Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 91–104

SYSTEMS CONTAINING CARCINOGENIC CrO_3 AND CELLULAR REDUCTANTS
Thermal and spectroscopic investigation

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(Received February 12, 2000; in revised form June 30, 2000)

Abstract

Two neutral and three anionic Cr(III) complexes have been isolated from the [CrO_3–non-enzymatic cellular reductants(CR)] binary and ternary systems (cellular reductant=ascorbic acid, cysteine and glutathione). Analytical data, thermal studies and infrared spectra allowed for a description of the chromium coordination sphere. Comparison with the results obtained earlier suggests strong dependence of the isolated complex composition upon the excluding Cr(VI) species.

Keywords: ascorbic acid, cellular reductants, CrO_3, cysteine, glutathione, infrared spectra, thermal decomposition

Introduction

The industrial use of chromium which causes an environmental pollution, has increased dramatically in the 20th century [1]. Among various chromium oxidation states those of Cr(III) and Cr(VI) are the most stable in natural systems [2, 3]. Whereas chromium(III) compounds are rather non toxic [4] or exhibit a low level of toxicity and mutagenicity [5], Cr(VI) chemicals are carcinogenic and mutagenic for humans [6–10]. However, detailed studies showed that Cr(VI) may be regarded rather as a promutagen. In the redox process *in vivo* and *in vitro* starting from Cr(VI) its harmful reactive metabolites i.e. Cr(V) and Cr(IV) and various oxygen and carbon based radicals are responsible for 'Cr(VI) carcinogenic effects' [11, 12].

Chromium(VI) is readily taken up by cells and reduced there to Cr(III) by biological reductants-cell constituents, e.g. NADPH, *L*-ascorbic acid, cysteine, glutathione, etc. [13]. Ascorbic acid is regarded as a principal non-enzymatic cellular reductant (CR) for Cr(VI) [14–15]. Among various forms of hexavalent chromium, CrO_3 seems to be of special interest since it is regarded as the most dangerous species in the chromium polluted air [1].

The present paper has two aims:

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

(i) to isolate the products of the interaction between chromium(VI) oxide and three main non-enzymatic cellular reductants: *L*-ascorbic acid (H_2Asc), cysteine (CYS) and glutathione (GSH) at various physical conditions (pH, temperature). As the system Cr(VI) – cellular reductant, where Cr(VI)=K_2CrO_4, $K_2Cr_2O_7$, $KCrO_3Cl$ and CrO_2Cl_2, was studied earlier by others [16–18] and us [19–21], the present investigation may provide an interesting comparison with regard to the influence of various Cr(VI) oxo forms on the chemical composition of the final products. The idea of the investigation also a mixture of the reductants arose after the observation of the synergism between H_2Asc and GSH in the process of the Cr(VI) reduction [22]. The results of this work are e.g. isolation for the first time neutral dimers from the CrO_3–ascorbic acid and from the CrO_3–ascorbic acid–glutathione systems.

(ii) to study in detail the thermal decomposition and the infrared spectra of the compounds referred in (i). According to the authors knowledge, no thermal investigations were carried out earlier on the products of the [Cr(VI)–CR] redox systems.

Experimental

Materials

L-ascorbic acid and chromium(VI) oxide have been purchased from POCH Gliwice (Poland), the reduced glutathione from Reanal (Hungary) and *L*-cysteine from Northampton (United Kingdom). The composition of the solid precipitates were established by microanalyses (C, H, N) and gave satisfactory results (Table 1).

Preparation of the complexes

In the procedure used, based on [23], the Cr(VI):CR reductant ratio was 1:10. In such conditions the reductant played a double role as a reducing and coordinating agent [19]. As the organic compound was added in large excess, the isolated complexes contained only its reduced form [3, 18, 20].

In the standard, experiment 10 ml of the CrO_3 water solution (0.1 M) was added upon stirring to 10 ml of *L*-ascorbic acid (1 M) or (ascorbic acid–cysteine), (ascorbic acid–glutathione) 1:1 solutions (0.25 M). For complexes B and E (Table 1) KOH 1 M solution was added to obtain pH about 7.4. The solid products were isolated by adding methanol (80 ml) to the water solutions of the reagent mixtures. After two weeks the resulting precipitate was filtered off, washed with methanol and dried in a desiccator over P_2O_5.

Two kinds of products have been isolated (Table 1): compounds A, C, D have been prepared at a temperature of ca –5°C and pH resulting from the reagent mixture, whereas complexes B and E were obtained at physiological conditions, i.e. pH ca 7.4 and temperature 37°C.

