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THERMAL ANALYSIS IN INORGANIC CHEMISTRY: PROGRESS REPORT

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ABSTRACT

Some recent advances in thermal analysis in inorganic chemistry are reviewed. New applications of sulphates have intensified research into their thermal stability. The decomposition of Cu_2SO_4 was shown to be complex owing to several competitive redox reactions. Among coordination compounds, new metal ammine complexes have been prepared and studied by TG and DTA. It was shown that for hexammine complexes the reduction of Co(III) to Co(II) occurs. Hydrates represent a very broad and widely studied class of compounds. Dehydration temperatures have often been used to propose the nature of bonding of water molecules. This correlation is not simple and should be used with caution. For the application of quantitative DTA, new computing techniques and new measuring cells have been proposed. Much work has been published on the kinetics of the oxidation of organic compounds by Ce(IV) in solution. The mechanism of the reactions between monocarboxylic acids and Ce(IV) has been evaluated.

INTRODUCTION

Thermoanalytical techniques have found very wide application in inorganic chemistry. In this short report some examples of recent advances in the field are outlined, particularly those connected with the poster sessions held at the 8th ICTA in Bratislava.

DISCUSSION

Inorganic sulphates have been extensively studied. In addition to academic interest, they have always played an important role in metallurgy. Recently, sulphates found new applications, such as the removal of sulphur oxides from combustion gases and the preparation of metal oxides with fine particle size.

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The thermal decomposition of inorganic sulphates is usually represented by two simultaneous equilibria:

$$MSO_4 = MO + SO_3$$

$$SO_3 = SO_2 + \tfrac{1}{2}O_2$$

There are a number of sulphates for which the decomposition stoichiometry appears to be more complex. For first-row transition metal sulphates the reactions are additionally complicated by redox reactions. Copper sulphates, especially Cu(I) sulphate, is a typical example.

Cu_2SO_4 disproportionates on heating in an inert atmosphere to give Cu and $CuSO_4$ at about 500 K [1]. The decomposition of Cu_2SO_4 in air yields $CuSO_4$ and Cu_2O in the same temperature range. At higher temperatures and under an inert atmosphere the products are also $CuSO_4$ and Cu_2O.

Debinski and Walszak [2] studied the decomposition of Cu_2SO_4 in an SO_2 atmosphere. They found that Cu_2SO_4 decomposes in three endothermic steps. Below 570 K, Cu_2SO_4 disproportionates mainly to Cu and $CuSO_4$. A small amount of Cu_2O has also been found as the decomposition product, indicating that there are at least two reactions taking place at lower temperatures. In the second step a considerable decrease in the amount of Cu and $CuSO_4$ in the sample has been detected, together with an increase in the amount of Cu_2O. In the last stage the remaining Cu and Cu_2SO_4 react completely to give Cu_2O. The whole process can be described by several competitive reactions having different kinetics.

Coordination chemistry is also a field where thermal analysis has widely been applied. Classical ammine complexes with anions other than fluoride are among the compounds studied most extensively. It is also a field where several other techniques such as magnetic measurements, infrared spectroscopy and polarography have been applied. It was shown, mainly by Wendlandt and co-workers [3–5], that the reduction of Co(III) to Co(II) occurs during the decomposition. For $[Co(NH_3)_6]X_3$ the decomposition stoichiometry depends on the nature of the anion. For $X = Cl$ the reaction is

$$6[Co(NH_3)_6]Cl_3 = 6CoCl_2 + N_2 + 6NH_4Cl + 28NH_3$$

but for $X = I$

$$2[Co(NH_3)_6]I_3 = 2CoI_2 + I_2 + 12NH_3$$

which is a good example illustrating the different oxidizing powers of halogens. With $X = F$ [6] the decomposition sequence is

$$[Co(NH_3)_6]F_3 \rightarrow [Co(NH_3)_5F]F_2 \rightarrow [Co(NH_3)_4F_2]F$$
$$\rightarrow [Co(NH_3)_3F_3] \rightarrow CoF_2$$

The last example shows that thermal decomposition can also be used as a method for the synthesis of new inorganic compounds.

The thermal decomposition of $[Co(NH_3)_6]MF_6$ [7] has been followed by TG, DTA, IR spectroscopy and X-ray powder diffractometry. The complexes with M = Al, Ga, V, Cr and Fe all decompose in two stages. In the first, ammonia reduces Co(III) to Co(II) to yield stable intermediate compounds of composition NH_4CoMF_6. These phases are cubic and isostructural with a group of complex fluorides of general formula $M^IM^{II}M^{III}F_6$. These substances are usually synthesized at high temperatures by the fluorination of a mixture of metal chlorides. By treatment with elemental fluorine, of course, no ammonium compounds can be prepared.

