Non-isothermal Studies of the Dehydration of Double Salt Hydrates and Their Deuterium Oxide Analogues. I

N. RAY CHAUDHURI, M. K. DASGUPTA, S. MITRA, and G. K. PATHAK

Inorganic Chemistry Laboratory, Indian Association for the Cultivation of Science, Calcutta 700032, India

(Received December 10, 1976)

Non-isothermal studies of the dehydration of double salt hydrates of the type $(NH_4)_2AB_4 \cdot M(II)SO_4 \cdot 6H_2O$ and their D_2O analogues in solid state were carried out with a derivatograph, where $AB_4 = BeF_4^{2-}$ or SeO_4^{2-}, M(II)=Mg(II), Mn(II), Co(II), Ni(II), Cu(II), or Zn(II). These salt hydrate molecules lost water/heavy water in single or multiple steps upon heating. Intermediate hydrates were isolated and characterised by elemental analysis and IR spectral measurements. The activation energy for each step of dehydration of the salt hydrate was evaluated from the analysis of TG, DTG, and DTA curves of the respective derivatograms. Enthalpy change was evaluated from the DTA peak area and the order of reaction was found to be unity for each step of dehydration. The nature of dehydration was little affected by deuteration. Thermal parameters for the $(NH_4)_2AB_4 \cdot M(II)SO_4 \cdot 6H_2O$ and their D_2O analogues were compared with the salt hydrates, $K_2AB_4 \cdot M(II)SO_4 \cdot 6H_2O$, $(NH_4)_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$ and their D_2O analogues.

Non-isothermal 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] Cs(I),[4] or Tl(I)[5] and M(II)=Mg(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), or Cd(II) and their D_2O analogues were carried out. Thermal studies on the dehydration of double salt hydrates of the type $K_2AB_4 \cdot M(II)SO_4 \cdot 6H_2O$, where $AB_4 = BeF_4^{2-}$ or SeO_4^{2-} and their D_2O analogues[6] were also reported. These studies showed that the thermal properties are affected by changes of univalent cation and/or anion contained in the double salt hydrates. The present paper deals with the dehydration of double salt hydrates of the type $(NH_4)_2AB_4 \cdot M(II)SO_4 \cdot 6H_2O$ where $AB_4 = BeF_4^{2-}$ or SeO_4^{2-}, M(II) =Mg(II), Mn(II), Co(II), Ni(II), Cu(II), or Zn(II) and their D_2O analogues, which was carried out in order to see the cation effect with change of K(I) by NH_4 (I) and the anion effect with change of SO_4^{2-} by BeF_4^{2-} or SeO_4^{2-} attached to the univalent cation. The values of activation energies of dehydration processes were evaluated from TG, DTG and DTA curves simultaneously, the order of reaction from TG, enthalpy changes from DTA peak area and the thermal stability from first DTG peak temperature. The effect of deuteration on the thermal properties is described. The role of divalent cation on the thermal properties of dehydration is also discussed.

Experimental

Preparation of $(NH_4)_2BeF_4 \cdot M(II)SO_4 \cdot 6H_2O$ where M(II) =Mg(II), Mn(II), Co(II), Ni(II), Cu(II), or Zn(II). These salts were prepared by the standard procedure.[7-9]

Preparation of $(NH_4)_2SeO_4 \cdot M(II)SO_4 \cdot 6H_2O$, where M(II)=Mg(II), Mn(II), Co(II), Ni(II), Cu(II), or Zn(II). These salts were prepared by crystallization from a mixture of equimolecular proportions of the corresponding single salts in water. D_2O analogues of the salt hydrates were prepared by dissolving the anhydrous single salts required in D_2O (99.5%) and subsequent crystallization. Elemental analysis of all the salt hydrates and their D_2O analogues was carried out before thermal analysis.

A Paulik-Paulik-Erdey type MOM derivatograph was used for the thermal analysis. The particle size of the sample was 150—200 mesh. A platinum crucible was used, the heating rate being maintained at 1.5 °C min^{-1}. The volume of the sample was nearly the same in each case.

The following abbreviations were used for the double salt hydrates of the present two series and also other series given in Results and Discussion.