Table 1 The analytical data and physical properties of the obtained compounds

Compound	pH	Colour of the sample	μ_{eff}[a]	Found (calculated)/%					
				C	N	H	S	Cr	K
(A) $Cr_2O_2(HAsc)_2 \cdot 9H_2O$	4.2	green	4.08 (3.62)	20.95 (21.56)	4.26 (5.43)			17.67 (16.76)	
(B) $K[Cr(HAsc)_2(OH)_2]KOH \cdot 3H_2O$	7.4	green	3.43 (3.20)	26.2 (25.41)	2.93 (3.73)			7.35 (8.16)	13.60 (13.75)
(C) $K_2[Cr(HAsc)(CYS)(OH)_2] \cdot 7H_2O$	11.5	grey	4.01 (3.67)	20.46 (20.38)	3.74 (4.18)	2.8 (2.64)	6.72 (6.04)	9.39 (9.8)	13.11 (14.7)
(D) $Cr_2O(HAsc)(GSH)_2 \cdot 7H_2O$	4.3	grey	3.49 (3.17)	30.09 (30.06)	5.30 (5.54)	8.34 (8.10)	6.50 (6.18)	9.3 (9.8)	
(E) $K[Cr(HAsc)(GSH)] \cdot 7H_2O$	7.4	grey	3.90 (3.53)	27.60 (27.59)	4.47 (5.06)	6.9 (6.03)	2.21 (4.60)	7.89 (7.46)	6.37 (5.61)

[a] μ_{eff} at 80 K were given in the parentheses
[b] The magnetic moments were calculated assuming less than water molecules in the compound composition due to same lost during the measurement

Physical measurements

Stoichiometries of the compounds were established by microanalyses using modified Kupman method (C, H, N, S) and Perkin Elmer AAS spectrophotometer (Cr, K). The TG, DTA and DTG curves were recorded simultaneously on a Paulik–Paulik–Erdey (MOM Budapest) derivatograph in a dynamic air atmosphere in the temperature range 20–1000°C. The sample mass was 100 mg, the heating rate was 5°C min^{-1}. The X-ray patterns of the final residues were obtained on DRON-2 diffractometer with CuK radiation lamp. The infrared spectra were recorded in a 4000–400 cm^{-1} spectral region on a Perkin Elmer 180 spectrophotometer in KBr pellets. Magnetic measurements were carried out in a temperature range of 80–300 K by the Gouy method using $Hg[Co(SCN)_4$ as a calibrant.

Warning: Chromium(VI) compounds are carcinogenic and should be handled with caution avoiding skin contact and inhalation.

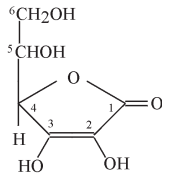
Results and discussion

The products of interaction between dissolved CrO_3 and *L*-ascorbic (H_2Asc) acid and the mixture of *L*-ascorbic acid with glutathione (GSH) or *L*-cysteine (CYS) are green (A, B) and grey (C–E) powder precipitates (Table 1). They are dimeric neutral (A, D) or monomeric anionic (B, C, E) type hydrated trivalent chromium complexes (Table 1). As the ligands were used in the 10 fold excess we assumed their presence in the complexes in reduced forms [18–21].

The magnetic moment analysis showed that the complexes exhibit both slightly lower (B, D) or higher (A, C, E) values than expected for an ideal O_h symmetry (i.e. 3.79 BM for three unpaired electrons). Thus the data support the Cr(III) pseudo-octahedral coordination (various oxygen atoms of H_2Asc coordinating to chromium in A, B and various ligands in C–E). In the literature both lower (3.16 BM) [19] and higher (4.05 BM) [24–25] values of magnetic moments were found for similar compounds.

Binary [CrO_3–H_2Asc] redox system

In this system, two Cr(III) complexes i.e. dimeric (A) and monomeric (B) have been obtained (Table 1).



