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THERMALLY INDUCED CHANGES IN THE OXIDATION STATE OF CERIUM(IV)
A study of carbonato and chloro complexes

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Abstract

Cesium hexachlorocerate(IV), Cs_2CeCl_6 (I) and sodium pentakis(carbonato)cerate(IV), $Na_6Ce(CO_3)_5 \cdot 12H_2O$ (II) have been investigated in air by simultaneous TG/DTA, FTIR and XRD in order to follow the oxidation state of cerium during their thermal treatment. The thermal decomposition of the hexachloro compound (I) is accompanied by a double change in the oxidation state of cerium. First, in an inner reduction-oxidation reaction, chlorine is evolved and a Cs_2CeCl_5 phase is obtained. The immediately starting oxidation of this Ce(III) species caused various phase transitions in the $CeCl_3$–CsCl system formed. The presence of Cs_3CeCl_6 above 400°C can also be assumed and finally this phase also oxidizes into CeO_2 with the formation of CsCl as by-product. In the case of the pentacarbonato complex (II), no Ce(III) species were detected. The final products of its decomposition were CeO_2 and Na_2CO_3.

Keywords: carbonato complex, cerium, chloro complex, oxidation-reduction

Introduction

Thermal decomposition of cerium(IV) salts, prepared from strong mineral acids, is in many cases accompanied by a double change in the oxidation state of cerium Ce(IV) $\rightarrow$ Ce(III) $\rightarrow$ Ce(IV) [1–7]. In our previous study, the effects of complexing anions and counter cations were investigated using four sulfato and nitrato complexes of Ce(IV) as samples [5]. In addition, other factors may also play a role in the oxidation-reduction sequence of reactions. These include traces of acids and solvents left in the crystals, as well as water evolving from the water of crystallization.

Here we present results obtained with two additional inorganic Ce(IV) complexes. One of them, Cs_2CeCl_6 (I) is a complex salt of a non-oxo acid, while the other

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$Na_6Ce(CO_3)_5 \cdot 12H_2O$ (II) is a salt of a weak oxoacid, which was prepared in a slightly alkaline medium. Both compounds have been studied by simultaneous TG/DTA in flowing air. FTIR and powder XRD were used to analyze the solid reaction intermediates and products.

Experimental

Preparation of Cs_2CeCl_6 *(I)*

To avoid difficulties which occurred in earlier preparations [8], we used relatively low temperature (4°C) during the precipitation of **I**. 101.0 mg (0.6 mmol) CsCl and 164.4 mg (0.3 mmol) $(NH_4)_2Ce(NO_3)_6$ were dissolved in 4 cm^3 32% (ca. 10 mol dm^{-3}) HCl at 4°C. The precipitate was filtered immediately and washed with 1 cm^3 of cooled 10 *M* HCl. The orange material was dried in air for several days at 15°C.

Preparation of $Na_6Ce(CO_3)_5 \cdot 12H_2O$ *(II)*

The preparation was also carried out near 0°C according to earlier investigations [9]. 329 mg (0.6 mmol) of $(NH_4)_2Ce(NO_3)_6$ was added into 10 cm^3 of 1 mol dm^{-3} solution of Na_2CO_3, precooled to 4°C. During the mixing NH_3 gas evolved. The obtained suspension was kept in refrigerator at 4°C overnight. The yellow crystals formed were filtered, washed with cold 1 *M* Na_2CO_3 solution and finally dried in desiccator over silica.

Thermal, FTIR and XRD studies

Thermal behaviour of **I** and **II** was studied in a Seiko TG/DTA 320 instrument. Sample size was 8–15 mg (**I**) and 25–30 mg (**II**). The heating rate was 10°C min^{-1} in both cases. The measurements were carried out in dynamic atmosphere of air (flow rate 80 ml min^{-1}) and, for comparison, in pure argon (99.95%).

FTIR and powder X-ray diffraction were used to study the reaction intermediates and products. The FTIR spectra were obtained in the 400–4000 cm^{-1} range with a Nicolet Magna IR 750 instrument using the KBr pellet technique. The X-ray powder patterns were recorded by a Philips MPD 1880 diffractometer using CuK_α radiation.

Results and discussion

Cs_2CeCl_6*. Double changes in the oxidation state of cerium*

There are some earlier reports [10, 11] on the thermal decomposition of Cs_2CeCl_6, which contains Ce(IV) octahedrally coordinated by chloride anions [12]. They agree that the first mass change by 330°C is caused by evolution of 1/2 Cl_2, but the Ce(III) species and phases occurring in the system were not unequivocally assigned, main problem being whether Cs_2CeCl_5 or $CeCl_3$ together with $2 \cdot CsCl$ was formed.

