Reduction of Chromium(VI) by D-Galacturonic Acid and Formation of Stable Chromium(V) Intermediates

MARIO BRANCA, GIOVANNI MICERA*

Dipartimento di Chimica, Universitá di Sassari, Via Vienna 2, 07100 Sassari, Italy

and ALESSANDRO DESSÍ

Istituto per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, C.N.R., Via Vienna 2, 07100 Sassari, Italy

(Received January 4, 1988; revised March 11, 1988)

Abstract

The interaction of dichromate with D-galacturonic acid in aqueous solution, as a function of pH, is described. The reaction involves the reduction of Cr(VI) to Cr(III), but the reaction rate is remarkably dependent on pH. In fact, the reduction of Cr(VI) to Cr(III) proceeds rather quickly in strongly acidic solutions, while it is slow in neutral or moderately acidic media. In all cases, according to the ESR evidence, Cr(V) species are found as intermediates. The stability of the Cr(V) species increases with increasing pH, so that it may be suggested that the overall reaction rate is controlled by the Cr(V) to Cr(III) conversion.

Introduction

Sugars play an essential role in bioinorganic processes since, besides acting as metal chelators, they may behave as biological reductants. For example, they have been proved to reduce iron(III) to iron(II) [1], thereby providing a mechanism of fundamental importance for the survival of plants. On the other hand, vanadium(V) is also reduced upon interaction with sugars [1–3], forming oxovanadium(IV) species which have biological activity different from that of vanadium(V) [4].

As a continuation of previous studies on the complexing and reducing properties of uronic and polyuronic acids [1–3, 5, 6] we have devoted our attention to the reaction of chromium(VI) with D-galacturonic acid. This choice was due to the fact that chromium(VI) originating from industrial wastes may contaminate soil, thus presenting a serious environmental hazard due to its toxicity and possible carcinogenity [7–10]. On the other hand, galacturonic acid is the major low-molecular-weight metabolite of pectic substances, which are widely diffuse in soil. Therefore, an understanding of the interaction of chromium(VI) with this sugar molecule could provide information on some ecological and biological implications of the presence of chromium in the environment.

*Author to whom correspondence should be addressed.

Experimental

Materials

D-Galacturonic acid (Sigma) solutions were prepared in doubly distilled water. The Cr(VI) source was potassium dichromate (Aldrich, ACS reagent), Typically, aqueous solutions of potassium dichromate and D-galacturonic acid, at varying molar ratios, were mixed and the pH was adjusted by addition of $HClO_4$ or NaOH. The samples were stored at 25 °C in stoppered vials in the presence of air. Aliquots were taken at timed intervals and submitted to electronic absorption and ESR measurements.

Physical Measurements

Electronic spectra were recorded with a Jarrel Jasco Model 610 spectrophotometer. X-band ESR spectra were taken at room temperature with a Bruker ER 220 spectrometer at *ca.* 9.40 GHz, using flat quartz cells. The spectrometer was interfaced to an ASPECT 2000 computer for data acquisition and handling. DPPH was used as a standard field marker.

Results and Discussion

Electronic Spectra

The reaction between Cr(VI) and D-galacturonic acid in aqueous solution was followed by changes in the UV–Vis spectra. At high acidity ($HClO_4 > 0.1$ M) and in the presence of an excess of D-galacturonic acid, the reaction was rather fast as the absorptions of dichromate ion (260, 350 and 440 nm) diminished quickly until they became no longer detectable after