Scheme 1

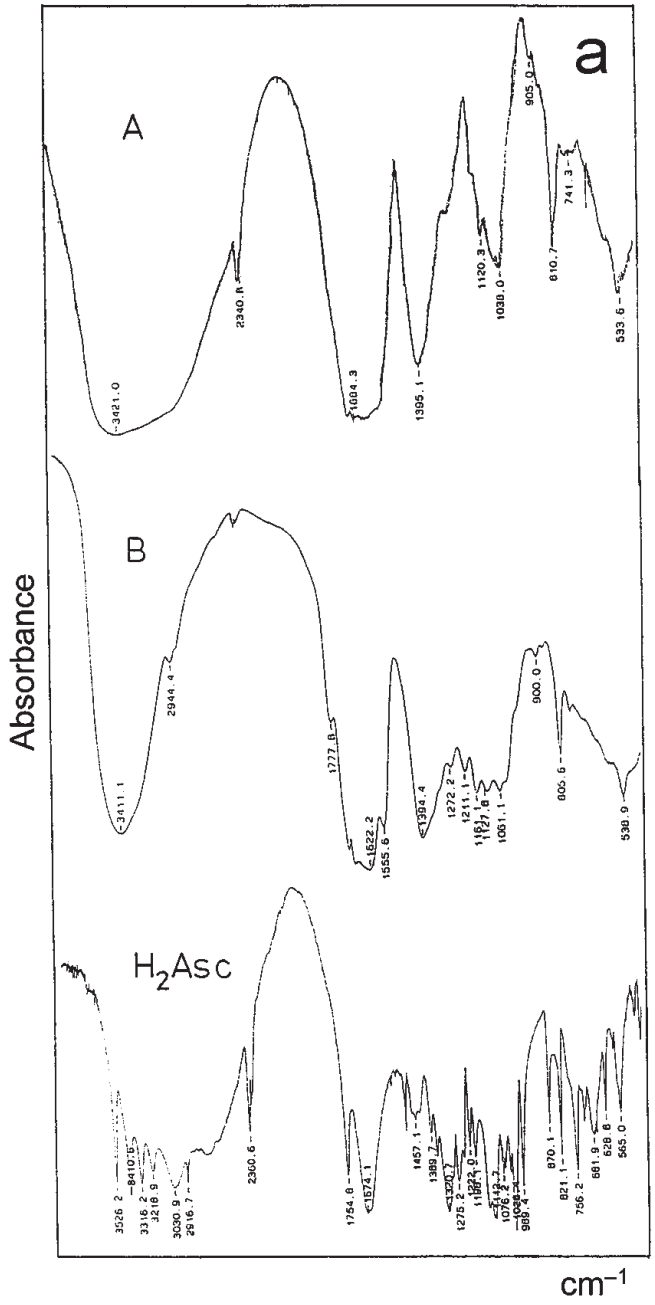


Fig. 1a IR spectra of complexes: A – $(Cr_2O_2(HAsc)_2 \cdot 9H_2O$; B – $K[Cr(HAsc)_2(OH)_2]KOH \cdot 3H_2O$ and free ligand; C – $K_2[Cr(HAsc)(CYS)(OH_2)] \cdot 7H_2O$ and free ligands; D – $Cr_2O(HAsc)(GSH)_2 \cdot 7H_2O$ and E – $K[Cr(HAsc)(GSH)] \cdot 7H_2O$ and free ligands

