Polyhedron 28 (2009) 2719–2729

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Oligo and polyuronic acids interactions with hypervalent chromium

Juan C. González [a], Silvia I. García [a], Sebastián Bellú [a], Ana María Atria [b], Juan Manuel Salas Pelegrín [c], Antal Rockenbauer [d], Lazlo Korecz [d], Sandra Signorella [a,*], Luis F. Sala [a,*]

[a] Instituto de Química de Rosario-CONICET, Universidad Nacional de Rosario, UNR, Suipacha 531, S2002LRK, Rosario, Argentina
[b] Facultad de Ciencias Químicas y Farmacéuticas-Universidad de Chile, Santiago de Chile, Chile
[c] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, Fuentenueva s/n, 18071 Granada, Spain
[d] Chemical Research Center, Hungary Academy of Sciences, Pusztaszeri street 59-67, H-1025 Budapest, Hungary

ARTICLE INFO

Article history:
Received 8 April 2009
Accepted 11 May 2009
Available online 19 May 2009

Keywords:
Chromium
Uronic acids
EPR
Redox chemistry
Kinetics

ABSTRACT

Selective oxidation of galacturonic residues of oligo and polyuronic acids by Cr^{VI} affords CO_2/HCO_2H, oxidized uronic acid, and Cr^{III} as final redox products. Kinetic studies show that the redox reaction proceeds through a mechanism combining $Cr^{VI} \rightarrow Cr^{IV} \rightarrow Cr^{II}$ and $Cr^{VI} \rightarrow Cr^{IV} \rightarrow Cr^{III}$ pathways. The mechanism is supported by the observation of free radicals, CrO_2^{2+} and Cr^{V} as reaction intermediates. The EPR spectra show that five- and six coordinated oxo-Cr^{V} intermediates are formed. Penta-coordinated oxo-Cr^{V} species are present at any $[H^+]$, whereas hexa-coordinated ones are only observed at pH <1. At low pH Cr^{V} predominating species are coordinated by carboxylate groups and O^{ring} (g_{iso} = 1.9783/5). At pH 7.5, the predominating ones are those coordinated by alcoholate groups of the ligand (g_{iso} = 1.9800). Polygal can reduce Cr^{VI} and efficiently trap Cr^{III}. This behaviour represents an interesting model for the study of biomaterials, which possess a high proportion of polygal, in order to remove chromium from polluted waters.

Published by Elsevier Ltd.

1. Introduction

Uronic acids are widespread distributed in vegetal kingdom, composing the wall cell of higher plants, under polyuronic acid form [1]. Galacturonic acid (galur) is the major low-molecular-weight metabolite of pectic substances. The determination of the ability of galur residues to reduce or stabilise high oxidations states of Cr, will contribute to understand its potential role in the biochemistry of this metal. A high percentage of vegetal carbohydrates come from uronic acids and includes all the pectin material, gums, mucilage, hemicelluloses present in plants and microbiological polysaccharides [1]. Generally, the carboxylate groups present in galur residues, are under the form of calcium and magnesium complexes. Acid saccharides interaction with cations could be of great biological implications because metal complexation is probably taking place on the cell wall surface, rich in this kind of polysaccharides [2–4].

The Cr^{VI} coming from industrial waste produces a serious ambiental risk due to its toxicity and carcinogenicity [5]. Understanding the interaction of the galur residues with $Cr^{VI/III}$ could afford information over the biological and ecological implicancies of the presence of Cr on the environment. Remediation processes to remove hypervalent chromium in contaminated waters as, filtration, chemical precipitation, adsorption, electrochemical reduction and ionic exchange processes have been reported [6,7]. Adsorption is a versatile and efficient method to eliminate chromium, especially if the adsorbents which were used are economical [8]. The biomaterials employed in remediation, such as bagasse and materials coming from cellulose degradation, are winning importance as an economic alternative for the treatment of chromium contaminated water. Taking into account the carbohydrate capacity to bond Cr^{III} and reduce Cr^{VI} to Cr^{III}, the use of material rich in polysaccharide acid, in particular polymers of uronic acids, could be a new alternative for the chromium elimination from effluents [9].