A: $(NH_4)_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$
B: $(NH_4)_2BeF_4 \cdot M(II)SO_4 \cdot 6H_2O$
C: $(NH_4)_2SeO_4 \cdot M(II)SO_4 \cdot 6H_2O$
A(K): $K_2SO_4 \cdot M(II)SO_4 \cdot 6H_2O$
B(K): $K_2BeF_4 \cdot M(II)SO_4 \cdot 6H_2O$
C(K): $K_2SeO_4 \cdot M(II)SO_4 \cdot 6H_2O$

The following abbreviations were used for representation of a particular salt of any series.

A-Mg(II): $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$
B-Mn(II): $(NH_4)_2BeF_4 \cdot MnSO_4 \cdot 6H_2O$
C-Co(II): $(NH_4)_2SeO_4 \cdot CoSO_4 \cdot 6H_2O$ *etc.*

Results

The derivatograms of B-Mg(II), B-Mn(II), and B-Co(II) are shown in Fig. 1. B-Mg(II) and B-Co(II) lose water molecules in a single step. The TG curve for the dehydration of B-Mn(II) shows dehydration taking place in a single step. However, the two DTA peaks partially overlap each other and two DTG peaks also partially overlap each other, indicating the existence of a thermally unstable intermediate product. The derivatograms of B-Ni(II), B-Cu(II), and B-Zn(II) are shown in Fig. 2. B-Ni(II) and B-Zn(II) show single step dehydration, whereas B-Cu(II) undergoes dehydration as follows: $(NH_4)_2BeF_4 \cdot CuSO_4 \cdot 6H_2O \rightarrow (NH_4)_2BeF_4 \cdot CuSO_4 \cdot H_2O \rightarrow (NH_4)_2BeF_4 \cdot CuSO_4$. The intermediate hydrate is not stable enough to be isolated. B-Mg(II) and B-Ni(II) start decomposition as soon as the dehydration ceases. The derivatograms C-Mg(II), C-Mn(II), and C-Co(II) are shown in Fig. 3. C-Mg(II) loses water molecules in a single step. C-Mn(II) becomes anhydrous passing through an unstable intermediate *i.e.*, dihydrate. The two DTA peaks and also the two DTG peaks overlap each other. C-Co(II) becomes anhydrous passing through an unstable hemihydrate. The derivatograms of C-Ni(II), C-Cu(II), and C-Zn(II) are shown in Fig. 4. C-Ni(II) and C-Zn(II) show dehydration in a single step, but the latter shows a shoulder in its DTA and DTG curves,