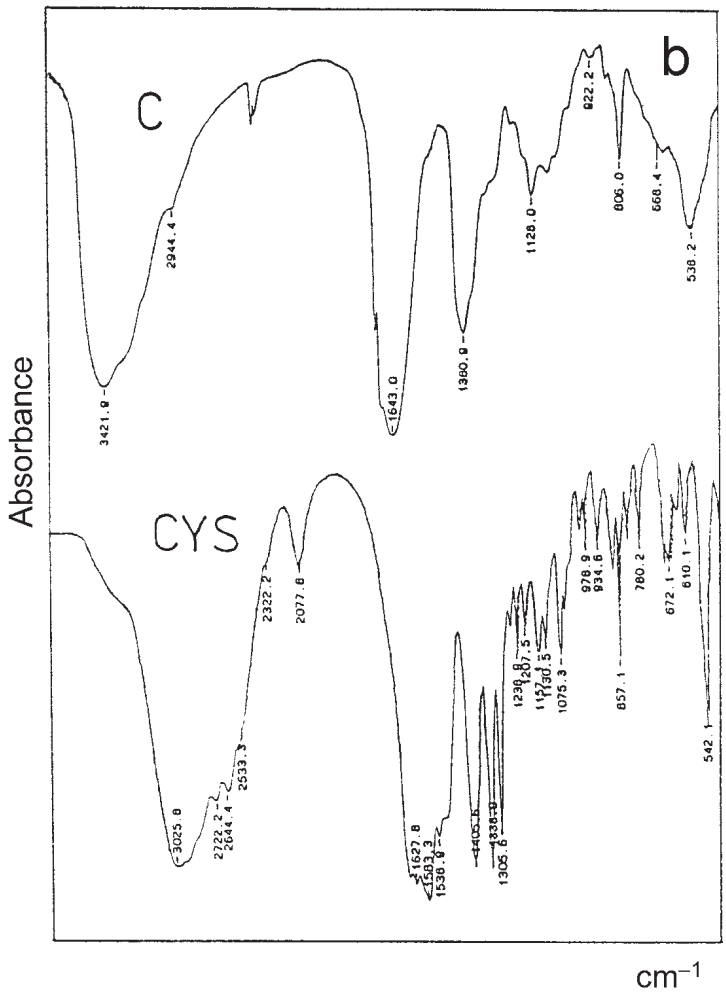


Fig. 1b IR spectra of complexes: A – $(Cr_2O_2(HAsc)_2 \cdot 9H_2O$; B – $K[Cr(HAsc)_2(OH)_2]KOH \cdot 3H_2O$ and free ligand; C – $K_2[Cr(HAsc)(CYS)(OH_2)] \cdot 7H_2O$ and free ligands; D – $Cr_2O(HAsc)(GSH)_2 \cdot 7H_2O$ and E – $K[Cr(HAsc)(GSH)] \cdot 7H_2O$ and free ligands

It is well known that the isolated *L*-ascorbic acid apart from C(3)–O, and C(2)–O binding sites uses carbonyl C(1)–O group as well as chain oxygen atoms for metal coordination [26–28].

Infrared spectra of A and B complexes

The IR spectra of the free *L*-ascorbic acid and its isolated Cr(III) complexes (A, B) have been presented in Fig.1a. Generally, the spectra of both compounds are similar and we will discuss them together. The whole region of spectra in A and B is much

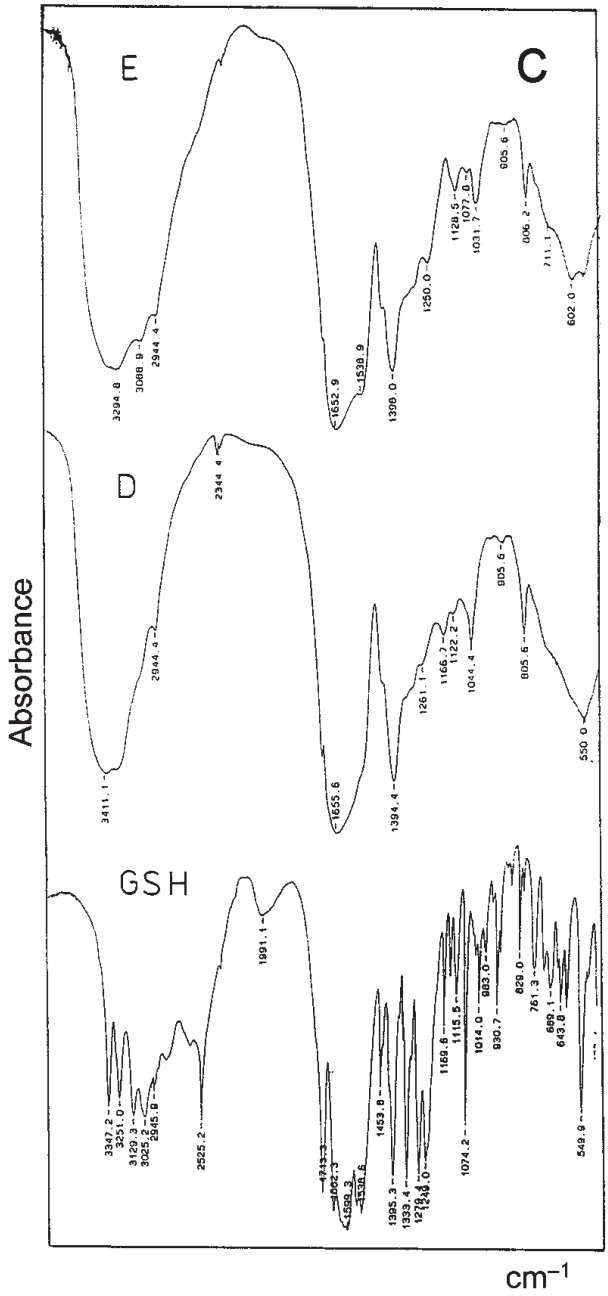


Fig. 1c IR spectra of complexes: A – $(Cr_2O_2(HAsc)_2 \cdot 9H_2O$; B – $K[Cr(HAsc)_2(OH)_2]KOH \cdot 3H_2O$ and free ligand; C – $K_2[Cr(HAsc)(CYS)(OH_2)] \cdot 7H_2O$ and free ligands; D – $Cr_2O(HAsc)(GSH)_2 \cdot 7H_2O$ and E – $K[Cr(HAsc)(GSH)] \cdot 7H_2O$ and free ligands

less resolved in comparison with that of free H_2Asc. Broadening of the bands is related to the complexation effect [19].

