 1.5H_2O$ and $Tl_2Co(SO_4)_2 \cdot 0.25H_2O$ which are indicated from the corresponding thermogram, are unique in the sense that these types of intermediates are not observed during the dehydration of other Tutton salts, though the former type intermediate is observed in the thermogram of $Tl_2Zn(SO_4)_2 \cdot 6H_2O$. The nature of dehydration of all Tutton salts of Co(II) remains unaltered on deuteration. With respect to the first DTG peak temperature of $M(I)_2SO_4 \cdot CoSO_4 \cdot 6H_2O$ where M(I) = NH_4(I), K(I), Rb(I), Cs(I) and Tl(I) the thermal stability follows the order NH_4(I) ⩾ Rb(I)>Tl(I)>Cs(I)>K(I), whereas, the activation energy for the first step of dehydration follows practically a reverse order; Cs(I)>K(I)>Tl(I)> Rb(I)>NH_4(I) with respect to the order followed in thermal stability. It is noticed that the above order of thermal stability and the activation energy for the first step of dehydration of the deuterated salt hydrates of Co(II) of the Tutton series remain practically unaltered; only the basic difference in the above order is the similarity in the value of activation energy of the corresponding K(I) and Tl(I) series. But on deuteration of this salt hydrate both enthalpy change and activation energy slightly increase. It is also noticed that the value of enthalpy change for the dehydration of the salt hydrate of the present series is minimum in comparison to other Tutton salts of Co(II).

The nature of dehydration of the double salt hydrate of Ni(II) of the present series is similar to that of other corresponding salt hydrates of Ni(II) of the Tutton series except $K_2Ni(SO_4)_2 \cdot 6H_2O$ which loses water molecules in two steps. The first step corresponds to 5.5 molecules of water and the second to the rest. The nature of

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*Average of the values obtained from TG, DTA and DTG curves.

dehydration of this salt hydrate is not effected on deuteration like the other Tutton salts of Ni(II) except the salt hydrate of the corresponding Rb(I) series, which on deuteration shows dehydration in two steps. The first step corresponds to four molecules of D_2O and the second step to the rest. The position of the thermal stability of the present salt hydrate with respect to the other corresponding Tutton salts of Ni(II) can be seen from: $Rb(I)>K(I)\geqslant Tl(I)>Cs(I)>NH_4(I)$. On deuteration, the above order remains unaltered except the salt hydrate of Rb(I), whose DTG peak temperature becomes lowest. This considerable decrease of thermal stability of Rb(I) is probably due to a complete change in the nature of dehydration on deuteration. The value of activation energy for dehydration of the $Tl_2Ni(SO_4)_2\cdot 6H_2O$ is close to those of other Tutton salts of Ni(II). On deuteration, the value remains practically unaltered but differs considerably from the value of the corresponding deuterated salt hydrate of Rb(I). It is noticed in our earlier works that where the deuteration effect completely changes the nature of dehydration of the salt hydrate, the value of activation energy alters noticeably and it is also noticed that the value increases with increase in the number of steps during dehydration and vice versa. The value of enthalpy change for the dehydration of this salt hydrate is slightly greater than that of K(I) and less than those of the other Tutton salts of Ni(II). On deuteration the value of enthalpy change is minimum with respect to other deuterated salt hydrates. This is due to the increase in the value of enthalpy change of the corresponding salt hydrate of the K(I) series due to deuteration, though the value of enthalpy change of the present salt hydrate remains unaltered.

