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Reduction of Trace Quantities of Chromium(VI) by Strong Acids

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O comportamento químico de Cr(VI) a baixas concentrações (10^{-4} to 10^{-7} mol L^{-1}) em vários ácidos fortes foi estudado utilizando-se ^{51}Cr(VI) de alta atividade específica como marcador. A especiação dos produtos destes sistemas foi realizada por cromatografia de troca iônica com eluição em etapas. Os resultados mostram que traços de Cr(VI), monitorados por radiocromo (^{51}Cr), são reduzidos na presença de ácidos minerais tais como perclórico, clorídrico, fluorídrico, sulfúrico, nítrico e trifluormetanosulfônico, mesmo na ausência de agentes redutores convencionais, produzindo várias espécies de Cr(III) diferentes, dependendo do ânion do ácido. Estudos detalhados com soluções de ácido nítrico mostram que a velocidade relativa da redução aumenta com o aumento da concentração do ácido ou com o decréscimo da concentração de Cr(VI).

The chemical behavior of Cr(VI) at low concentrations (10^{-4} to 10^{-7} mol L^{-1}) in several strong acids was studied using high specific activity ^{51}Cr(VI) as a tracer. The speciation of the products from these systems was carried out by ion exchange chromatography with stepwise elution. The results show that trace quantities of Cr(VI), monitored by means of radiochromium (^{51}Cr), are reduced in the presence of mineral acids such as perchloric, hydrochloric, hydrofluoric, sulfuric, nitric and trifluoromethanesulfonic acids, even in the absence of conventional reducing agents, producing different measureable Cr(III) species, depending on the acid anion. Detailed studies of the reduction of low concentrations of Cr(VI) with nitric acid have shown that the relative rate of reduction increases as the concentration of the acid increases or as the concentration of the Cr(VI) decreases.

Keywords: chromium, chromate, speciation, ion exchange chromatography, acid reduction

Introduction

The acid reduction of Cr(VI) is a little known aspect of chromium chemistry even though the reduction of Cr(VI) by hydrochloric acid has been known since the discovery of the element by Vauquelin in 1797. He described the formation of a green solution of Cr(III) when dissolving the mineral chrocoite, $PbCrO_4$, in muriatic acid.[1] In the 40's, Feigl[2] suggested the reaction of hydrochloric acid and potassium chromate, with manganese dioxide as catalyst, as a spot reaction experiment for educational purposes.

The oxidation of organic compounds by Cr(VI) in acidic media has been studied and reviewed by many authors.[3-6] A great variety of Cr(VI) compounds have proved to be versatile reagents capable of oxidizing almost every oxidizable organic functional group. Beattie and Haight[7] reviewed Cr(VI) oxidations of inorganic substrates, while Fendorf *et al.*[8] concerned themselves with the role of biological and abiological processes in chromium(VI) reductions.

The reduction of Cr(VI) by many acids, including the so-called "oxidizing acids", has also been reported.[9-19] Detailed studies of the reduction of low concentrations (less than 10^{-3} mol L^{-1}) of Cr(VI) with several different acids, including HNO_3,[13,14] $HClO_4$,[17] CF_3SO_3H,[17] H_2SO_4,[18] and HCl,[18] have shown that the relative rate of reduction increases as the concentration of the acid increases or as the concentration of the Cr(VI) decreases. Similar reductions have been reported for Cr(VI) present in natural waters, after acidification of the sample for storage.[20,21] These results are apparently not consistent with the well-known use of acidic Cr(VI) solutions as titrimetric and spectrophotometric standards.[22]

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A number of mechanisms have been proposed for reduction of Cr(VI) involving combinations of one-, two and three-electron elementary processes. The variety of species of chromium(VI) in acid solution, the passage of chromium through transient, unstable species of Cr(V) and Cr(IV), and the formation of complexes of chromium(III) all combine to give systems of considerable complexity. Thus, King and coworkers[23,24] suggested a sequence of three one-electron steps for the reduction of Cr(VI) to Cr(III), with the step from Cr(V) to Cr(IV) being the slowest, due to the change in coordination number from four to six, while Khan and Din[25] propose a single, three-electron reduction after the formation of a diester. Esters have also been implicated in the oxidation of organic substrates by Cr(VI).[3]

Haight *et al.*[26] attributed the reduction in perchloric acid to the action of water. However, this is not likely to be the case as the rate of reduction increases with a decrease in the activity of water, as seen in the extreme cases of 98% H_2SO_4[18] and 99% CF_3SO_3H.[17] Stollenwerk and Grove[21] suggest that the electrons for the Cr(VI) reduction could be provided by the oxygen in $HCrO_4^-$ while Espenson[27] suggests the addition of protons, two for the first step (Cr(VI) to Cr(V)) and one for the second (Cr(V) to Cr(IV)). However, no satisfactory overall reaction mechanism for the acid reduction of Cr(VI) has yet been proposed.