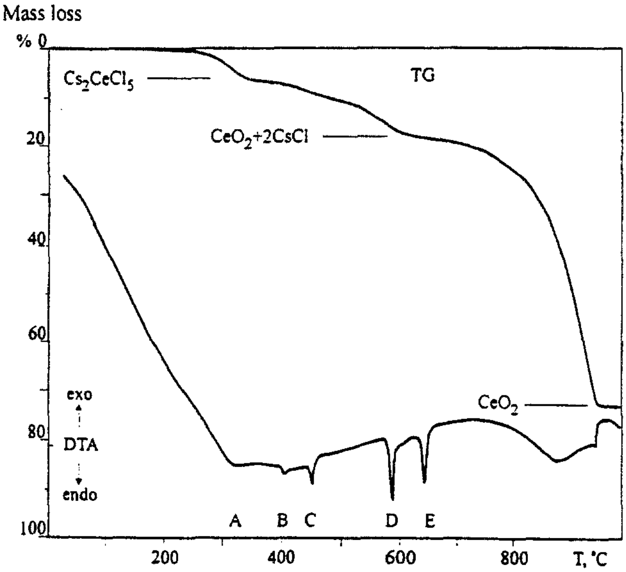

Fig. 1 Simultaneously recorded TG and DTA curves of Cs_2CeCl_6 (I) in air (80 ml min^{-1}) at heating rate of 10 K min^{-1}, initial mass 14.95 mg. Marked endothermic effects at A-320, B-407, C-456, D-590, E- 649°C. The theoretical (calculated) mass levels are also marked

Our TG run obtained in flowing air (Fig. 1) shows also the mass loss due to $0.5Cl_2$ (theoretically 5.73%), but the step is not sharp because of slow, but continuous thermally induced further changes in mass, indicating that after reduction of Ce(IV) probably an immediately starting, but slow oxidation of Ce(III) species and phases follows. An exchange of three chloride ions into two oxide ions seems to be responsible for the decrease in mass. The overall process, to be discussed in more detail below, can be summarised in the following way:

$$Cs_2CeCl_6 \rightarrow 0.5Cl_2 + Cs_2CeCl_5(CeCl_3 \cdot 2CsCl) \xrightarrow{(O_2)} CeO_2 + 2CsCl \qquad (1)$$

The $CeCl_3$:CsCl ratio decreases in the system continuously due to CeO_2 formation. The theoretical mass loss of complete oxidation is 17.7%. This mass loss, when the $CeCl_3$ molar fraction equals to zero, is reached experimentally at 650°C (Fig. 1). At the same temperature the fusion of the formed CsCl was observed and then the liquid CsCl evaporated totally, accompanied by a sharp (Fig. 1, peak E) and a prolonged endothermic effect, respectively. At 950°C only CeO_2 remains in the system (theoretical residue is 27.82%).

On the DTA curve, the heat of the first reaction occurred as a small endothermic effect on the declining baseline (Fig. 1, peak A), while the exothermic effect of oxidation of Ce(III) species into CeO_2 is observed as monotonous slow increase of the DTA baseline between 350 and 650°C. The total molar fraction of the Ce(III) species decreased slowly from 0.333 to zero due to the formation of CeO_2. The observed $CeCl_3$ molar fraction – temperature points give a curve on the equilibrium phase diagram of $CeCl_3$–CsCl system (Fig. 2, dashed line). In the above mentioned compositional and temperature range several phase equilibria are expected [13]. In

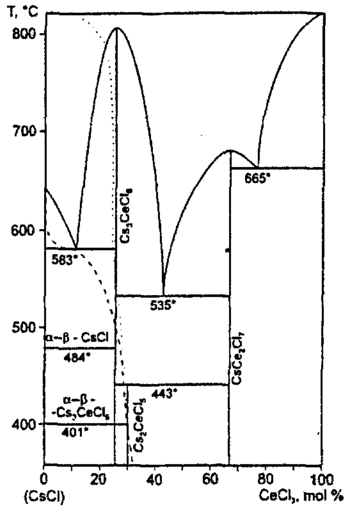

Fig. 2 Routes of compositional changes in air (dashed line) and in argon (dotted line) followed on the phase diagram of $CeCl_3$–CsCl system (redrawn after Ref.[13])