0020-1693/88/$3.50

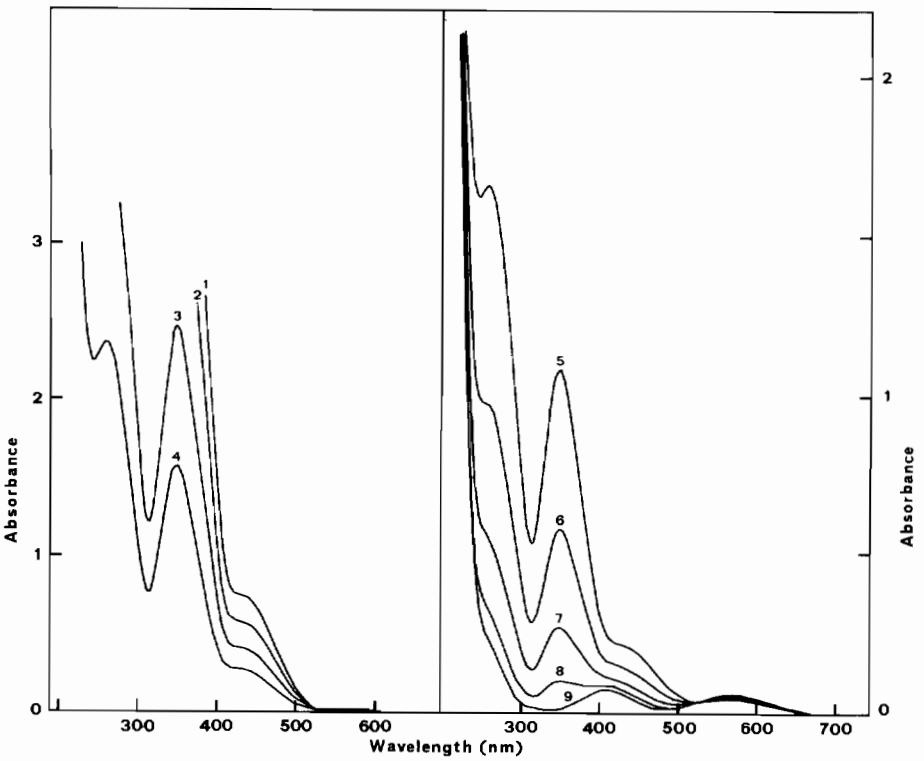

Fig. 1. Time-dependence of electronic spectra in the Cr(VI) oxidation of D-galacturonic acid. Conditions: 4×10^{-3} M $K_2Cr_2O_7$, 1.2×10^{-2} M D-galacturonic acid, 0.25 M $HClO_4$. Spectra were recorded consecutively at 30-min intervals.

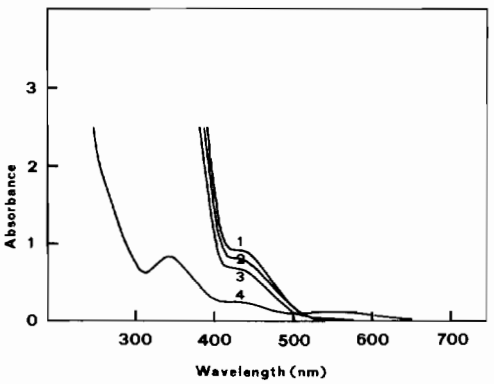

Fig. 2. Time-dependence of electronic spectra in the Cr(VI) oxidation of D-galacturonic acid. Conditions: reactant concentrations the same as for Fig. 1, pH 4. Spectra were recorded at the beginning of the reaction and after 7, 11 and 18 days, respectively.

a few hours (see Fig. 1). Under these conditions the reaction showed a pseudo-first-order dependence on the chromium(VI) concentration. Finally, bands at 410 and 570 nm were observed (ϵ = 13 and 16 M^{-1} cm^{-1}, respectively), attributable to the octahedral $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions in O_h symmetry, respectively, which are distinctive of the free Cr(III) aqua-ion.

With increasing pH values, the reaction became much slower and apparently required an induction time. For example, at pH about 1 the conversion of Cr(VI) into Cr(III) was complete within 24 h at 25 °C, while at pH 4 the Cr(VI) bands disappeared completely only after several days (see Fig. 2). In addition, chromium(III) bands which were shifted and exhibited higher extinction coefficients, compared to those of the free ion, were detected. Typically, at pH around 4 the absorptions were at 425 and 560 nm, with ϵ values of about 46 and 39 M^{-1} cm^{-1}, respectively.