Studies of the reaction of solid CrO_3 with concentrated $HClO_4$,[15] HNO_3[19] or HCl[28] show that the acid-reduction process depends on the solubilization of the Cr(VI). Low concentrations of Cr(VI) in the solution phase lead to a very rapid reduction, but Cr(VI) concentrations above 10^{-2} mol L^{-1} are also reduced, although the process is slower. The rate of reduction in the CrO_3-37% HCl system is very rapid, when compared to the rates for the CrO_3-70% $HClO_4$ and CrO_3-65% HNO_3 systems, probably due to the presence of the oxidizable chloride ion. Based on ion exchange analysis and aquation experiments, it was concluded[28] that the initial identifiable species produced by the reduction reaction is $[Cr(H_2O)_3Cl_3]$, which undergoes aquation to produce $[Cr(H_2O)_4Cl_2]^+$, $[Cr(H_2O)_5Cl]^{2+}$ and, finally, $[Cr(H_2O)_6]^{3+}$.

These results show the importance of Cr(VI) concentrations to the acid reduction process. Which species of Cr(VI) are present in acidic solution, their spectra and their equilibria are the subjects of considerable discussion in the literature.[29,30] Besides the divergences regarding the existence of the protonated species, $HCrO_4^-$ and H_2CrO_4, there are also differences of opinion about the range of predominance of each species as a function of pH, Cr(VI) concentration and ionic strength.[30-32] From all these discussions, it is possible to propose some general guidelines for the existence and distribution of the different Cr(VI) species. In the pH range from 1 to 6, the $HCrO_4^-$ ion predominates when the [Cr(VI)] is $<10^{-3}$ mol L^{-1}. $Cr_2O_7^{2-}$ becomes important only at higher Cr(VI) concentrations. The species dihydrogen chromate, H_2CrO_4, may also exist at pH <1. Moreover, the Cr(VI) equilibria depend on the nature of the acid used. Changes in the electronic absorption spectra of $HCrO_4^-$ in the presence of various acids, such as H_2SO_4, H_3PO_4, HCl, and $H_2C_2O_4$, are interpreted[7] as indicating formation of the esters $CrSO_7^{2-}$, $HCrPO_7^{2-}$, CrO_3Cl^-, and $H_2CrO_3C_2O_4$.

On the other hand, the wide utilization of chromium and its compounds by modern industry results in the discharge of large quantities of this element into the environment. In view of its paradoxical roles as an essential micronutrient in human and animal nutrition at low concentrations, as Cr(III), and as a known carcinogen at elevated levels, as Cr(VI), there is a growing concern about the fate and effects of chromium in the environment.[33] Thus, chromium speciation is an important analytical operation for laboratories that determine chromium in natural water, in drinking water or in other consumables. Although chromium can be present in aqueous solutions as Cr(VI) or as any of various kinetically stable forms of Cr(III), whose distribution depends on the chemical history of the aqueous sample, most chromium speciation procedures in the literature consider only Cr(VI) and Cr(III) (as the hexaaquo species) as significant. Thus, a number of liquid chromatographic methods have recently been proposed to separate Cr(VI) and the several Cr(III) species.[34,35]

This paper discusses the reduction of Cr(VI) in several concentrated mineral acids, in the absence of any other reducing agent, and the determination of its products by ion exchange procedures. These procedures have been used in the fraction collection mode, with radiometric detection of Cr-51-labelled species.

Experimental

Reagents

Triply-distilled and deionized water (Nanopure, Barnstead or Milli-Q, Millipore) was used in all procedures. For the acid reduction experiments, analytical grade 70% perchloric (Aldrich, 99,999% pure), 40% hydrofluoric (Nuclear), 37% hydrochloric (Merck), 65% nitric (CPQ), 98% sulfuric (Merck), and 99% trifluoromethanesulfonic acids (Aldrich) were used.

^{51}Cr(VI) was obtained as an aqueous solution of $Na_2^{51}CrO_4$ (Amersham, England). The specific activity was 400 GBq mol^{-1}. All samples were submitted to multichanel

(EG&G Ortec 918) radionuclidic analysis which utilized the 0.320 MeV peak of ^{51}Cr. Open column cation-exchange radiochromatography[36] was carried out to show that more than 99% of the ^{51}Cr was initially present as Cr(VI).

