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THERMAL BEHAVIOUR OF SOME PHOSPHORUS/CHROMIUM POLYOXOANIONS

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ABSTRACT

The thermal degradation of $K_2HPCr_2O_{10}$, $Na_3PCr_3O_{13} \cdot 3H_2O$, $K_3PCr_4O_{16}$ and $(NH_4)_3PCr_4O_{16}$ has been investigated by TG and DTA methods. The main decomposition process for the three firstly mentioned compounds occurs at around 400°C and is associated with the rupture of P–O–Cr bonds. The ammonium salt shows a different behaviour and decomposes explosively at 230°C. In the case of $K_2HPCr_2O_{10}$ a new polyoxoanion of formula $K_4P_2Cr_4O_{19}$ is generated as an intermediate during the thermal degradation. Detailed stoichiometries, sustained by the TG/DTA results as well as by the chemical and infrared spectroscopic analyses of the solid residues could be given. It is shown that, in all cases, $CrPO_4$ is one of the decomposition products.

INTRODUCTION

An important number of recent crystallographic studies [1–9] have brought definitive evidence for the existence and structural characteristics of an interesting series of simple polyoxoanions of the types $PCr_nO_{3n+4}^{3-}$ and $AsCr_nO_{3n+4}^{3-}$.

As part of our present studies on the spectroscopic and thermal properties of simple iso- and heteropolyanions (cf. [10–13]) we have now investigated the thermal behaviour of crystalline species containing the following anions: $PCr_2O_{10}^{3-}$, $PCr_3O_{13}^{3-}$ and $PCr_4O_{16}^{3-}$.

Structurally, these species are essentially built from a central PO_4-tetrahedron sharing two, three or four corners with CrO_4-tetrahedra.

EXPERIMENTAL

Syntheses of the compounds

$K_2HCr_2PO_{10}$ was obtained from $K_2Cr_2O_7$ and concentrated H_3PO_4 [1] and $Na_3PCr_3O_{13} \cdot 3H_2O$ from a Na_2HPO_4/CrO_3 mixture in a 1/3 molar

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ratio [2]. From the quaternary phosphates, the potassium salt, $K_3PCr_4O_{16}$, was obtained from concentrated 1:4 K_3PO_4/CrO_3 solutions [4] and the corresponding ammonium compound from a 2:1 $(NH_4)_2Cr_2O_7/H_3PO_4$-mixture [3,14]. The purity of the substances was checked by chemical analysis and X-ray diffractometry [1,2,4,14].

TG and DTA measurements

Thermogravimetric and differential thermal analyses were carried out simultaneously on a Rigaku thermoanalyzer (type YLDG/CN 8002 L2) using a Pt–Pt/Rh thermoelement and working under normal atmosphere at a heating rate of 5°C min^{-1}. Al_2O_3 was used as a DTA standard; sample weight ranged between 20–40 mg. The maximum heating temperature was 500°C. In order to allow the further characterization of the pyrolysis residues or intermediates, samples of the different compounds were also heated at selected and well controlled temperatures in a crucible furnace, according to the information obtained from the thermograms.

IR and X-ray measurements

The infrared spectra were recorded on a Perkin Elmer 580 B spectrophotometer using the KBr-pellet technique. X-ray powder diagrams were obtained with a Philips PW 1010 diffractometer, using Cu-K_α radiation (Ni-filtered) and NaCl as an external calibration standard.

RESULTS AND DISCUSSION

The TG and DTA traces recorded in typical experiments for $K_2HPCr_2O_{10}$, $Na_3PCr_3O_{13} \cdot 3H_2O$ and $K_3PCr_4O_{16}$ are presented in Fig. 1. As the ammonium salt $(NH_4)_3PCr_4O_{16}$ decomposes explosively, its diagram is not included in the figure.

$K_2HPCr_2O_{10}$

As seen in Fig. 1A, the DTA-curve of this compound shows two well defined endothermic peaks at 195 and 405°C. The first one is associated with a mass loss of 2.38% whereas that corresponding to the second peak lies around 4.5% but the mass decrease continues slowly with rising temperature.

The heating of the samples in a crucible furnace, at fixed controlled temperatures, shows the following behaviour: after 5 min at 250°C, 2.4% of weight loss; subsequent heating and maintenance of the sample during one hour at 400°C, 4.4% loss more. Finally, after heating at 600°C one hour more, a further loss of ca. 1.2% was registered.