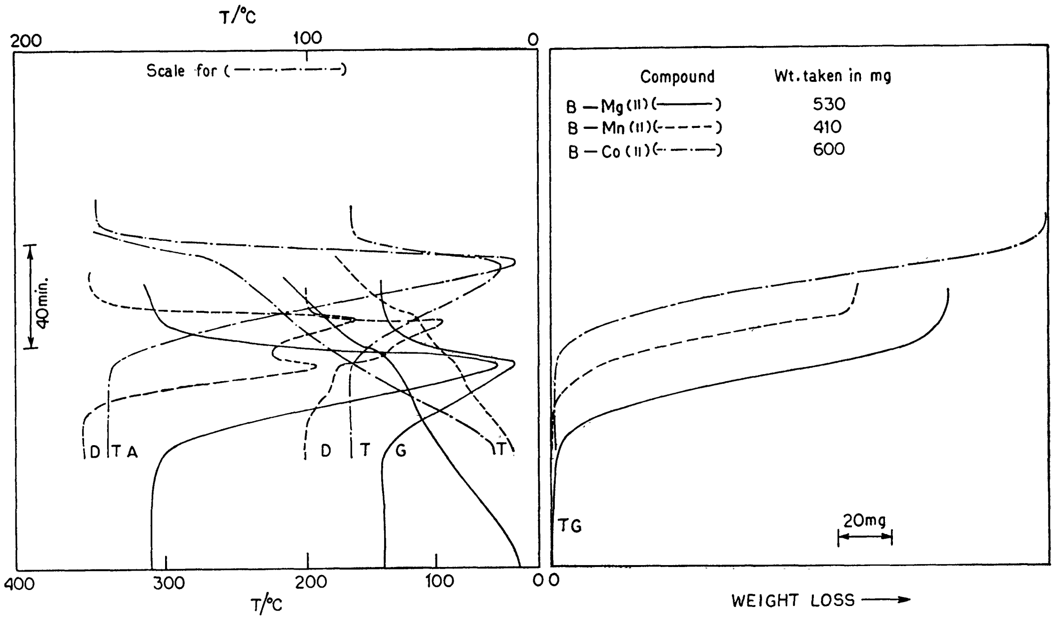

Fig. 1. Derivatograms for $(NH_4)_2BeF_4 \cdot MgSO_4 \cdot 6H_2O$[B-Mg(II) (——)], $(NH_4)_2BeF_4 \cdot MnSO_4 \cdot 6H_2O$[B-Mn(II) (— — —)], and $(NH_4)_2BeF_4 \cdot CoSO_4 \cdot 6H_2O$[B-Co(II) (—·—·—)].

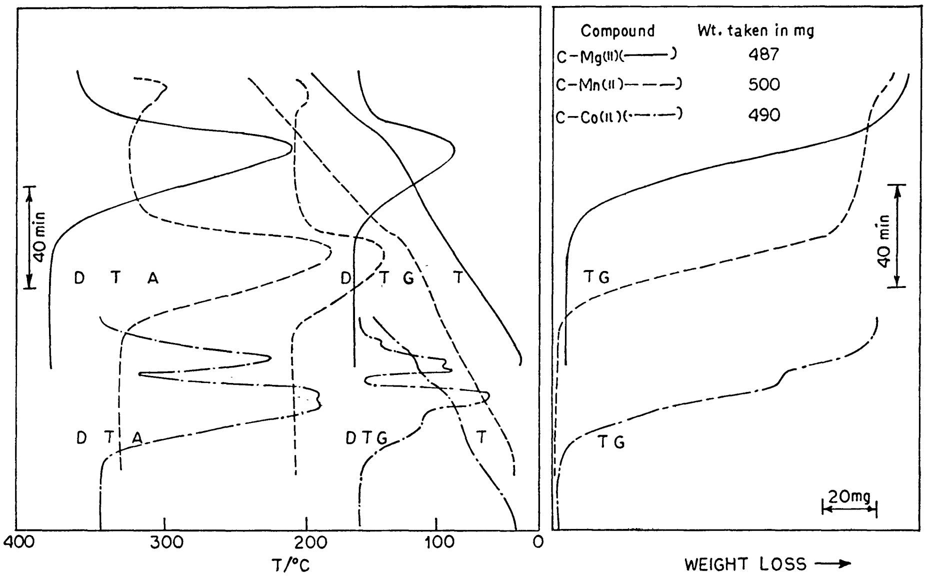

Fig. 3. Derivatograms for $(NH_4)_2SeO_4 \cdot MgSO_4 \cdot 6H_2O$[C-Mg(II) (——)], $(NH_4)_2SeO_4 \cdot MnSO_4 \cdot 6H_2O$[C-Mn(II) (—·—·—)], and $(NH_4)_2SeO_4 \cdot CoSO_4 \cdot 6H_2O$[C-Co(II) (————)].

indicating a very unstable intermediate hydrate. C-Cu(II) dehydrates through an unstable dihydrate. The derivatograms of the deuterated salt hydrates are not given since the nature of dehydration remains unaltered.

DTG peak temperatures and the temperature ranges of dehydration of the double salt hydrates of "B" and "C" and their D_2O analogues are given in Tables 1 and 2, respectively. Enthalpy changes for each step of dehydration of the double salt hydrates and their D_2O analogues were evaluated by the method used by Tsuchiya *et al.*[10] using copper sulfate pentahydrate as a standard. When the peaks are too much overlapped, the values are evaluated from the overall area of the DTA curves. 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 equation.[11] The activation energies for each step of dehydration were evaluated from the analysis of DTG curves using the method of Dave and Chopra[12] and also from that of DTA curves using the equation of Brochardt and Daniels[13] for first order reactions. In a few cases the values of activation energy obtained from TG curves appear high in comparison with those determined from the corresponding DTA and DTG curves (Table 2). As a result, we evaluated the activation energy also from TG curves