Reaction of trace Cr(VI) with concentrated acids

To 5 mL screw-capped Erlenmeyer flasks were added 1.0 mL of acid (70% HClO$_4$ or 40% HF or 37% HCl or 65% HNO$_3$ or 98% H$_2$SO$_4$ or 99% CF$_3$SO$_3$H) and 100 μL of high specific activity ^{51}Cr(VI). The initial concentrations of Cr(VI) varied from 1 x 10^{-5} to 2.3 x 10^{-5} mol L^{-1}. The solutions were homogenized and maintained at room temperature (19.6-20.6 °C). After appropriate time periods, 10 μL aliquots were taken and immediately analyzed or diluted in water ("aquation solutions") for later analysis by ion exchange chromatography.

Reaction of trace Cr(VI) with nitric acid solutions

A set of acidic solutions of Cr(VI) with concentrations from 10^{-7} to 10^{-3} mol L^{-1} were prepared in nitric acid whose concentration varied from 2 to 10^{-5} mol L^{-1}. The 10^{-7} to 10^{-5} mol L^{-1} Cr(VI) solutions were prepared directly from the radioactive solution, whereas those of 10^{-4} and 10^{-3} mol L^{-1} Cr(VI) were prepared from a stock solution of K$_2$Cr$_2$O$_7$ and spiked with ^{51}Cr(VI). All the solutions were stored in glass flasks in the absence of light. After appropriate time periods, aliquots of these solutions were analyzed by ion exchange chromatography.

Speciation by open column ion exchange chromatography

Ion exchange columns were prepared by placing 0.5 mL of pretreated[37] cation (Bio-Rad AG50Wx8, 100-200, Na$^+$ form) or anion (BioRad AG1x8, 200-400 mesh, Cl$^-$ form) resins in glass columns (40-80 mm x 5 mm) fitted with a PTFE stopcock and having a small (7-8 mL) open reservoir at the top.[38] Just prior to use, the cation resin was treated with 0.5 mL of a 0.02 mol L^{-1} Na$_2$Cr$_2$O$_7$ solution (to eliminate possible reducing impurities) and washed with 6 mL of 0.01 mol L^{-1} HClO$_4$ and 10 mL of deionized water. Then, 0.01 mL of sample solution containing a few micromoles of the ionic species, as carrier, was added to 4 mL of deionized water contained in the open reservoir. This procedure is required to decrease the high initial acid concentration. After the liquid level reached the top of the resin bed, a small portion of the first eluent was used to carefully rinse the walls. The elution was carried out using the following sequence of eluents: 12 mL of 0.01 mol L^{-1} HClO$_4$ for the elution of neutral and anionic species; 20 mL of 0.1 mol L^{-1} HClO$_4$ for the elution of +1 species; 20 mL of 1 mol L^{-1} HClO$_4$ for the elution of +2 species; 24 mL of 0.25 mol L^{-1} Ca(ClO$_4$)$_2$ at pH 2 (adjusted with HClO$_4$) for the elution of +3 species; 24 mL of 0.5 mol L^{-1} Ca(ClO$_4$)$_2$ at pH 2 and 24 mL of 1 mol L^{-1} Ca(ClO$_4$)$_2$ at pH 2 for the elution of dimeric, trimeric and polimeric species.[36]

Two mL fractions of the eluates were collected (ISCO 328 fraction collector) for radioactivity measurements. The resin (R) was also counted to estimate possible non-eluting species. In some experiments, to distinguish between the anionic (A) and neutral (N) species which co-elute in the first fraction, a 0.01 mL aliquot of this fraction was analyzed by anion exchange chromatography on Bio-Rad AG-1 resin, using 8 mL of 0.01 mol L^{-1} HClO$_4$ as eluent. The 0.320 MeV gamma rays from the decay of ^{51}Cr were measured using a well type NaI(Tl) detector (Bicron) coupled to a modular single channel gamma analyzer (Hewlett-Packard 5583A). The counting time was determined by the sample activities to give errors below 1%, as counting statistics give an estimate of the measurement standard deviation as $\pm \sqrt{N}$, where N is the number of counts recorded.