This behaviour is not explainable if one only takes into account the formation of complexes between Cr(III) and the excess of galacturonic acid. In fact, a spectrophotometric study of the Cr(III)–D-galacturonic acid system, as a function of pH, while exhibiting analogous band shifts, showed only a minor intensity increase of the absorptions (Table I). However, after acidifying the reaction solution with mineral acid, the Cr(III) bands were restored to intensity values comparable to those of the aqua-ion. This indicated that except for strongly acidic conditions, the reduction requires a rather long lapse of time before going to completion and, in addition, the intensity increase of chromium(III) bands may originate from the presence of underlying absorptions due to reaction intermediate species, as well as from

TABLE I. Electronic Absorption Data for the Cr(III)–D-Galacturonic Acid System in Aqueous Solution[a]

pH	Absorption maxima (nm)[b]
1	410(16), 575(13)
2.5	410(18), 575(14)
3	420(20), 575(14)
4	430(27), 575(16)
5	435(34), 565(20)

[a]D-Galacturonic acid:Cr(III) molar ratio = 2. [b]Extinction coefficients (M^{-1} cm^{-1}) are in parentheses.

the involvement of the trivalent ion in complex formation. Based on the ESR results (see later), the underlying absorptions may be assigned to Cr(V) species, in agreement with literature data which report bands in the above range for Cr(V) complexes of O-donor ligands [11, 12].

To determine the stoichiometry of the reaction, solutions with various Cr(VI)-to-galacturonic acid molar ratios were studied. Complete reduction of Cr(VI) to Cr(III), as deduced by the disappearance of the 350 nm-peak and the quantitative formation of Cr(III), occurred only at dichromate:galacturonic acid molar ratios higher than 3.3–3.5. This finding suggests that, at least under very acid conditions, the overall reaction involves the full oxidation of carbon atoms of the sugar molecule to yield carbon dioxide and water.

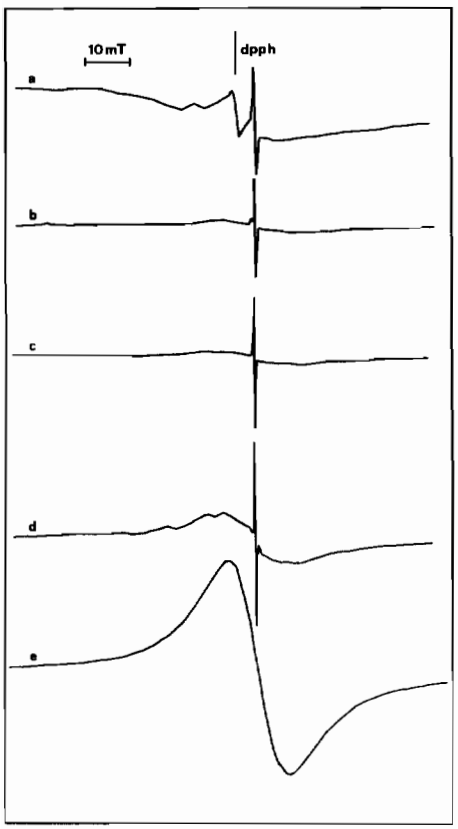

Fig. 3. Time-dependence of the ESR spectra, recorded at room-temperature, in the Cr(VI) oxidation of D-galacturonic acid. Conditions: 4×10^{-3} M $K_2Cr_2O_7$, 1.2×10^{-2} M D-galacturonic acid, pH 1. Spectra were recorded immediately after mixing the reactants (a) and after 1 h (b), 2 h (c), 3 h (d) and 19 h (e).

ESR Spectra

ESR spectra of the reaction mixtures, recorded at room temperature, are shown in Figs. 3–5. At high acidity ($HClO_4 > 0.1$ M) a sharp signal ($g_o = 1.977$) which can be attributed to Cr(V) was observed immediately at the beginning of the reaction. The measured ^{53}Cr hyperfine coupling constant of 1.85 mT is very close to the literature values for Cr(V) complexes with O-donor ligands [13–15]. A broader band at g_o about 1.98, which is attributable to Cr(III), showed up with elapsing time, while the narrow Cr(V) resonance first appeared superimposed on the Cr(III) band and then vanished as the reaction went to completion.