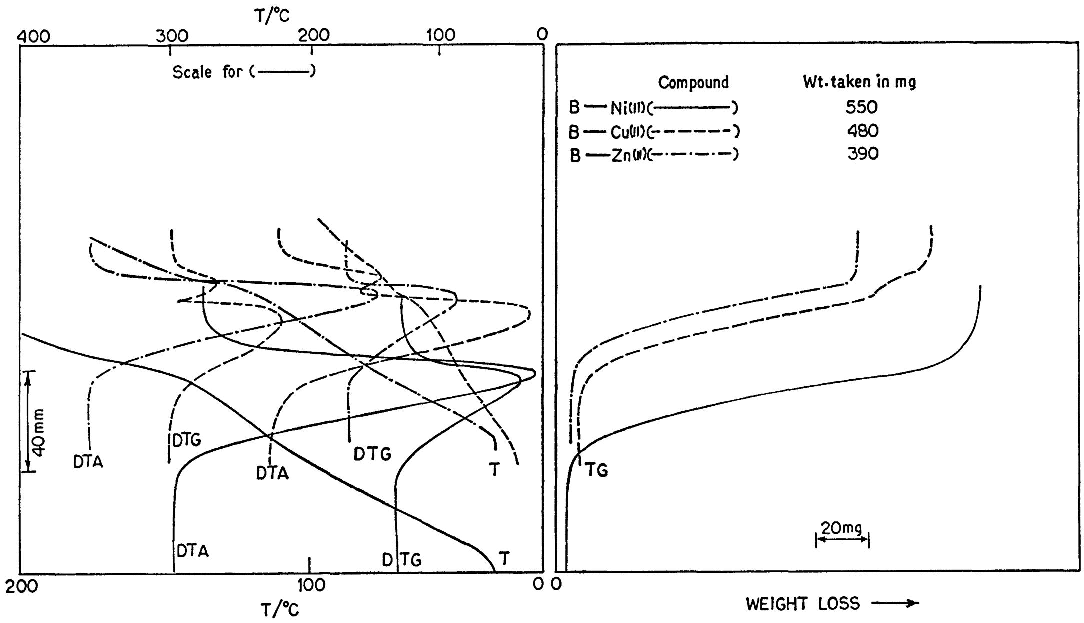

Fig. 2. Derivatograms for $(NH_4)_2BeF_4 \cdot NiSO_4 \cdot 6H_2O$[B-Ni(II) (——)], $(NH_4)_2BeF_4 \cdot CuSO_4 \cdot 6H_2O$ [B-Cu(II) (— — —)], and $(NH_4)_2BeF_4 \cdot ZnSO_4 \cdot 6H_2O$[B-Zn(II) (—·—·—)].

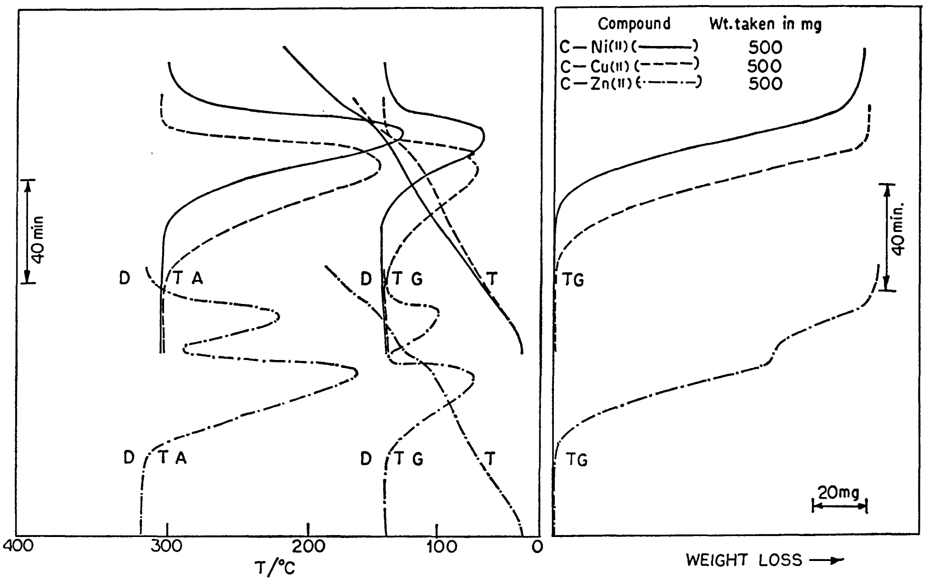

Fig. 4. Derivatograms for $(NH_4)_2SeO_4 \cdot NiSO_4 \cdot 6H_2O$[C-Ni(II) (——)], $(NH_4)_2SeO_4 \cdot CuSO_4 \cdot 6H_2O$[C-Cu(II) (—·—·—)], and $(NH_4)_2SeO_4 \cdot ZnSO_4 \cdot 6H_2O$[C-Zn(II) (————)].