Dehydration of all the Cu(II) salt hydrates of the Tutton series occurs in multiple steps. The nature of dehydration of $Tl_2Cu(SO_4)_2\cdot 6H_2O$ is similar to that of the corresponding salt hydrate of the $NH_4(I)$ series. It is observed that the nature of dehydration remains practically the same in all the deuterated Tutton salts of Cu(II) except $K_2Cu(SO_4)_2\cdot 6D_2O$ where the first endotherm splits into two and the resolution of the second endotherm decreases. The thermal stability with respect to the first DTG peak temperature of the present salt hydrate is less than the corresponding salt hydrate of the $NH_4(I)$ and Cs(I) series and greater than those of the K(I) and Rb(I) series. The order of thermal stability of the Tutton salts of Cu(II) is as follows: $Cs(I)>NH_4(I)>Tl(I)>K(I)\geqslant Rb(I)$. It is observed that this order is maintained even on deuteration. The value of activation energy for the first step of dehydration of $Tl_2Cu(SO_4)_2\cdot 6H_2O$ is less than those of the corresponding Rb(I) and $NH_4(I)$ series and greater than those of Cs(I) and K(I). The decreasing order of the values of activation energies of the salt hydrates of Cu(II) is as follows: $Rb(I)>NH_4(I)>Tl(I)>Cs(I)\geqslant K(I)$. On deuteration of this salt hydrate the activation energy remains practically the same but the above order slightly changes as follows: $NH_4(I)>Rb(I)>Tl(I)>Cs(I)>K(I)$. The order in the value of enthalpy change for these Tutton salts of Cu(II) is as follows: $NH_4(I)>Rb(I)>K(I)>Tl(I)>Cs(I)$. On deuteration the value of enthalpy change slightly increases, but the above order is maintained.

The nature of dehydration of the double salt hydrate of Zn(II) of the present series is quite different from that of the other salt hydrates of the present series and also from the other Tutton salts of Zn(II), though the first step of dehydration is similar to that of the salt hydrate of Co(II) of the present series. The third step of dehydration of this salt hydrate is very complicated. On deuteration, the nature of dehydration changes but the last step of dehydration is similar to that of its H_2O analogue. However, it is observed that there is little effect on the nature of dehydration of the other Tutton salts of Zn(II) due to deuteration. The thermal stability is similar to that of the Cs(I) series but less than those of NH_4(I) and Rb(I) and greater than that of K(I) and the order is as follows: NH_4(I)>Rb(I)>Cs(I) ⩾Tl(I)>K(I). On deuteration, this order is maintained except Cs(I), where the thermal stability increases due to deuteration. The position of the value of activation energy of dehydration with respect to other Tutton salts of Zn(II) follows from: K(I)> Rb(I)>Tl(I)>Cs(I)>NH_4(I). On deuteration of this salt hydrate, the value of activation energy for the first step of dehydration increases though it is observed in our earlier work that the value of activation energy decreases where the number of step decreases for dehydration of the salt hydrates due to deuteration. However, the order of the activation energy is maintained on deuteration. The overall ΔH value is minimum with respect to those of other Tutton salts of Zn(II). On deuteration, the value of enthalpy change, which is not the overall value, but the value calculated for five molecules of D_2O, increases.

The relative thermal stability of all the salt hydrates of the present series is as follows: Ni(II)>Mg(II)=Co(II)>Zn(II)>Cu(II). On deuteration this order is not maintained but is as follows: Ni(II)>Co(II)>Mg(II)>Zn(II) ⩾Cu(II). The value of activation energy of the salt hydrates of the Tl(I) series decreases in the order: Mg(II)>Co(II)>Cu(II) ⩾ Ni(II)>Zn(II), but this order alters on deuteration as: Mg(II)>Co(II)>Zn(II) ⩾Cu(II)>Ni(II). This change in the order of activation energy is due to the change in the nature of dehydration of Zn(II) of the present series. The values of activation energies of the salt hydrates do not follow any relation with increase or decrease of ionic size or atomic number or 2nd ionisation potential of the divalent cation. The average ΔH values are, in general, low in comparison to those of other series. It is also observed that the value of activation energy for the later step of dehydration is always higher than the former step which is observed in our earlier works.

The differences in the thermal properties of dehydration from the salt hydrates of other series are due to a natural cause, i.e., slight difference in ionic size of monovalent cations. We attempted to isolate the double salt hydrate of Cd(II) and Mn(II) of the present series but could not succeed. The salt hydrate of Mn(II), though isolable, becomes anhydrous as soon as the crystals are removed from the mother liquor.

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