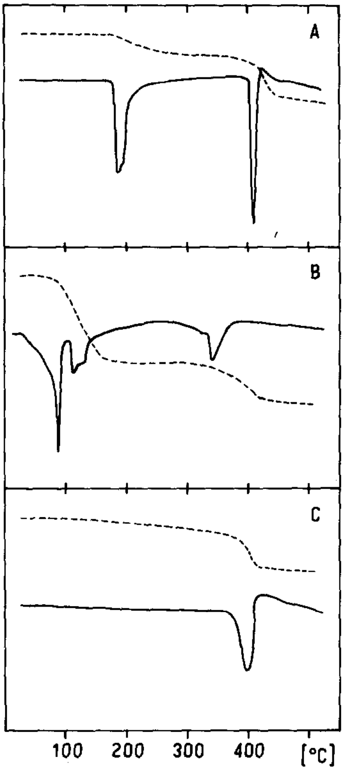

Fig. 1. DTA (———) and TG (— — —) traces for $K_2HPCr_2O_{10}$ (A), $Na_3PCr_3O_{13}\cdot 3H_2O$ (B) and $K_3PCr_4O_{16}$ (C). All the DTA-peaks correspond to endothermic processes.

The X-ray powder diagrams of samples collected after the three mentioned heat treatments, show that the materials were amorphous. But their IR spectra gave rather different patterns.

The analysis of the TG/DTA and crucible furnace experiments, together with the IR results points to the following sequence of events during the thermal degradation of this sample.

In the first step, intramolecular water is liberated, and the generation of a new polyoxoanion occurs

$$2\ K_2HPCr_2O_{10} \rightarrow K_4P_2Cr_4O_{19} + H_2O \qquad (1)$$

The theoretical weight loss of 2.4% coincides perfectly with the values found experimentally at the temperature of the first endothermic DTA signal.

On the other hand, the chemical analysis and the IR and Raman spectra, show unambiguously the presence of a new polyoxoanion, not reported up to now, containing a P–O–P bridge and supporting two CrO_4 tetrahedra and a free oxygen over each of the phosphorus atoms [13].

In the second step, the degradation of this intermediately generated species takes place, according to

$$K_4P_2Cr_4O_{19} \rightarrow 2\ CrPO_4 + K_2Cr_2O_7 + K_2O + 1.5\ O_2 \qquad (2)$$

The theoretical weight loss of this stage would be 6.57%. The fact, that the experimentally found values, always lie around 4.5% and the slow ulterior mass loss, suggest that not all of the potassium is bound as K_2O. Some of them probably forms KO_2, which subsequently decomposes with the release of more oxygen (cf. also [15]).

The determination of the oxidative power of the pyrolysis residues (by iodometry [16]), support this supposition, because the determined values are always slightly higher than those expected from only one mole $K_2Cr_2O_7$ in the mixture.

On the other hand, a synthetic 2:1 mixture of $CrPO_4$ and $K_2Cr_2O_7$ gave the same infrared spectral pattern as that of the residues collected after the heat treatment at 400°C, supporting, additionally, the proposed stoichiometry.

Finally, during the heating up to 600°C, not only the primarily generated KO_2 is decomposed, but also other material, and more complex changes occur. The IR spectra of both, the residues collected after heating at this last temperature, and those of the 2:1 synthetic $CrPO_4/K_2Cr_2O_7$ mixture also heated up to 600°C, gave the same general spectral pattern, which is very complex and not easily interpreted. It must be assumed that a reaction between $CrPO_4$ and $K_2Cr_2O_7$ occurs, because neither the pure phosphate nor the pure dichromate alone decomposes at this temperature.

$Na_3PCr_3O_{13} \cdot 3H_2O$

This compound is very hygroscopic and, therefore, very difficult to manipulate. As shown in Fig. 1B, the thermogram presents three endothermic peaks. The second one is, apparently, a superposition of two others not totally resolved. The first peak, centered at 90°C corresponds to the liberation of adsorbed water and the subsequent even mentioned doublet ($\sim$ 120, $\sim$ 135°C) is associated with the loss of the three molecules of crystal water (experimental weight loss = ca. 10.5%, theoretical = 10.43%).

The further degradation of the anhydrous polyoxoanion is associated with the endothermic peak, located at 348°C, and is accompanied by a weight loss of 4.8%. The weight loss continues also in this case in a very slow form up to the maximum temperature reached.

The heating of samples in a crucible furnace up to 400°C, during varying periods of time always gave total weight losses around 15%.

These results together with the information obtained from the IR spectroscopic analysis of the residues of the thermolysis experiments, allow to propose the following decomposition scheme

$$Na_3PCr_3O_{13} \cdot 3H_2O \rightarrow Na_3PCr_3O_{13} + 3\ H_2O \qquad (3)$$

$$Na_3PCr_3O_{13} \rightarrow Na_2Cr_2O_7 + CrPO_4 + 1/2\ Na_2O + 0.75\ O_2 \qquad (4)$$

This proposition is supported by the following additional evidence:
—The theoretical weight loss expected according to eqn. (4) is 5.17%.
—The oxidative power of the residues collected after the heating treatments at 400°C practically coincides with that expected for the mixture generated according to eqn. (4).
—The IR spectrum of a synthetic 1 : 1 $Na_2Cr_2O_7$: $CrPO_4$ mixture is totally similar to that of the pyrolysis residues.