2. Experimental

2.1. Materials

Sodium polygalacturonate (Sigma, 95%), digalacturonic acid (digal) (Sigma, 98%), trigalacturonic acid (trigal) (Sigma, 98%), potassium dichromate (Mallinckrodt), perchloric acid (A.C.S. Baker), 1,5-diphenylcarbazide (Aldrich, p.a.), acrylonitrile (Fluka 99%), 4-(2-hydroxyethyl-1-pyperazineetanesulfonic acid (Hepes) (Aldrich, 99.5%), diphenylpicrylhydrazyl (dpph) (Aldrich p.a.) glutathione, (GSH) (reduced form, Sigma 99.0%), oxygen peroxide

* Corresponding authors. Tel./fax: +54 341 4350214.
E-mail addresses: signorella@iquir-conicet.gov.ar (S. Signorella), sala@iquir-conicet.gov.ar (L.F. Sala).

0277-5387/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.poly.2009.05.018

(Merk, p.a.), chromium(III) nitrate nonahydrate (Aldrich 99%) and sulfuric acid (Cicarelli, p.a.), oxygen (99.99%). Aqueous solutions were prepared in milliQ deionised water (HPLC quality).

In experiments performed at pH 1–3, the pH of the solutions was achieved by addition of $HClO_4$ solution. In experiments at pH 7.0–7.5 the buffer used was 4-(2-hydroxyethyl-1-pyperazineetanesulfonic acid (Hepes). Concentration of stock solutions of $HClO_4$ was determined using standards analytical methods.

Caution: Cr^{VI} are human carcinogens, and Cr^{V} complexes are mutagenic and potential carcinogens [10]. Contact with skin and inhalation must be avoided. Acrylonitrile is a carcinogen and must be handled in a well-ventilated fume hood [11].

2.2. Methods

2.2.1. Spectrophotometric measurements

Spectrophotometric measurements were performed by monitoring absorbance changes using a Jasco-V-550 spectrophotometer with a fully thermostated cell compartment (±0.2 °C). Disappearance of Cr^{VI} in reactions with digal and trigal was followed spectrophotometrically at 350 nm under pseudo-first-order conditions, using at least a 50-fold molar excess of substrate over Cr^{VI}. Reactant solutions were previously thermo stated and transferred into a 1.0 cm path length cell immediately after mixing. Experiments were performed at 33 °C unless otherwise stated and mixtures of sodium perchlorate and perchloric acid were used to maintain a constant ionic strength (I) 1.0 M. The disappearance of Cr^{VI} was followed until at least 80% conversion. In the kinetic measurements, the initial concentration of Cr^{VI} was kept at 6.0×10^{-4} M and the digal/trigal concentration was varied from 0.03 to 0.09 M, [$HClO_4$] was kept constant at 0.2 M. Multiple measurements showed the reproducibility of the method. Rate constant (k_6, k_5) were deduced from multiple determinations and were within ±10% error for each other. The first-order dependence of the rate upon [Cr^{VI}] was verified in a set of experiments where the $[Cr^{VI}]_0$ was varied between 0.3 and 0.6 mM but temperature, $[digal]_0$ or $[trigal]_0$, [H^+] and I were kept constant.

The presence of superoxoCr^{III}, CrO_2^{2+}, in mixtures of digal or trigal/Cr^{VI} was investigated by periodic scanning UV–Vis spectrophotometry in the 220–500 nm region of O_2-saturated solutions, 1.26 mM, containing 0.1 M digal or trigal, [$HClO_4$] = 0.2 M, [Cr^{VI}] = 0.047 mM, I = 1.0 M at 25 °C. Periodic scanning of the reaction mixture showed that the Cr^{VI} band at 350 nm decreased in intensity, while new peaks at 290 and 247 nm, characteristic of CrO_2^{2+} grew in.

2.2.2. Chromium determination in polygal/Cr^{VI} supernatant mixtures

Perchloric acid used in the reaction mixture of polygal/Cr^{VI} protonates the carboxylate groups of polygal, producing its aggregation in particles of different sizes, which depends on the experimental conditions. In all experiences, polygal was generated by direct reaction of sodium polygalacturonate solutions with perchloric acid. Different mass of sodium polygalacturonate (25–1200 mg) were dissolved in 31.0 mL of distilled water at 60 °C, with constant stirring. 1.10 mL of $HClO_4$ 3.83 M was added to a heterogeneous mixture, which was then incubated for 10 min. Finally, 2.0 mL Cr^{VI} 0.30 M was added. The final composition of the mixture was [$HClO_4$] = 0.12 M, [Cr^{VI}] = 0.0176 M, [polygal] = 0.73–35.2 g/L. Reaction mixture was kept in close recipients thermostitazed at 60 °C. After 24 h of stirring, 2.0 mL aliquot of the suspension were centrifuged during 30 min at 5000 rpm. About 200–300 μL of the clear supernatant were taken and dried in a porcelain cap and calcinated until total elimination of organic material. The yellow solid [12] was taken up to a final volume of 5.0 mL with H_2SO_4 0.10 N and measurements of the absorbance at 350 nm allowed calculation of the [Cr^{VI}].