The further decomposition of NH_4CoMF_6 gives a mixture of both fluorides. For manganese and iron, reduction to MnF_2 and FeF_2 has been observed. The appearance of NH_4^+ ion can be followed conveniently by measuring the deformation absorption band at 1420 cm^{-1}, active in the IR region.

Hydrates are of importance for inorganic chemists. Water is present in the structure of a hydrate either as coordinated water in the inner coordination sphere or as structural water, also called lattice water, which is usually bound with hydrogen bonds. There are also more detailed classifications of the water molecules in hydrates based on the coordination of lone-pair orbitals [8]. It is an interesting question whether the mode of bonding of water molecules can be determined by thermal analysis.

There are proposals in the literature for correlating the structures of hydrates with decomposition temperature. Structural water should be eliminated below 150°C and coordinated water above 200°C. There are also arguments for and against the applicability of this correlation [9].

In a study in our laboratory, a series of relatively simple compounds of general formula $K_2MF_5 \cdot H_2O$ were used [10]. The compounds belong to two structural types. For M = Al and Mn the tervalent metals are coordinated only by fluorine atoms, and water molecules lie in the lattice between the anionic chains. For M = V, Cr, Fe and Ga the water molecule takes part in the coordination sphere of the central atom. Al and Mn compounds are not isostructural but the structural motive is the same. The other compounds all belong to the same monoclinic space group.

DTA curves for the dehydration of all $K_2MF_5 \cdot H_2O$ compounds have been recorded under the same experimental conditions. The dehydration temperatures vary considerably, the lowest values being those for Al and Fe, which have structural and coordination water, respectively. The second compound with structural water dehydrates at a higher temperature than do some compounds with coordinated water. Similar results have been obtained for the reaction enthalpies. Evidently, these data cannot be used to distinguish between the two types of water molecules. By plotting the dehydration temperatures or the dehydration enthalpies as a function of the *d*-electron configuration of M^{3+} ions, a typical diagram has been obtained that shows the correlation between the hydration enthalpies of trivalent cations and crystal field stabilization energies for their high-spin configurations in an octahedral environment. It means that even with isomorphous compounds with the same dehydration stoichiometry, the results of thermal analysis could be significantly different and should be used with caution when interpreting structures.

Parallel to the application of quantitative DTA in inorganic chemistry, there is also constant interest from both theoretical and methodological points of view. There are a number of theories that correlate enthalpy changes with DTA peak areas. Hložek [11] proposed a computing technique for the calculation of enthalpy changes. A graphical interpretation of Kirchoff's law was used in order to express the temperature dependence of the reaction enthalpy. $CaCO_3$ decomposition was used to illustrate the method.

The determination of the thermodynamic characteristics of melts is an area of interest where the DTA method has been applied. A special problem is the measurement of enthalpies of mixing in a multi-component system with volatile and chemically active components. Mechkovski et al. [12] designed a quantitative DTA apparatus for measurements in the range 300–1300 K. Two different measuring cells were constructed that allow the determination of enthalpies by direct mixing of liquid samples, by dissolving a solid component in a liquid component and by dropping a solid volatile component into a melt of the others. Estimated errors in the determination of enthalpies of mixing do not exceed 3% for binary systems and 5% for ternary systems.

For solutions, thermoanalytical techniques have mainly been used to study reaction mechanisms. Much work has been published on the kinetics of the oxidation of organic compounds by Ce(IV) in various media [13–15]. Cerium(IV) is used as an oxidant not only in analysis, but also in organic chemistry. The hydrated ion $[Ce(H_2O)_n]^{4+}$, which is a strong acid, exists only in concentrated perchloric acid solution. In other acid media the anions coordinate with Ce(IV). In sulphate solutions the reactions are sufficiently slow for investigation by conventional methods. The predominant species in these solutions are sulphatocerium(IV) complexes. There has been some controversy as to the precise nature of the oxidant, the complex ions $[Ce(SO_4)]^{2+}$ and $[Ce(SO_4)_2]$ being more favoured.

Guindy et al. [16] studied spectrophotometrically the kinetics of reduction of Ce(IV) by a series of monocarboxylic acids in aqueous suphuric acid solutions. They found the reaction to be first order for both reactants with the rate constant being independent of Ce(III) concentration. A mechanism of the reaction was proposed that involves the formation of intermediate complexes between Ce(IV) and organic acids. The reactivity of acids was attributed to their chelating power.

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