Different behaviour was found when the pH was raised. The ESR resonances due to Cr(V) were weaker

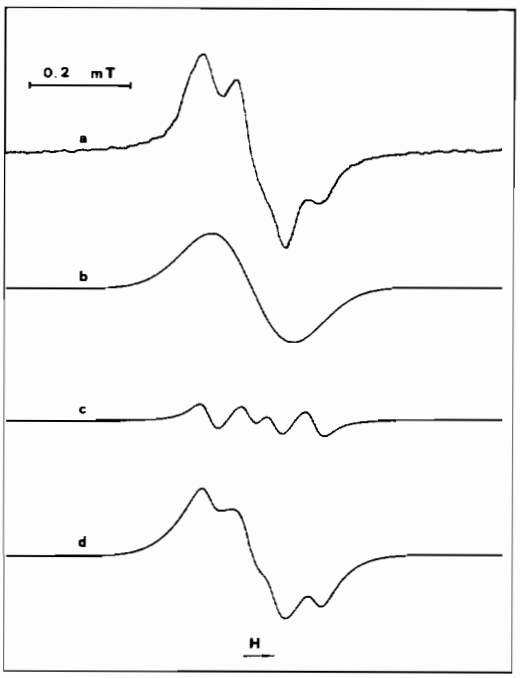

Fig. 4. Experimental (a) and computed (b, c and d) ESR spectra at room-temperature of Cr(V) species formed at pH 2. The spectrum (d) was obtained by assuming the superimposition of resonances (c) due to the coupling with two unequivalent protons ($a_H = 0.13$, $a_{H'} = 0.08$ mT) on the isotropic band (b). Instrumental settings: microwave frequency 9.40 GHz, field set 338.6 mT and sweep 1 mT.

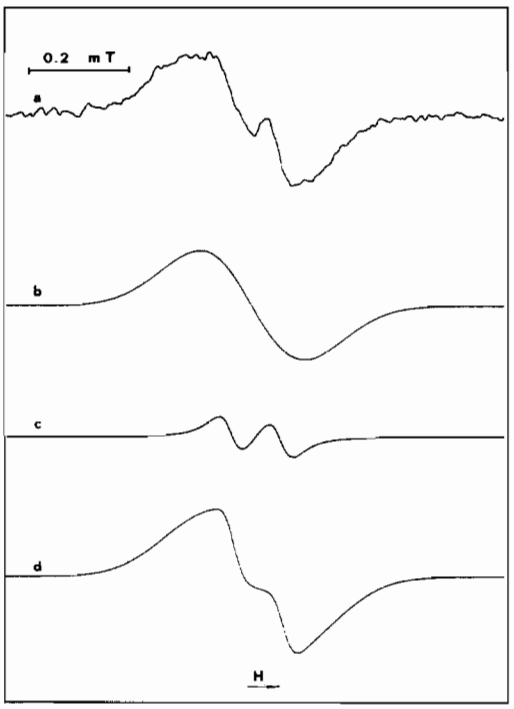

Fig. 5. Experimental (a) and computed (b, c and d) ESR spectra at room-temperature of Cr(V) species formed at pH 5. The spectrum (d) was obtained by assuming the superimposition of resonances (c) due to the coupling with one proton ($a_H = 0.10$ mT) on the isotropic band (b). Instrumental settings: microwave frequency 9.40 GHz, field set 338.6 mT and sweep 1 mT.

and required pH-dependent incubation times. Also their decay rate showed a remarkable pH-dependence: in particular, the higher the pH, the more persistent was the signal. In fact, the Cr(V) signals were still observable even after months in solutions stored at pH 5–7 room temperature. This finding represents striking evidence for the presence, in solution, of Cr(V) species having remarkable stability.

Evidence for the presence of complexed Cr(V) was obtained from the fact that the ESR resonances, which varied with pH, showed detectable splittings of about 0.1 mT (Figs. 4 and 5), similar to those observed by Goodgame and Joy on other Cr(V)–sugar complexes [15], indicating the superhyperfine coupling of metal with ligand protons and, possibly, the existence of more than one species. In any case, the asymmetric shape of the spectra may be explained by the superimposition of a hyperfine structure on an isotropic resonance, the corresponding g values being slightly different. For example, by simulating the combination of an isotropic band with the set of resonances due to the interaction of Cr(V) with one proton ($g_o = 1.976$, $a_H = 0.10$ mT) at pH 5 and two unequivalent protons ($g_o = 1.977$, $a_H = 0.08$ and $a_{H'} = 0.13$ mT) at pH 2, satisfactory fits were obtained (Figs. 4 and 5).