In the 3500–2700 cm^{-1} spectral region all sharp bands assigned to the O–H stretching vibrations in free acid are overlapped with water OH group vibrations present in A and B. The differences in the broadness of the band at ca 3400 cm^{-1} with respect to A and B can be due to the significant difference in the number of water molecules found in the complexes (Table 1). In the 1700–700 (carbonyl and ring vibrational region) the sharp band at 1754 cm^{-1} found in the free acid was bathochromically shifted to about 1709 cm^{-1} in the complexes. That means that the carbonyl C(1)=O group participates in coordination [26–28]. Similarily, the broad, strong band at ca 1674 cm^{-1} in the *L*-ascorbic acid attributed to the C=O and C=C stretching vibrations is shifted to ca 1620 cm^{-1} upon complexation.

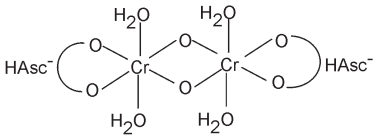
The complexation effect is also seen in the 500–600 cm^{-1} frequency region. In this region the 533 and 539 cm^{-1} bands attributed to the metal ligand vibration can be observed in A and B, respectively.

These results suggest the binding of chromium through oxygen C(1) and C(3) atoms in complexes A and B.

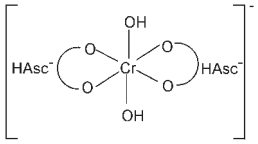
Thermal decomposition of A and B complexes

Table 2 and Fig. 2 illustrate the process of thermal decomposition of the complexes investigated. On increasing temperature compound A loses all hydration water in the first stage (20–120°C). Over the range 120–620°C the complex undergoes a complete degradation to Cr_2O_3. The X-ray diffraction data showed that the final products of decomposition is solid Cr_2O_3.

The decomposition of B is more complicated due to the presence of extra potassium ions in the molecule. There are three steps of decomposition (Table 2 and Fig. 2). The TG and DTA curves of B show that in the first step B loses hydration water and in the following steps a partial decomposition of the coordination sphere of chromium takes place. The release of the last portion of mass is accompanied by a total decomposition of the compound (exothermic effect on the DTA curves) and the oxidation process of chromium (Fig. 2). Finally, the presence of K_2CrO_4 as the only solid product has been found by X-ray diffraction method. The thermal decomposition of A and B is in line with the structure proposed from analytical and spectroscopic studies.



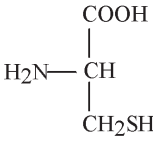
Scheme 2



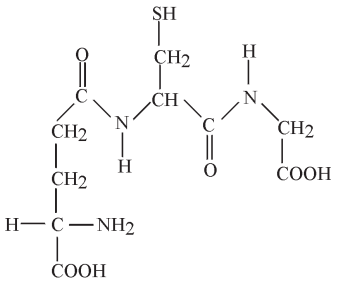
Scheme 3

Ternary [CrO_3–H_2Asc–GSH(CYS)] redox system

Cysteine and glutathione (Scheme 4 and 5) are potentially tridentate chelating ligands binding through sulphur, oxygen and nitrogen atoms [16, 29–31].



Scheme 4



Scheme 5

One ternary complex with ascorbic acid and cysteine (C) and two complexes with ascorbic acid and glutathione (D and E) have been isolated (Table 1).

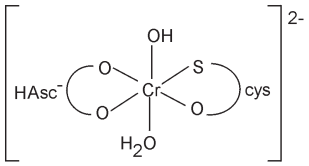
Infrared spectra of C, D and E complexes

The IR spectrum of grey product C is broad and unresolved in comparison to that of free cysteine (Fig. 1b). Several absorption regions were of interest, namely those characteristic for ν(OH), ν(SH) and ν(NH) and δ(NH) vibrations. A broad, strong band at 3400 cm^{-1} corresponds to ν(OH) in water and ascorbic acid molecules [32, 33].

The difference of 263 cm^{-1} between ν_a (1643 cm^{-1}) and ν_s (1380 cm^{-1}) for C=O in carboxyl group vibrations in *L*-cysteine shows that there is a unidentate binding between the metal ion and the carboxyl group of free cysteine [33]. A broad band at 542 cm^{-1} can be tentatively assigned to the metal-ligand (Cr–O) vibrations [16, 30]. In potassium ascorbatocysteinato-chromate(III) (C) the S–H vibrations characteristic of cysteine disappeared upon complexation thus the Cr{O,S} coordination in (C) was proposed.