A further heating of the pyrolysis residues up to 600°C generates Cr_2O_3, by decomposition of the $Na_2Cr_2O_7$, and a mixture of $CrPO_4$ and Cr_2O_3 could be clearly identified by IR spectroscopy.

$K_3PCr_4O_{16}$

As can be seen from Fig. 1C, the mass loss for this compound begins at a relatively low temperature. This first and slow loss reaches approximately 2.5% up to 380°C. The main decomposition process, associated with the well defined endothermic peak at 400°C, begins at this temperature and a further and rapid weight loss of ca. 4% more is observed. As in the other two cases, the loss continues slowly with the subsequent temperature increase.

The initial mass loss is probably associated with a small release of oxygen. This is comprehensible, because this substance is the most oxygenated one. This first stage can probably be formulated as

$$K_3PCr_4O_{16} \rightarrow \text{“}K_3PCr_4O_{15}\text{”} + 1/2\ O_2 \qquad (5)$$

for which a theoretical weight loss of 2.61% is expected.

Therefore, the main decomposition process may be:

$$\text{“}K_3PCr_4O_{15}\text{”} \rightarrow CrPO_4 + K_2Cr_2O_7 + \text{“}CrO_2\text{”} + 1/2\ K_2O + 0.75O_2 \qquad (6)$$

for which the expected mass loss is 4.02%.

Notwithstanding, the process appears to be much more complex than that described by the simple eqn. (6). First, the real chemical state of the species formulated as "CrO_2" is not clear. But it is known, that pure CrO_3 slowly liberates oxygen at temperatures above its melting point (197°C) generating species such as Cr_3O_8, Cr_2O_5, CrO_2, etc. [17]. On the other hand, a partial reduction of the four Cr(VI) atoms can be postulated in the first step, as indicated in eqn. (5). Therefore, the $K_2Cr_2O_7$ postulated in eqn. (6) is very probably not totally stoichiometric. This supposition is in accordance with the experimental finding that the oxidative power of the pyrolysis residues were always lower than expected for the mixture generated according to eqn. (6). It is also possible that some other products, present only in very small quantities, can be generated during this process.

On the other hand, the IR spectrum of a synthetic 1 : 1 : 1 mixture of $K_2Cr_2O_7$, $CrPO_4$ and CrO_3 (previously heated at 400°C) is very similar, but not totally identical, to those obtained for the pyrolysis residues. A better characterization of the residues was unfortunately impossible, due to the fact that they were amorphous to X-rays.

Finally, it is interesting to comment that a further heating of the residues to 600°C generates a very complex IR-pattern, which is similar to that obtained after heating the decomposition products of $K_2HPCr_2O_{10}$ at the same temperature. This fact supports the presence of the same main decomposition products in both compounds.

$(NH_4)_3PCr_4O_{16}$

This compound is practically stable up to 230°C, although a negligible mass loss can be observed even at lower temperatures. At the mentioned temperature an explosive reaction, associated with a strong exothermic process, takes place. This decomposition can be formulated as follows

$$2\,(NH_4)_3PCr_4O_{16} \rightarrow 2CrPO_4 + 3Cr_2O_3 + 3N_2 + 12H_2O + 1.5O_2 \qquad (7)$$

This means, that the process resembles to some extent the thermal degradation of $(NH_4)_2Cr_2O_7$ [18], but it is additionally complicated due to the liberation of O_2 and the generation of $CrPO_4$ as a second solid residue, together with Cr_2O_3.

The proposed stoichiometry is supported by the fact that the IR spectrum of the collected solid residues closely resembles that of a synthetic 2 : 3 mixture of $CrPO_4$ and Cr_2O_3.

CONCLUSIONS

It is evident, that all the investigated polyoxoanions, with the exception of the ammonium salt of $PCr_4O_{16}^{3-}$, undergoes a very similar thermal degradation. The main process is undoubtedly associated with the rupture of P–O–Cr bonds, which occurs at temperatures around 400°C.

Notwithstanding, some smaller differences should be remarked. In the case of $K_2HPCr_2O_{10}$ the final degradation is preceded by a condensation process with the formation of a more complex, higher weight intermediary. In the case of $K_3PCr_4O_{16}$, the intrinsic instability, associated with the great number of $Cr^{VI}O_3$-groups present in the structure, can be visualized by an oxygen loss which occurs before the final bond rupture takes place. The same effect apparently occurs also during the first heating stages of the corresponding ammonium salt. The fact that in the case of $Na_3PCr_3O_{13} \cdot 3H_2O$ the main decomposition process occurs at somewhat lower temperature than in the other two cases, can be related with the presence of a different cation and with the previous release of crystal water, which can probably produce some type of "activation" of the main decomposition reaction.

The further degradation of the primarily generated solid residues is also different in the case of the sodium and the potassium salts.

Finally, the production of $CrPO_4$ in all of the investigated processes is very interesting. This compound, belonging to the $CrVO_4$ structural-type, is a very stable phase and can usually be obtained by solid state reactions at much higher temperatures than those reached during the thermolysis experiences [19,20].

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