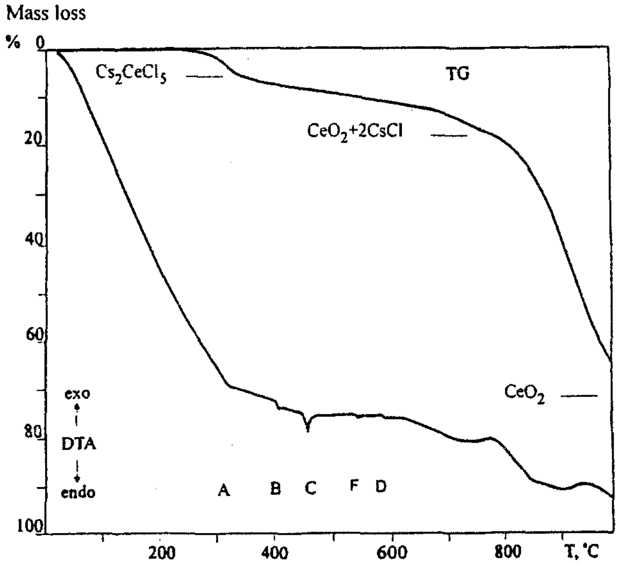

Fig. 3 Simultaneous TG and DTA curves of Cs_2CeCl_6 (I) in Ar (120 ml min^{-1}), at heating rate of 10 K min^{-1}, initial mass 8.70 mg. Marked endothermic heat effects at A-320, B-410, C-456, F-540, D-590°C. The theoretical (calculated) mass levels are also marked

our reaction system three endothermic heat effects are recorded on the DTA curve (Fig. 1, peaks B-D) at 407, 456, and 590°C, which agree quite well with transition temperatures observed in the pure $CeCl_3$–CsCl system at 401, 443, and 583°C. The differences are probably caused by the formation and accumulation of CeO_2 in the sample or rather the equilibrium is not reached perfectly.

When heating was carried out in an argon atmosphere under a much reduced partial pressure of oxygen (the oxygen content of the inert gas was less than 0.05%) the first reaction was not affected, while the subsequent oxidation became slower (Fig. 3). The oxidation ended at 780°C, which is higher temperature than in air as seen in the DTA baseline which is in this case slightly declining above 350°C, compared to the rising baseline observed in air atmosphere (Fig. 1). Because of the slow and prolonged oxidation in argon four phase transitions occurred as endothermic peaks of DTA at 410, 456, 540 and 590°C (Fig. 3, peaks B, C, F, D) agreeing again with the transition temperatures at 401, 443, 535, and 583°C of the pure $CeCl_3$–CsCl system (Fig. 2, dotted line). These enthalpy changes are weaker than in air, for the overall composition of the system remains quite near those of Cs_3CeCl_6, and only a small amount of other phases are expected to occur as equilibrium partner of Cs_3CeCl_6. In addition an elongated (650–780°C) endothermic effect occurs because of slow dissolution of the assumed solid phase, Cs_3CeCl_6 in the quite small amount of eutectic liquid formed by 590°C (Fig. 2, dotted line).

X-ray phase analysis

The XRD peak positions of the starting material (I) were in good agreement with the calculated pattern found in the literature (JCPDS cards No. 200064 and 280286). XRD patterns of intermediate solid phases obtained in Ar after cooling back from various temperatures are shown on Fig. 4. The solid product of the first reaction step was identified as Cs_2CeCl_5 (JCPDS card No. 381317). This phase was present already

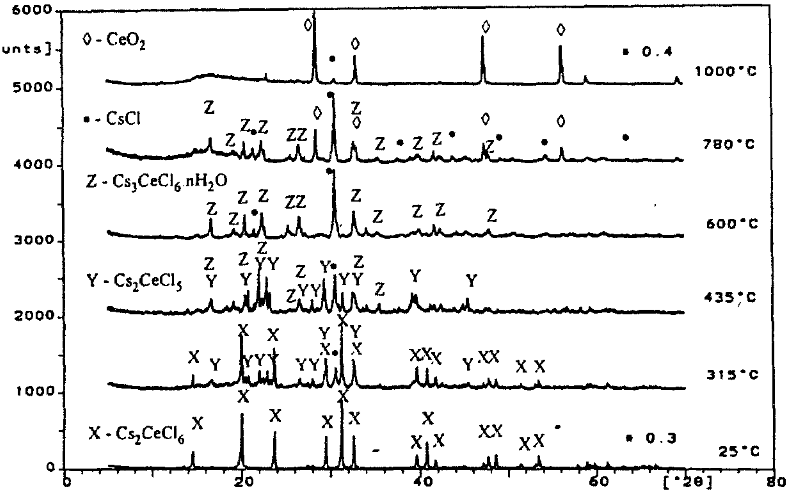

Fig. 4 Phases observed by *ex situ* XRD recordings when Cs_2CeCl_6 (I) is heated in Ar from 25 to 1000°C