On the other hand, the Cr(III) ESR bands were not immediately evident from examination of spectra recorded on samples stored at pH above 3, even in the presence of Cr(V) decay. This finding was in accordance with the results of an ESR investigation which showed that the Cr(III) bands, either in the presence or absence of D-galacturonic acid, become broader and weaker with increasing pH. However, again, the addition of mineral acid allowed the reaction to go to completion, as judged from the complete disappearance of the Cr(V) signals and the detection of the Cr(III) isotropic band typical of the free aqua-ion.

Conclusions

The results of this study show that galacturonic acid converts Cr(VI) into Cr(III) and the reaction is favoured by acidic conditions. In all cases, Cr(V) species are generated as intermediates. However, the rate of Cr(V) decay appears to be remarkably dependent on pH, probably due to the extent of the involvement of the ion in complex formation with the substrate or with intermediate oxidation products, if any. The decay rate decreases with increasing pH, so that it may be suggested the Cr(V) complexes formed at various pH values have different kinetic stabilities toward subsequent reduction. Thus, long-lived Cr(V) complex species may be generated by the interaction of Cr(VI) with sugars. Judging from our experiments, the stability of these species, which is reasonably dependent on the relative formation and decay rates, increases with increasing pH until it becomes significant under neutral or moderately acidic conditions.

In conclusion, this study further substantiates recent evidence [13–15] showing that, under environmental conditions, the interaction of chromium(VI) with natural substances may be responsible for the formation and accumulation of water-soluble Cr(V) species stable enough to enter into ecological cycles and produce toxic effects. Further, it is known that plants, at the root level, are provided with an extra-cellular macromolecular apparatus composed mainly of galacturonic units [16]. Thus, it is conceivable that, in polluted soils, accumulation of Cr(V) species, generated by Cr(VI) reduction, can take place inside the plant roots, constituting a further vehicle of environmental contamination.

References

1 C. Gessa, M. L. De Cherchi, A. Dessí, S. Deiana and G. Micera, *Inorg. Chim. Acta, 80*, L53 (1983).
2 C. Gessa, M. L. De Cherchi, S. Deiana, A. Dessí and G. Micera, *J. Chromatogr., 268*, 539 (1983).
3 G. Micera, S. Deiana, A. Dessí, A. Pusino and C. Gessa, *Inorg. Chim. Acta, 100*, 49 (1986) and refs. therein.

4 N. Sutin and P. Gütlich, *Comments Inorg. Chem., 2,* 1 (1982).
5 S. Deiana, L. Erre, G. Micera, P. Piu and C. Gessa, *Inorg. Chim. Acta, 46,* 249 (1980).
6 S. Deiana, G. Micera, G. Muggiolu, C. Gessa and A. Pusino, *Colloids Surfaces, 6,* 17 (1983).
7 L. Tomatis, C. Agthe, W. Bartesch, J. Huff, R. Montisano, R. Saracci, E. Walker and J. Wilbourn, *Cancer Res., 38,* 877 (1978).
8 J. M. Davies, *Lancet,* 384 (1978).
9 A. Fürst, M. Schlauder and D. P. Sasmore, *Cancer Res., 36,* 1779 (1976).
10 A. G. Levis and F. Majone, *Br. J. Cancer, 44,* 219 (1981).
11 M. Krumpolc and J. Roček, *J. Am. Chem. Soc., 99,* 137 (1977).
12 V. Srinivasan and J. Roček, *J. Am. Chem. Soc., 96,* 127 (1974).
13 D. M. L. Goodgame, P. B. Hayman and D. E. Hathaway, *Inorg. Chim. Acta, 91,* 113 (1984).
14 S. L. Boyko and D. M. L. Goodgame, *Inorg. Chim. Acta, 123,* 189 (1986).
15 D. M. L. Goodgame and A. M. Joy, *Inorg. Chim. Acta, 135,* L5 (1987).
16 R. Ramamoorthy, *J. Theor. Biol., 66,* 527 (1977).