The characteristic of the $–NH_2$ group frequencies were found to be less indicative due to an extensive hydrogen bonding operating in such a system [19].

Thus the IR spectrum shows that in $K_2[Cr(HAsc)(CYS)(OH)_2]\cdot 7H_2O$ obtained at pH=11.5, ascorbic acid is in the diionic form $(CYS)^{2-}$ binds to the Cr(III) ion via O and S atoms (Scheme 6). The Cr–S coordination was found previously in the electronic spectra of similar compound i.e. $[Cr(HAsc)(CYS)_2]$ [20].

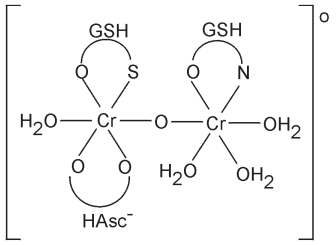


Scheme 6

The rather complicated situation found in the IR spectra of ternary complexes D and E (Fig. 1c) is due to the complexity of the GSH molecule. The tripeptide glutathione H_5L (Scheme 5) apart from various donor groups (N, O, S) available for coordination exhibits also various degree of deprotonation [29].

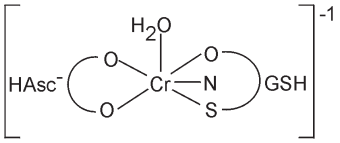
Compound D was isolated at low pH region and, similarily to A, it was found to be a dimer.

The lack of bands assigned to the SH vibrations present in free GSH molecule (2525) points to the Cr–S coordination. The frequency difference between asymmetric and symmetric carbonyl group vibrations indicates unidentate coordination of the carboxylate group in the GSH molecule. The presence of bending NH_2 vibration at 1538 cm^{-1} supports the Cr{O, S} coordination in complex D. However, the presence of the band at 448 cm–1 assigned to the νCr–N vibration showed also the Cr–N coordination (Scheme 7). Thus, as in [29], the GSH molecules are coordinated in the form of H_3L^{2-} and H_4L^{-} anions (Scheme 7).



Scheme 7

In complex E, monomeric anionic species of H_2L^{3-} type were found for GSH coordination. The lack of the 983 cm^{-1} (S–H), 3347, 1538 cm^{-1} (N–H) and the shift of C=O vibrations showed that the complex contains coordinated GSH through sulphur, nitrogen and unidentately coordinated carboxylic group. Ascorbic acid is most probably coordinated through C(1)O and C(3)O atoms (Scheme 8).



Scheme 8

Thermal decomposition of C, D and E complexes

Table 2 contains the proposed mechanism for decomposition of the Cr(III) ternary complexes C, D and E. As all complexes precipitated as hydrates we observed that in the first step of the thermal decomposition (25–170°C) the compounds lose the water of hydration (endothermic effects at DTA trace). The TG and DTA curves of C, D and E showed that in the second and third step (at temperatures over ca 200°C) the

decomposition and destruction of coordination sphere takes place. The release of the last portion of ligand is mostly accompanied by a total decomposition of the compounds (exothermic effect on the DTA curves) (Fig. 2).

Table 2 Thermal decomposition process characteristics

	Decomposition	Stage	Effect	TG/°C	Mass loss/%	
					found	calcd.
A	$[Cr_2O_2(HAsc)_2\cdot 4H_2O]\cdot 5H_2O$ ↓	I	endo	20–120	14.40	13.90
	$Cr_2O_2(HAsc)_2\cdot 4H_2O$ ↓	II	exo	120–620	61.40	62.30
	Cr_2O_3		endo			
B	$K[Cr(HAsc)_2(OH)_2]KOH\cdot 3H_2O$ ↓	I	endo	25–100	6.48	6.34
	$K[Cr(HAsc)_2(OH)_2]KOH$ ↓	II	exo	100–480	58.31	58.18
	$K[Cr(HAsc)_{0.4}]KOH$ ↓	III	endo	490–1000	4.70	5.50
	K_2CrO_4					
C	$K_2[Cr(HAsc)(CYS)(OH)_2\cdot(H_2O)]\cdot 6H_2O$ ↓	I	endo	20–195	13.49	13.59
	$K_2[Cr(HAsc)(CYS)(OH)_2(H_2O)]$ ↓	II	exo	230–460	38.50	39.6
	$K_2[Cr(CYS)]$ ↓	III	endo	480–1000	8.10	7.55
	$K_2SO_4+½Cr_2O_3$					
D	$[Cr_2O(HAsc)(GSH)_2\cdot 4H_2O]\cdot 3H_2O$ ↓	I	endo	20–140	12.18	12.20
	$[Cr_2O(HAsc)(GSH)_2$ ↓	II	exo	190–340	59.04	59.15
	$[CrO(HAsc)Cr]$ ↓	III	endo	350–630	16.87	16.86
	Cr_2O_3					
E	$K[Cr(HAsc)(GSH)\cdot H_2O]\cdot 6H_2O$ ↓	I	endo	20–220	15.75	15.50
	$K[CrO(HAsc)(GSH)\cdot H_2O]$ ↓	II	exo	220–330	27.00	27.7
	$K[CrO(GSH)]$ ↓	III	endo	340–1000	31.50	31.2
	$0.5Cr_2O_3+0.5K_2SO_4$					

