Thermochimica Acta, 92 (1985) 561-562
Elsevier Science Publishers B.V., Amsterdam

INVESTIGATION OF THERMAL STABILITY AND NATURE OF PROTON CONTAINING GROUPS IN COMPOUNDS OF ZIRCONIUM AND HAFNIUM WITH INORGANIC LIGANDS

Zinaida N. Prozorovskaya, Moscow State University,
Department of Chemistry
Moscow,USSR
Lidia N. Komissarova, Moscow State University,
Department of Chemistry
Moscow, USSR
Olga I. Erohina, Moscow State University,
Department of Chemistry
Moscow, USSR

Dehydration kinetics of zirconium and hafnium bisulphate tetrahydrates, oxinitrate hexahydrates and zirconium basic carbonates in isothermic conditions on air has been studied. Kinetic regions of dehydration processes have been located, rate constants and activation energies E^* have been calculated.

Dehydration kinetics of mentioned crystallohydrates have been investigated also in polythermal conditions on derivatograph, reaction orders n and E^* have been calculated. Values of E^* (kcal/mol) and n are listed below (M is Zr or Hf): 50±3 for $M(SO_4)_2 \cdot H_2O$ (n=1), 33±3 for $M(SO_4)_2 \cdot 4H_2O$ (n=1), 23±1 for $MO(NO_3)_2 \cdot 6H_2O$ (n=1), 17±1 for $MO(NO_3)_2 \cdot 2H_2O$ (n=1) and for $Zr_2O_3CO_3 \cdot 5.5H_2O$ (n=2) and 15±1 for $Zr_2O_3CO_3 \cdot 3H_2O$ (n=1).

Dehydration enthalpies and entropies have been calculated by DTA and tensometric methods. Values of enthalpies (kcal/mol) are listed below: 30±2 for $M(SO_4)_2 \cdot H_2O$, 20±2 for $M(SO_4)_2 \cdot 4H_2O$ (tens. 17), 17±1.5 for $MO(NO_3)_2 \cdot 6H_2O$ (tens. 13), 12±1 for $MO(NO_3)_2 \cdot 2H_2O$ and 8±0.7 for carbonates. Changes in values of E^* and enthalpies are in accordance with changes in bond strength of H_2O in compounds considered.

Proceedings of ICTA 85, Bratislava

All examined compounds have been studied by methods of IR and PMR spectroscopies , by which composition formulas of carbonates and oxinitrates have been obtained, i.e. $MO(NO_3)_2 \cdot 2H_2O$ can be represented as $[M_2O(OH)_2(NO_3)_x \cdot 3H_2O](NO_3)_{4-x}$. Interprotonic distances of water molecules have been calculated. These distances define degree of deformation and bond strength in compounds and alter in following order : $M(SO_4)_2 \cdot H_2O$ > $MO(NO_3)_2 \cdot 2H_2O$ (obtained by heat treatment of hexahydrate) > $M(SO_4)_2 \cdot 4H_2O$ > $MO(NO_3)_2 \cdot 6H_2O$ > > $MO(NO_3)_2 \cdot 2H_2O$ (obtained from solution). This order coincides with changes of E^* and enthalpies of dehydration processes.