at 315°C and reached its maximum amount at 435°C. Taking into account the chlorine evolution, the reaction can be described with the following equation:

$$Cs_2CeCl_6 \rightarrow Cs_2CeCl_5 + 0.5Cl_2 \qquad (2)$$

At about 600°C instead of Cs_2CeCl_5, a new phase occurred, that was expected to be Cs_3CeCl_6, but its XRD pattern was completely different from those published earlier (JCPDS card No. 381315 or 381316). We assume that the phase observed after cooling at room temperature is another polymorph of Cs_3CeCl_6 or possibly its partially hydrated form for its IR spectra indicated clearly the presence of water of crystallization. This phase was also detected at 780°C accompanied by CsCl and CeO_2. Cesium chloride (JCPDS card No. 50607) occurred already at 315°C and it reached its maximum amount at 780°C as a by-product of the oxidation of Ce(III) species, while the main product, CeO_2 could be identified in crystalline form only above 700°C in argon.

The detected new Cs_3CeCl_6 phase is also present together with CsCl and CeO_2, when a mixture of $CeCl_3{\cdot}7H_2O$ and CsCl in 1:3 molar ratio were melted together at 850°C in N_2 to obtain anhydrous Cs_3CeCl_6. This sample showed the same phase transitions starting from 400°C, and the same XRD pattern at 850°C, as I did.

$Na_6Ce(CO_3)_5{\cdot}12H_2O$. Decomposition without valence changes

In this complex the Ce(IV) ions are ten-coordinated by five bidentate carbonate groups and the sodium cations are surrounded by loosely bonded water molecules

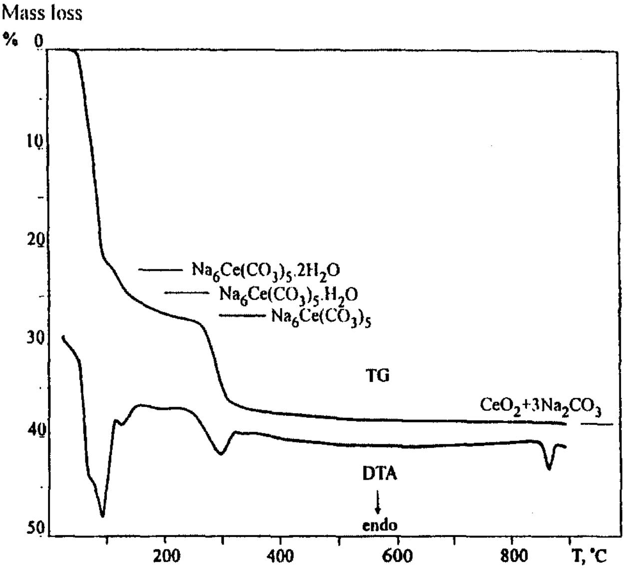

Fig. 5 Simultaneous TG and DTA curves of $Na_6Ce(CO_3)_5{\cdot}12H_2O$ (II), in air (80 ml min^{-1}), at heating rate 10 K min^{-1}, initial mass 26.16 mg. The theoretical (calculated) mass levels are marked

in an irregular octahedral configuration [14]. The bidentate nature of the carbonate group was confirmed by its IR spectrum showing a large splitting of ν_3 carbonate frequency [9].

The thermal decomposition of this complex was found to be quite straightforward (Fig. 5), and showed only the effect of a faster heating rate (10°C $\min^{-1}$) compared to the literature data (2.5°C $\min^{-1}$) [15]. Between 50°C and 105°C about 9–10 molecules of water vanished, while the rest of water evolved in two steps much more slowly by 225°C. The next mass loss step corresponds to the evolution of two molecules of carbon dioxide at about 300°C, but this process showed a tailing up to 600°C. An endothermic heat effect at 866°C indicates the presence and melting of Na_2CO_3 formed during the decomposition.