using Horowitz and Metzger's equation[14] and a modified Dharwadkar and Phandnis equation.[15] The results are given in Table 2 within parentheses. The order of reaction is found to be unity for the dehydration of all the double salt hydrates and their D_2O analogues. The IR spectra of the salt hydrates and their D_2O analogues were taken to confirm the fact that the deuteration of the hydrates takes place to the desired extent.

Discussion

The patterns of elimination of water molecules of B-Mg(II) and C-Mg(II) are similar to each other, but differ from that of A-Mg(II). The mode of dehydration of B-Mg(II) does not differ from that of B(K)-Mg(II), but that of C-Mg(II) differs from that of C(K)-Mg(II) where dehydration takes place in double steps. B-Mn(II) differs from C-Mn(II), but shows similarity to A-Mn(II) with respect to the pattern of elimination of water molecules. B-Co(II) shows similarity to A-Co(II), but differs from C-Co(II) with respect to the elimination of water molecules. Our earlier work shows that the patterns of elimination of water molecules for both B-Co(II) and C-Co(II) differ from those of B(K)-Co(II) and C(K)-Co(II). The modes of elimination

TABLE 1. THERMAL PARAMETERS OF DEHYDRATION OF SALT HYDRATES (B) AND THEIR DEUTERIUM OXIDE ANALOGUES

	Decomposition reaction	Temp. range (°C)	DTC peak temp (°C)	Activation energy[a] (kcal mol^{-1})				Enthalpy change (kcal mol^{-1})
				TG	DTG	DTA	m[b]	
I	$(NH_4)_2BeF_4 \cdot MgSO_4 \cdot 6H_2O \longrightarrow (NH_4)_2BeF_4 \cdot MgSO_4$	75—181	120	29.6	26.5	33.0	30.6	12.5
I′	$(NH_4)_2BeF_4 \cdot MgSO_4 \cdot 6D_2O \longrightarrow (NH_4)_2BeF_4 \cdot MgSO_4$	72—174	117	26.3	30.6	29.9		14.4
II	$(NH_4)_2BeF_4 \cdot MnSO_4 \cdot 6H_2O \longrightarrow (NH_4)_2BeF_4 \cdot MnSO_4$	49—130	112	34.5	—	—		14.7[c]
II′	$(NH_4)_2BeF_4 \cdot MnSO_4 \cdot 6D_2O \longrightarrow (NH_4)_2BeF_4 \cdot MnSO_4$	47—130	107	34.5	—	—		11.1[c]
III	$(NH_4)_2BeF_4 \cdot CoSO_4 \cdot 6H_2O \longrightarrow (NH_4)_2BeF_4 \cdot CoSO_4$	70—164	126	23.4	24.5	23.4	46.0	16.0
III′	$(NH_4)_2BeF_4 \cdot CoSO_4 \cdot 6D_2O \longrightarrow (NH_4)_2BeF_4 \cdot CoSO_4$	68—160	120	23.0	28.7	30.6		15.3
IV	$(NH_4)_2BeF_4 \cdot NiSO_4 \cdot 6H_2O \longrightarrow (NH_4)_2BeF_4 \cdot NiSO_4$	84—200	145	21.2	26.8	22.0	34.1	13.3
IV′	$(NH_4)_2BeF_4 \cdot NiSO_4 \cdot 6D_2O \longrightarrow (NH_4)_2BeF_4 \cdot NiSO_4$	81—195	145	20.8	23.0	21.0		12.7
Va	$(NH_4)_2BeF_4 \cdot CuSO_4 \cdot 6H_2O \longrightarrow (NH_4)_2BeF_4 \cdot CuSO_4 \cdot H_2O$	55—120	107	34.5	34.5	—	40.2	13.4[c]
Vb	$(NH_4)_2BeF_4 \cdot CuSO_4 \cdot H_2O \longrightarrow (NH_4)_2BeF_4 \cdot CuSO_4$	120—185	145	133.4	—	—		
V′a	$(NH_4)_2BeF_4 \cdot CuSO_4 \cdot 6D_2O \longrightarrow (NH_4)_2BeF_4 \cdot CuSO_4 \cdot D_2O$	53—120	108	32.4	32.4	—		13.9[c]
V′b	$(NH_4)_2BeF_4 \cdot CuSO_4 \cdot D_2O \longrightarrow (NH_4)_2BeF_4 \cdot CuSO_4$	120—181	145	128.8	—	—		
VI	$(NH_4)_2BeF_4 \cdot ZnSO_4 \cdot 6H_2O \longrightarrow (NH_4)_2BeF_4 \cdot ZnSO_4$	59—142	117	20.0	23.0	23.0	25.2	12.5
VI′	$(NH_4)_2BeF_4 \cdot ZnSO_4 \cdot 6D_2O \longrightarrow (NH_4)_2BeF_4 \cdot ZnSO_4$	55—140	115	20.9	24.7	25.1		10.9