Thermal data show, that in compound D where gluthatione was found to be a bidentate ligand (see the IR data), the GSH is eliminated as a first one.In the complex E tridentate gluthatione must be bound more strongly with central metal than ascorbate acid is. Hence, in E the gluthatione molecules were eliminated during the last step of decomposition (Table 2). In the same step at a temperature over 350°C,

the destruction and combustion of *L*-ascorbic acid also takes place. The results of the thermal analysis show that the release of ligands is a three-step process (Fig. 2).

The final products obtained is Cr_2O_3 (D) and the mixture of Cr_2O_3 and K_2SO_4 (C and E).

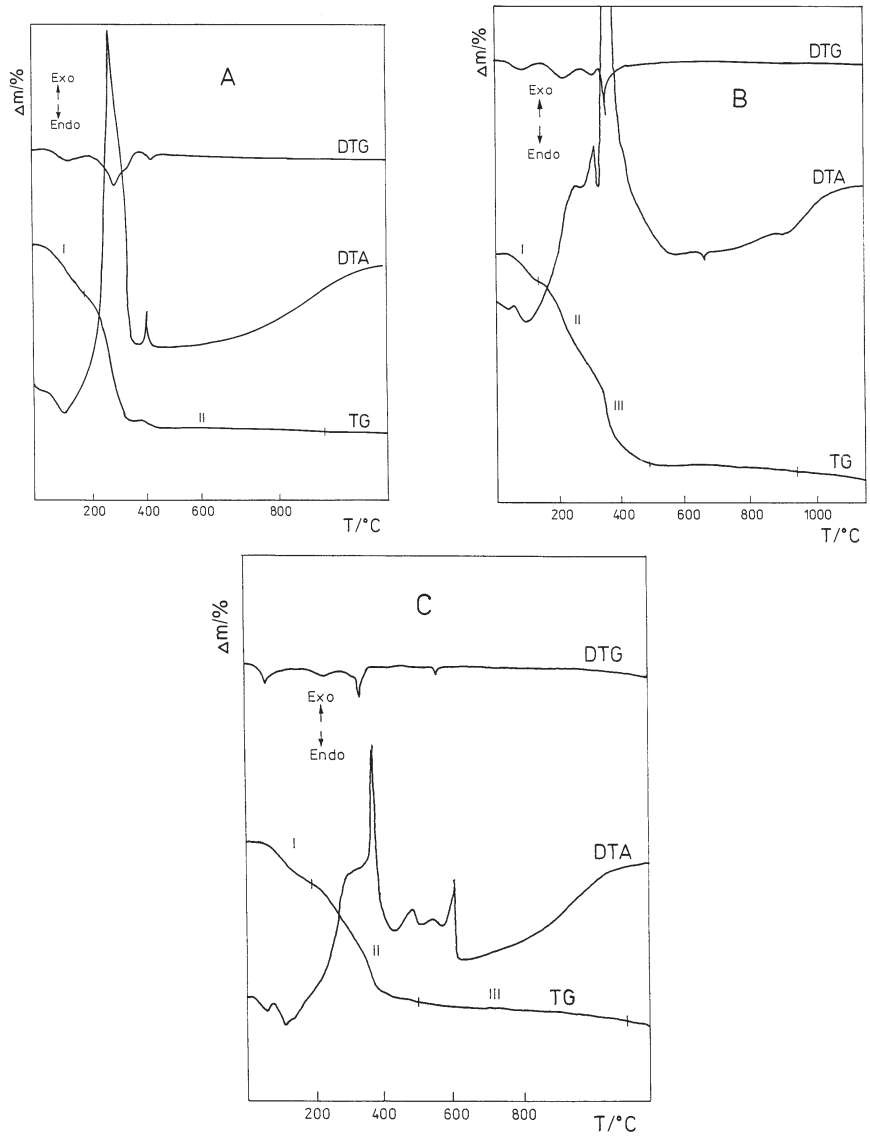


Fig. 2 DTA, TG and DTG traces for complexes: A – $Cr_2O_2(HAsc)_2 \cdot 9H_2O$, B – $K[Cr(HAsc)_2(OH)_2]KOH \cdot 3H_2O$, C – $K_2[Cr(HAsc)(CYS)(OH)_2] \cdot 7H_2O$

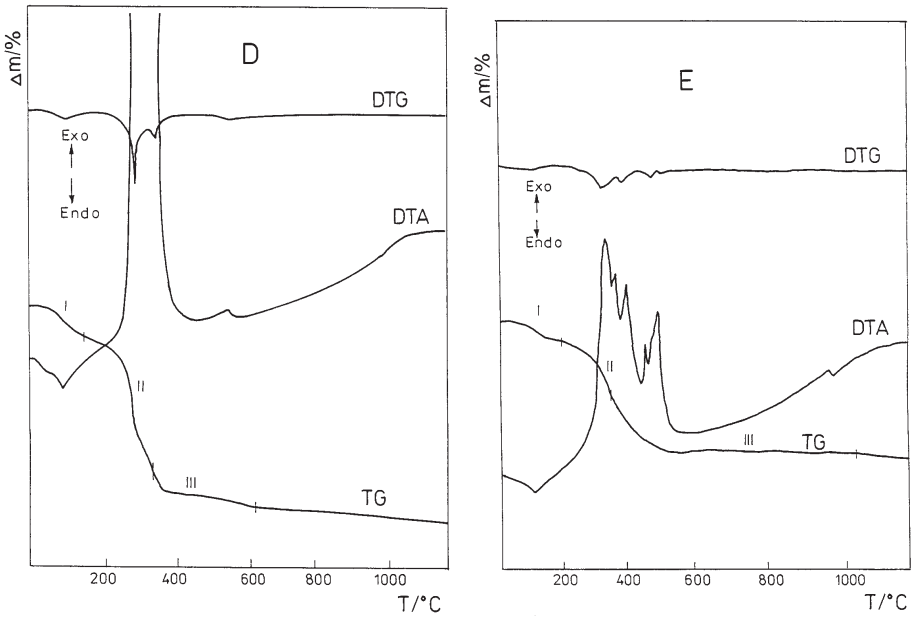


Fig. 2 Continued: D – $Cr_2O(HAsc)(GSH)_2 \cdot 7H_2O$, E – $K[Cr(HAsc)(GSH)] \cdot 7H_2O$

Conclusions

The interaction between chromium(VI) oxide and low molecular mass non-enzymatic cellular reductants resulted in isolation of monomeric anionic type and dimeric neutral Cr(III) complexes. The systems studied are very complicated because depending on the solution acidity:

1. various forms of Cr(VI) (mono- and polymeric) and various form of organic anions (e.g. mono, double or triple-charged) were present in the isolated complexes.

