Non-isothermal Studies of Dehydration of Double Selenate Hydrates of Potassium with Divalent Metal Ions & Their Deuterium Oxide Analogues

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Non-isothermal studies of dehydration of double selenate hydrates of the type $M(I)_2SeO_4.M(II)SeO_4.6H_2O$ and their $D_2O$ analogues have been carried out (where $M(I) = K(I)$ and $M(II) = Mg(II)$, Co(II), Ni(II), Cu(II) or Zn(II)). Activation energy has been evaluated for each step of dehydration from TG, DTA and DTG curves simultaneously. Enthalpy change has been evaluated from the DTA peak area. Order of reaction for dehydration is found to be unity. The nature of dehydration is affected in the case of Mg(II), Ni(II) and Zn(II) salt hydrates on deuteration. Thermal parameters have been compared with the corresponding double sulphate hydrates.

Earlier, we reported non-isothermal studies on the dehydration of double sulphate hydrates of the type $M(I)_2SO_4.M(II)SO_4.6H_2O$, where $M(I) = NH_4(I)$, K(I), Rb(I), Cs(I) or TI(I) and $M(II) = Mg(II)$, Mn(II), Co(II), Ni(II), Cu(II), Zn(II) or Cd(II) and their $D_2O$ analogues. We also reported the thermal studies of dehydration of double salt hydrates of the type $K_2AB_4.M(II)SO_4.6H_2O$ where $AB_4 = BeF_2$ or $SeO_4^2$ and their $D_2O$ analogues. These studies indicated that the thermal parameters of the isomorphous salt hydrates were affected with change of monovalent cation of the double salt hydrates and also with change of anion. The non-isothermal dehydration of double selenate hydrates of potassium series and their $D_2O$ analogues has now been investigated. We report in this paper (i) values of activation energies of dehydration processes evaluated from TG, DTG and DTA curves simultaneously, (ii) order of reaction from TG, (iii) enthalpy change from DTA peak area, (iv) thermal stability from first DTG peak temperature, (v) effect of deuteration on the thermal properties, and (vi) the role of divalent cation of the present series on the thermal properties of dehydration. Thermal parameters have been compared with the corresponding double sulphate hydrates.

Materials and Methods

Double selenate hydrates were prepared by dissolving the equimolecular proportions of single salts in water and subsequent crystallization. $D_2O$ analogues were prepared by dissolving the anhydrous double selenates in $D_2O$ (99.5%) and subsequent crystallization. A Paulik-Paulik-Erdey type MOM derivatograph has been used for thermal analysis. A platinum crucible was used and the heating rate was maintained 1.5° min⁻¹. The particle size of the samples was within 150-200 mesh.

Results

The derivatograms of double selenate hydrates of Mg(II), Co(II) and Ni(II) are shown in Fig. 1. All these salt hydrates become anhydrous passing through a thermally stable dihydrate. The DTG curves for the first step of dehydration of Co(II) and Ni(II) provide indications of thermally unstable intermediate hydrates. The salt hydrate of the TG curve for the dehydration of Cu(II) salt hydrate shows dehydration taking place as follows: $K_2Cu(SeO_4)_2.6H_2O \rightarrow K_2Cu(SeO_4)_2.5H_2O \rightarrow K_2Cu(SeO_4)_2$ (Fig. 2), whereas corresponding DTA and DTG curves for the first step of dehydration overlap indicating the existence of thermally unstable intermediate. The salt hydrate of Zn(II) shows dehydration similar to that of Co(II) (Fig. 2). The DTG curves for the first step of dehydration of the salt hydrate of Mg(II) and its deuterated analogue overlap showing the formation of an intermediate deuterated hydrate. The nature of dehydration of salt hydrate of Ni(II) and its deuterated analogue is identical to the behaviour exhibited by salt hydrates of Mg(II). However, the derivatogram in the case of Ni(II) salt hydrates show that the range of thermal stability of the intermediates in the case of deuterated analogue is less as compared to that of aqurated salt. In the case of Zn(II) salt hydrate the DTA and DTG curves for the second step of dehydration splits into two in the case of deuterated analogue.

DTG peak temperatures and temperature ranges of dehydration of the double selenate hydrates and their $D_2O$ analogues are listed in Table 1. Enthalpy changes for each step of dehydration of the double selenate hydrates and their $D_2O$ analogues are evaluated by the method of Sano using copper sulphate pentahydrate as the standard and the values are tabulated in Table 1. $\Delta H$ values are
Evaluated from the overall area of the DTA curves, where the peaks are too much overlapped. Activation energies for each step of dehydration of the salt hydrates and their D$_2$O analogues are evaluated from the analysis of TG curves using Freeman and Carroll's equation$^9$. The results are given in Table 1. The activation energies for each step of dehydration are also evaluated from the analysis of DTG curves using the method of Dave and Chopra$^{10}$ and also from the analysis of DTA curves using Brochardt's equation$^{11}$ for first order reactions. All these values are recorded in Table 1. The IR spectra of the salt hydrates and their D$_2$O analogues are taken to ensure the deuteration of the hydrates has taken place to the desired extent. X-ray diffraction patterns show that the salt hydrates and their corresponding D$_2$O analogues are isomorphous to each other.