a) In some cases thermal parameters could not be calculated due to very poor resolution of the curve. b) Activation energy for the first step of dehydration of B(K). c) Overall enthalpy change where DTA curves overlap too much.

of water molecules of B-Ni(II) and C-Ni(II) are similar to each other and are also similar to A-Ni(II). B-Ni(II) shows no change in the elimination of water molecules due to the change of cation K by NH_4, but in C-Ni(II) a difference is observed from C(K)-Ni(II) where dehydration takes place in double steps. The patterns of elimination of water molecules of B-Cu(II) and C-Cu(II) differ from each other, and also from A-Cu(II) where dehydration takes place in three steps. Both B-Cu(II) and C-Cu(II) differ in the nature of dehydration from B(K)-Cu(II) and C(K)-Cu(II), respectively. Apparently A-Zn(II), B-Zn(II), and C-Zn(II) show no difference in the nature of dehydration, but in C-Zn(II) a slight difference is observed. B-Zn(II) shows similarity to B(K)-Zn(II). C-Zn(II) difffers from C(K)-Zn(II) with respect to the elimination of water molecules.

Salt hydrates of "B" show no dihydrate, whereas our earlier work on the dehydration of the salt hydrates of "B(K)" shows thermally stable dihydrates in the cases of Co(II) and Cu(II). On the other hand, salt hydrates of "C" show the existence of thermally unstable dihydrates in the cases of Mn(II) and Cu(II), and the salt hydrates of "C(K)" show thermally stable dihydrates in the cases of Mg(II), Co(II), Ni(II), and Zn(II).

No noticeable change in the nature of dehydration due to deuteration is observed in the salt hydrates of "A", "B", and "C". In the salt hydrates of "B(K)" a slight deuteration effect was observed in the case of Cu(II) only, whereas appreciable deuteration effect was observed in C(K)-Ni(II) and C(K)-Cu(II).

The first DTG peak temperature of the salt hydrates of "B" shows thermal stability to be in the order: Ni(II)>Co(II)>Mg(II)>Zn(II)>Mn(II)>Cu(II) and that of "C" in the order: Ni(II)>Mg(II)>Co(II)>Zn(II)>Cu(II)>Mn(II). In both series thermal stability of Ni(II) is appreciably high. This phenomenon is observed in "A" and also in "B(K)" and "C(K)" we reported.

In our works on non-isothermal studies on the dehydration of salt hydrates we evaluated the value of activation energy and order of reaction (n) from TG using Freeman and Carroll's equation,[11] reaction order always being found to be unity. It was observed that the specific rate constant of the reaction at different temperatures can be ascertained from the equation of Dave and Chopra[12] as follows:

$$k = \frac{\left(\frac{A}{N_0}\right)^{n-1}\left(-\frac{dx}{dt}\right)}{(A-a)^n},$$

where k=specific rate constant,

N_0=number of molecules of the sample at the time when DTG peak appears,

A and a=the total peak area and the area swept up till time t,

dx/dt=the displacement of DTG curve from the base line at time t,

and n=the order of reaction.