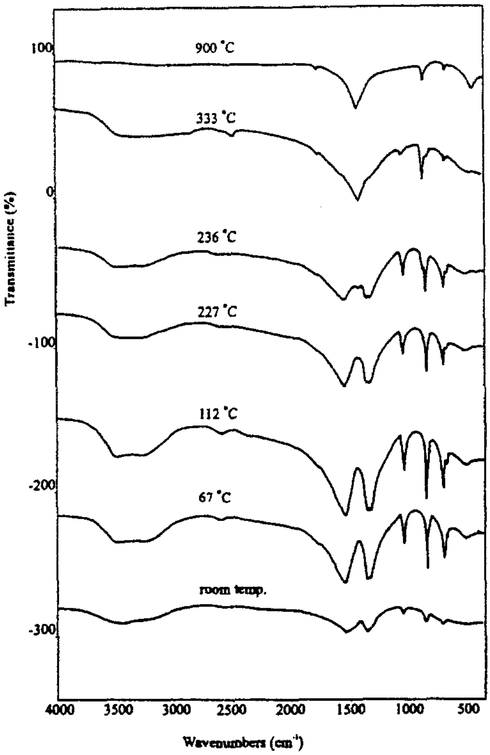

Fig. 6 Changes in FTIR spectra of $Na_6Ce(CO_3)_5 \cdot 12H_2O$ (II) during its decomposition

The IR spectra of the dehydration products at various stages were practically the same (Fig. 6). The decomposition of the anhydrous pentacarbonato structure was indicated already at 235°C by occurrence of the most intense band of sodium carbonate between the two split ν_3 vibration bands of the pentacarbonate. The latter two bands gradually decreased and disappeared with the rising temperature. Above 600°C only the bands of Na_2CO_3 could be seen.

The XRD pattern of the sample changed suddenly at 50°C (Fig. 7). Thereafter the peak positions and the obtained patterns remained similar to each other till the

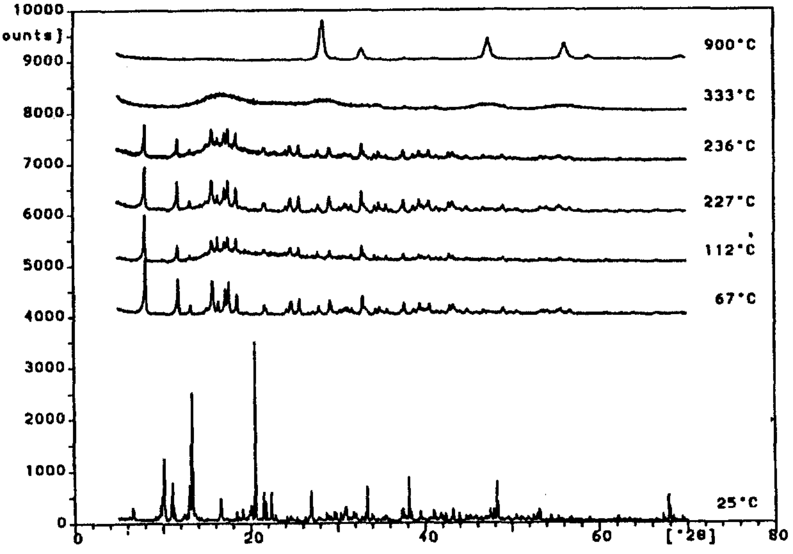

Fig. 7 XRD patterns of $Na_6Ce(CO_3)_5 \cdot 12H_2O$ (II) at various stages of thermal decomposition

end of the dehydration process. The common lines of these similar XRD patterns may indicate a stable structural skeleton of the anhydrous complex and its lower hydrates. This stable structure is destroyed by the evolution of CO_2 at 290°C where only amorphous material remained yielding at higher temperatures CeO_2 and Na_2CO_3.

Conclusions

In the case of Cs_2CeCl_6 (I) a double change in the oxidation state of cerium occurred. First a reduction of the Ce(IV) into $Cs_2Ce(III)Cl_5$ was observed accompanied by chlorine evolution. Then the oxidation into CeO_2 started but the overall reaction scheme was complex due to the phases and phase transitions in the $CeCl_3$–CsCl system formed. The rate of the oxidation of Ce(III) species largely depended on the oxygen content of the surrounding atmosphere. That is, the oxidizing agent in this case must have been atmospheric oxygen whilst in the case of complexes with oxoanions of strong acids, the oxidation took place using oxygen coming from the decomposition of the anion even in the absence of oxygen. In the latter cases no significant difference could be observed between the thermal curves obtained in air and in inert atmosphere [5].

In the case of $Na_6Ce(CO_3)_5 \cdot 12H_2O$ (II) prepared from slightly alkaline solution, no Ce(III) species could be detected among the decomposition intermediates by thermal, FTIR and XRD analysis. The carbonic acid seems not to be strong enough to increase the oxidation potential of the Ce(IV)/Ce(III) system. After the loss of the water molecules two molecules of CO_2 evolved, Na_2CO_3 and CeO_2 being the final products. It should be noted here that the decomposition of **II** starts and is completed at much lower temperature as compared with **I** and especially with the complexes studied earlier [5–7].

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