2. various forms of coordination preferences (e.g. monodentately, bidentately) has been found for the ligands [16, 26–28].

The dimeric neutral Cr(III) products in the CrO_3 – ascorbic acid and CrO_3 – ascorbic acid – GSH systems were obtained for the first time.

All complexes crystallized as hydrates. The presented data illustrate that CrO_3 – biological ligand system are strongly influenced by pH, as expected.

The comparison of these results to those obtained earlier shows that the stoichiometries of the isolated species depend on the substrates used i.e. at low pH the products are chromium monomers and dimers for K_2CrO_4 [19] and CrO_3 (this work), respectively.

The thermal decomposition processes of these complexes are in line with the spectroscopic results. Final solid products of the dimeric Cr(III) species are chromium(III) oxide (A and D) whereas for the monomers the potassium sulphate and chromium(III) oxide (C and E) and potassium chromate(VI) (B) were found. The potassium sulphate(VI) and chromate(VI) are the results of the strong oxidation process ($S^{-2} \rightarrow S^{+6}$ and $Cr^{+3} \rightarrow Cr^{+6}$) operating during heating in the dynamical air atmosphere.

The authors are indebted to dr. W. Surga for making X-ray. One of the authors (M.C-G.) thanks to the University of Technology in Wrocław for financial support (grant No 342-049).

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