The values of log k are plotted against the reciprocal of the absolute temperature assuming different values of n, the correct one resulting in a straight line. The slope of the line gives the value of activation energy for the order of reaction. The value of n evaluated by this method is in good agreement with the value determined from Freeman and Carroll's equation. When the value of n becomes greater or less than unity, evaluation of the specific rate constant by means of Brochardt and Daniel's equation becomes very difficult. We did not face this difficulty as we observe unit value of n evaluated from the plot of Freeman and Carroll's equation. As a result we chose Freeman and Carroll's equation instead of other kinetic equations, *e.g.*,

TABLE 2. THERMAL PARAMETERS OF DEHYDRATION OF SALT HYDRATES (C) AND THEIR DEUTERIUM OXIDE ANALOGUES

	Decomposition reaction	Temp range (°C)	DTG peak temp (°C)	Activation energy[a] (kcal mol^{-1}) TG	DTG	DTA	m[b]	Enthalpy change (kcal mol^{-1})
I	$(NH_4)_2SeO_4\cdot MgSO_4\cdot 6H_2O \longrightarrow (NH_4)_2SeO_4\cdot MgSO_4$	85—200	132	28.8, (29.7),[c] (25.5)[d]	30.6	27.6	69.0	10.1
I′	$(NH_4)_2SeO_4\cdot MgSO_4\cdot 6D_2O \longrightarrow (NH_4)_2SeO_4\cdot MgSO_4$	80—195	130	27.6	20.9	24.3		10.8
IIa	$(NH_4)_2SeO_4\cdot MnSO_4\cdot 6H_2O \longrightarrow (NH_4)_2SeO_4\cdot MnSO_4\cdot 2H_2O$	50—90	87	32.8	—	—		12.2[e]
IIb	$(NH_4)_2SeO_4\cdot MnSO_4\cdot 2H_2O \longrightarrow (NH_4)_2SeO_4\cdot MnSO_4$	108—142		64.4	—	—		
II′a	$(NH_4)_2SeO_4\cdot MnSO_4\cdot 6D_2O \longrightarrow (NH_4)_2SeO_4\cdot MnSO_4\cdot 2D_2O$	50—92	88	35.8	—	—		10.6[e]
II′b	$(NH_4)_2SeO_4\cdot MnSO_4\cdot 2D_2O \longrightarrow (NH_4)_2SeO_4\cdot MnSO_4$	92—150	120	43.3	—	—		
IIIa	$(NH_4)_2SeO_4\cdot CoSO_4\cdot 6H_2O \longrightarrow (NH_4)_2SeO_4\cdot CoSO_4\cdot 0.5H_2O$	87—200	121	64.4, (24.5),[c] (25.5)[d]	21.2	24.7	54.4	11.8
IIIb	$(NH_4)_2SeO_4\cdot CoSO_4\cdot 0.5H_2O \longrightarrow (NH_4)_2SeO_4\cdot CoSO_4$	200—245	235	—	—	—		
III′a	$(NH_4)_2SeO_4\cdot CoSO_4\cdot 6D_2O \longrightarrow (NH_4)_2SeO_4\cdot CoSO_4\cdot 0.5D_2O$	87—200	118	69.0, (26.6),[c] (25.3)[d]	28.7	28.3		10.8
III′b	$(NH_4)_2SeO_4\cdot CoSO_4\cdot 0.5D_2O \longrightarrow (NH_4)_2SeO_4\cdot CoSO_4$	200—245	237	—	—	—		
IV	$(NH_4)_2SeO_4\cdot NiSO_4\cdot 6H_2O \longrightarrow (NH_4)_2SeO_4\cdot NiSO_4$	97—200	145	29.0	27.0	33.0	37.1	10.6
IV′	$(NH_4)_2SeO_4\cdot NiSO_4\cdot 6D_2O \longrightarrow (NH_4)_2SeO_4\cdot NiSO_4$	98—200	142	36.1	21.9	25.8		12.3
Va	$(NH_4)_2SeO_4\cdot CuSO_4\cdot 6H_2O \longrightarrow (NH_4)_2SeO_4\cdot CuSO_4\cdot 2H_2O$	60—115	102	28.8	30.6	—	23.0	13.9
Vb	$(NH_4)_2SeO_4\cdot CuSO_4\cdot 2H_2O \longrightarrow (NH_4)_2SeO_4\cdot CuSO_4$	125—165	145	64.4, (46.0),[c] (32.2)[d]	42.4	—		
V′a	$(NH_4)_2SeO_4\cdot CuSO_4\cdot 6D_2O \longrightarrow (NH_4)_2SeO_4\cdot CuSO_4\cdot 2D_2O$	50—120	100	26.3	25.1	—		11.7
V′b	$(NH_4)_2SeO_4\cdot CuSO_4\cdot 2D_2O \longrightarrow (NH_4)_2SeO_4\cdot CuSO_4$	120—180	145	76.6, (40.2),[c] (36.8)[d]	39.4	—		
VI	$(NH_4)_2SeO_4\cdot ZnSO_4\cdot 6H_2O \longrightarrow (NH_4)_2SeO_4\cdot ZnSO_4$	60—140	115	23.0	24.8	23.0	23.0	12.9
VI′	$(NH_4)_2SeO_4\cdot ZnSO_4\cdot 6D_2O \longrightarrow (NH_4)_2SeO_4\cdot ZnSO_4$	70—140	120	26.3	23.0	27.6		14.0