2.2.3. EPR measurements

The EPR spectra were obtained on a Bruker EMX0 spectrometer operating at X-band frequencies (~9–10 GHz). Microwave generation was means with a Bruker 04 ER and measured with a Bruker EMX 048T frequency meter. Spectra were recorded as first derivatives of the microwave absorption in 1024 point at 20 ± 1 °C using 10 mW microwave power, 100 kHz modulation frequency, and 0.29–2.00 G modulation amplitude. g-Values were determined by reference to (dpph) (g_{iso} = 2.0036) as an external standard. In EPR measurements, scanning speed and scans number were fixed in order to reduce the time used in each measurement. This was done to avoid fluctuations in the EPR signal during the sample scanning. Power values used in the EPR experiments did not overcome 10 mW in order to avoid signal saturation.

Long-lived oxo-Cr^{V}-oligouronic and polygal complexes were generated by reaction of $K_2Cr_2O_7$ with an aqueous solution containing GSH at 25 °C. In the experiments [Cr^{VI}] = [GSH]. Final concentration in mixtures polygal/GSH/Cr^{VI}, where [Cr^{VI}] = [GSH] = 0.012–0.014 M; [polygal] = 19.2–23.0 g/L.

All the EPR spectra were simulated using the PEST WINSIM [13] program assuming 100% Lorentzian line shapes. The spectral parameters for each Cr^{V} species were similar in all simulations, with a maximum deviation of ±0.0001 in the g_{iso} values. Values for a_{iso} (^{1}H) were included in the simulations only when were greater than the line width of the oxo-Cr^{V} species.

2.2.4. Polymerization test

The presence of free radicals in the reactions of digal and trigal with Cr^{VI} was tested by acrylonitrile polymerization test. About 0.2 mL of acrylonitrile was added to a solution of Cr^{VI} (0.0027 mmol) and digal/trigal (0.07 mmol) in $HClO_4$ 0.20 M (0.5 mL). After a few minutes at 33 °C, a white precipitate appeared. 0.5 mL of acrylonitrile was added to a reaction mixture containing 53.1 g/L of polygal and 8.0 mM of Cr^{VI}, in 2.0 mL of $HClO_4$ 0.01 M. The mixture was left 2.0 h at 60 °C. After this time, the white precipitate could be seen. ^{13}C NMR of a D_6-DMSO solution of the white solid and FT-IR of the solid showed the pattern characteristic of polyacrilonitrile. Blank experiments with either Cr^{VI} or polygal gave no detectable white precipitates. Control experiments (without Cr^{VI} or reductant present) did not show the formation of a precipitate. The possible reaction of Cr^{V} or Cr^{IV} with acrylonitrile was tested with Na[Cr^{V}O(ehba)$_2$] [14] and [Cr^{IV}O(ehba)$_2$] [15] (ehba = 2-ethyl-2-hydroxybutanoic acid). No precipitation occurred on mixing the Cr^{V} or Cr^{IV} complexes with acrylonitrile under the same conditions as those used in the Cr^{VI} + digal/trigal/polygal reactions.

2.2.5. Effect of external reducing agent (Na_2SO_3) in polygal/Cr^{VI} mixture

Reaction mixture of polygal and perchloric acid were 35.2 mg/L and 0.12 M, respectively. About 0.9 mmol of Na_2SO_3 and 2.0 mL of Cr^{VI} solution 0.3 M were added to 34.1 mL of the reaction mixture.

2.2.6. HCO_2H and CO_2 determination in polygal/Cr^{VI} mixtures

Supernatant of polygal/Cr^{VI} reaction mixture was employed to analyse oxidation products. Carbon dioxide was measured in 35.0 g/L polygal and Cr^{VI} 2.90 mmol/L mixture, in $HClO_4$ 0.12 M. The reaction mixture was continuously stirred and flushed with pure nitrogen at 60 °C. Gaseous products were passed trough three flasks containing NaOH solution. Once the reaction finished, NaOH solutions were titrated with standard HCl in order to determine the carbon dioxide generated. Supernatant was filtered employing a 0.2 μm of porous diameter membrane and analysed by HPLC, showing the presence of formic acid with retention time (R_t) 13.20 min. An aminex HPX-87H column at 25 °C and 0.6 mL/min flow, detection at 220 nm, was used for this experiment. Co