Discussion

The nature of dehydration of double selenate hydrates of Mg(II) differs from that of double sulphate hydrates where dehydration has been shown to take place in three steps showing thermally stable tetrahydrate and dihydrate as intermediates. It has earlier been observed that on deuteration of
The double sulphate hydrate of Mg(II) dehydration takes place in a single step. The nature of dehydration of salt hydrate of Co(II) differs a little from the corresponding double sulphate hydrate where no sign of overlapping nature of the DTA and DTG curves for the first step dehydration has been observed. In the case of Ni(II), the nature of dehydration differs from that of double sulphate hydrates which show an unstable hemihydrate as an intermediate. The double selenate hydrates of Cu(II) also differ in the nature of dehydration from that of double sulphate hydrates which become anhydrous in two steps passing through a thermally stable dihydrate as an intermediate and the corresponding DTA and DTG curves for both the steps are found to overlap. On deuteration of the double sulphate hydrate of Cu(II), the first endotherm has been found to split into two and the resolution of the second endotherm becomes diffused. The nature of dehydration of double selenate of Zn(II) differs a little from that of double sulphate hydrate where DTA and DTG curves for the second step of dehydration are of overlapping nature. Besides this deuteration effect has not been observed in the case of double sulphate hydrates.

The first DTG peak temperature of the salt hydrates of the present series shows the following order of thermal stability: Ni(II) > Mg(II) > Cu(II) = Zn(II) > Co(II). The thermal stability of Ni(II) is appreciably high. This was also observed in the corresponding double sulphate hydrates. The thermal stabilities of the dihydrates of Mg(II), Co(II) and Cu(II) are comparable. The dihydrate of Zn(II) is less stable. This is in accord with the behaviour of the corresponding double sulphate hydrates. On deuteration the double selenate hydrates show the following order of thermal stability: Ni(II) > Zn(II) > Mg(II) > Cu(II) > Co(II).

The value of activation energy evaluated for the first step of dehydration of Mg(II) is less than that of the corresponding double sulphate hydrate and is appreciably high as compared to its D$_2$O analogue. We observed in our earlier works that the value of activation energy was low where the dehydration took place in single step and the value was high where dehydration took place in more than one step. In the case of double sulphates of Mg(II), aquated salt lost water molecules in three steps, whereas, its D$_2$O analogue lost all its D$_2$O molecules in a single step. The activation energy for the D$_2$O analogue was about 30 kcal mole$^{-1}$ and for the aquated salt it was 69.0, 103.0 and 168.0 kcal mole$^{-1}$ respectively. The value of activation energy for the first step of dehydration of double selenate hydrate of Co(II) is high when compared with that of double sulphate hydrate, but the value for the second step of dehydration is close. Table 1 shows that the value of activation energy evaluated from TG using Freeman and Carroll's equation are comparable to those obtained from the analysis of the corresponding DTG and DTA curves. However, Ni(II) shows deviation in that the value obtained from TG is appreciably high than that obtained from DTA curves. In this case we applied modified Coats and Redfern's method and found the value to be comparable with the value obtained from DTA curve. In our earlier and also present works we have emphasized on Freeman and Carroll's equation because of the fact that this equation gives order of reaction directly, whereas other TG methods do not give order of reaction.
directly and activation energy is calculated assuming the order of reaction to be unity. In the corresponding double sulphate hydrates the values of activation energy are almost same for deuterated analogues, whereas in the present series, values are appreciably high for deuterated analogues though the nature of dehydration remains the same. The value of activation energy of the double selenate hydrate of Cu(II) is appreciably high in comparison to that of double sulphate hydrate. In the case of Zn(II) the value of $E_a$ for the first step of dehydration is close to that of double sulphate, whereas the value for the second step is appreciably high in comparison to that of double sulphate.

It is observed that the value of enthalpy change of dehydration of salt hydrate is in the range 12-18 kcal mole$^{-1}$. The value of enthalpy change is effected in the case of deuterated analogues of Mg(II) and Ni(II).

We observe differences in the thermal behaviour of the salt hydrates of the present series and also differences between the salt hydrates of double selenates and double sulphates. For a suitable explanation of the difference we have analysed the crystal constants of the salt hydrates given by Tutton$^{13}$. In the present series axial angles of Co(II), Ni(II) and Zn(II) are very close whereas the value in the case of Mg(II) is appreciably high and is low by about a degree in the case of Cu(II). This trend is reflected in the thermal stabilities of the double selenate hydrates of Co(II), Ni(II) and Zn(II) of the present series, which are quite close. The similarity in the thermal stability in the case of Mg(II) is hard to account from the value of crystal constants. The difference exhibited by Cu(II) is probably due to difference in the value of axial angle as stated already.

The values of crystal constants of double selenate hydrate$^{13}$ of Mg(II) are appreciably high as compared to that of double sulphate hydrate. The magnitude of this difference is higher in the case of Cu(II) where axial angle of double selenate hydrate is 103°19' as compared to the value 75°32' for double sulphate hydrate. In the case of Ni(II) crystal constants for double sulphates and double selenates were evaluated by two groups of workers. Tutton's values of the axial angles differ about a degree whereas the values given by the other workers differ by about 15°. This may account for the difference in the thermal behaviour between the double selenate hydrates and double sulphate hydrates of Mg(II), Ni(II) and Cu(II). The crystal constants of the double selenate and double sulphate hydrates of Co(II) are very close. Similar closeness is observed in the case of Zn(II) and these are reflected in their thermal behaviour.

References