a) In some cases thermal parameters could not be calculated due to very poor resolution of the curve. b) Activation energy for the first step of dehydration of C(K). c) Evaluated by method of Horowitz and Metzger. d) Evaluated by modified method of Dharwadkar and Phadnis. e) Overall ethalpy change.

Horowitz and Metzger,[14] modified Dharwadkar and Phadnis[15] *etc.* for TG curves where the value of n is based on assumption. The value of n obtained by using Freeman and Carroll's equation appears greater or less than one besides the unit value in number of cases observed by different workers.[16–18] However, in our works on salt hydrates[1–6] and the adduct molecules of metallic halides[19–23] with oxo compounds we did not find the order of reaction other than unity, and found a closeness of values of activation energy evaluated using Freeman and Carroll's equation for TG, Dave and Chopra's equation for DTG and Brochardt and Daniel's equation for DTA. This is also observed in most of the cases of the present two series. In a few cases (see Table 2) Freeman and Carroll's equation shows values appreciably high in comparison with the values evaluated from DTA and DTG curves. In such cases on application of two other standard equations, Horowitz and Metzger's equation and modified Dharwadkar and Phadnis equation, to the TG curve, the value of activation energy becomes closer to those obtained from DTA and DTG curve. However, when the value of activation energy obtained by using Freeman and Carroll's equation does not differ much from that evaluated from DTA and DTG curves, application of other two methods to the TG curve gives comparable values. Under such context we have emphasised Freeman and Carroll's equation because of its advantage over the other kinetic equation for TG curve.

The activation energy for the first step of dehydration of salt hydrates of "A" increased with increase in atomic number in the order Mg(II)<Mn(II)<Co(II)<Ni(II), reaching a maximum in Cu(II) and decreasing as Zn(II)>Cd(II). This trend is not observed in both of the present series. The values of activation energy for the first step of dehydration of B-Mg(II), B-Mn(II) and B-Cu(II) are very close and the values of B-Co(II), B-Ni(II), and B-Zn(II) are close to each other respectively, but the former values are appreciably high (Table 1). The highest value of activation energy is observed in C-Mn(II). The values of activation energies of C-Mg(II), C-Ni(II), and C-Cu(II) are close to each other. Those of C-Co(II) and C-Zn(II) are also close, but the former values are higher than those of latter such as the salt hydrates of "B" (Table 2). B-Ni(II) shows considerably low value of activation energy due to change of K by NH_4, though the pattern of dehydration hardly differs. The difference in the value of activation energy between the salt hydrates of "B" and "C" is not so prominent as was observed for the salt hydrates of "B(K)" and "C(K)" (Tables 1 and 2).

No deuteration effect is observed on the value of activation energy in both the salt hydrates of "B" and "C". It was observed in the salt hydrates of "B(K)" and more clearly in the salt hydrates of "C(K)".

The values of enthalpy changes of dehydration of the salt hydrates of "B" and "C" are ≈ 10—≈ 16 kcal mol^{-1}. Deuteration causes no marked effect on the value of ΔH.

In the salt hydrates of "A", "B", and "C" for particular divalent cation except Mg(II) and Cu(II) we observed pronounced anion effect with respect to elimination of water molecules, whereas this effect was observed for each divalent cation amongs the salt hydrates of "A(K)", "B(K)", and "C(K)".

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