Results and Discussion

The reaction of trace Cr(VI) with hydrochloric acid

The cation exchange chromatogram of the products formed when a high specific activity ^{51}Cr(VI) solution was placed in concentrated hydrochloric acid, and stored for 60 min, is shown in Figure 1. In this case, 85% of the ^{51}Cr eluted with the initial solution, indicating the presence of anionic or neutral species, smaller amounts of ^{51}Cr appearing in subsequent fractions. The anion exchange analysis confirmed the presence of only neutral species, with no residual ^{51}Cr(VI), suggesting that the species eluted in the initial cation fraction is Cr(H$_2$O)$_3$Cl$_3$. In addition, when the reaction product mixture was stored in 0.05 mol L^{-1} HCl, the composition of the mixture slowly changed, indicating aquation of the Cr(III)-chloride complexes. Initially, Cr(H$_2$O)$_4$Cl$_2$$^+$ and Cr(H$_2$O)$_5$Cl^{2+} were produced but, after 168 h, nearly 30% of the product was hexaaquochromium(III), Cr(H$_2$O)$_6$$^{3+}$ (Figure 1 and Table 1). The identities of the species as Cr(H$_2$O)$_4$Cl$_2$$^+$ and Cr(H$_2$O)$_5$Cl^{2+} are based on cation exchange determinations, with spectrophotometric confirmation, using aqueous solutions of CrCl$_3$.[39]

As has been known for many decades, Cr(VI) reduction in concentrated HCl involves the oxidation of chloride to chlorine.[40] Krauss *et al.*[41] studied the HCl/CrO$_3$ reaction in acetic acid spectrophotometrically and proposed a one-
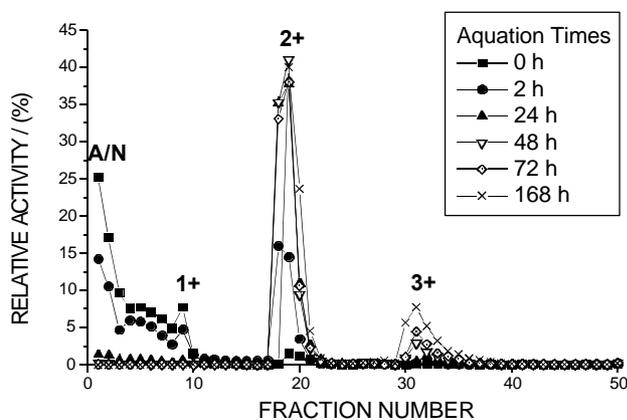
Figure 1. Cation exchange chromatograms of the products from the reaction (1 h) of high specific activity ^{51}Cr(VI) and 37% HCl and after post reduction aquation.

Table 1. Summary of products (%), observed after different reaction times, t(conc), and after specified aquation times, t(dil), from trace ^{51}Cr(VI) reacting with concentrated HCl

t (conc)	t (dil)	Anionic/ Neutral	Charge 1+	Charge 2+	Charge 3+	Resin
1 h	0	85.4	9.7	3.8	0.8	0.3
1 h	2 h	53.2	10.6	35.2	0.8	0.3
1 h	24 h	6.1	1.5	88.0	3.9	0.5
1 h	48 h	1.0	0.4	89.7	8.3	0.7
1 h	72 h	0.4	0.3	85.6	13.0	0.7
1 h	168 h	0.2	0.3	71.0	27.6	0.9
840 h	0	80.9	11.8	7.3	—	—

Figure 2. Cation exchange chromatograms of the products from the reaction (1 h) of high specific activity ^{51}Cr(VI) and 40% HF and after post reduction aquation.

Table 2. Summary of products (%), observed after different reaction times, t(conc), and after specified aquation times, t(dil), from trace ^{51}Cr(VI) reacting with concentrated HF

| t (conc)	t (dil)	Anionic/ Neutral	Charge 1+	Charge 2+	Charge 3+	Resin
1 h	0	90.8	4.6	2.3	1.5	0.7
1 h	2 h	85.1	8.4	4.5	1.3	0.6
1 h	72 h	85.5	8.6	4.5	0.9	0.5
1h	192 h	80.9	13.8	2.8	0.9	0.5

electron reduction mechanism, with the formation of $[Cr^VOCl_5]^{2-}$ and further reduction to $H_2[Cr(H_2O)Cl_5]$. Thus, in the Cr(VI)-HCl system, the oxidation of chloride to chlorine by Cr(VI) may be an important reaction but other paths may also contribute.

The reaction of trace Cr(VI) with hydrofluoric acid

The results for the immediate (5 min) cation exchange analysis showed that 91% of the ^{51}Cr was eluted as anionic and/or neutral species, 5% as 1+ species, 2% as 2+ species and <2% as 3+ species (Figure 2 and Table 2). The chromatographic profile was very similar to that obtained for the Cr(VI) – HCl system, so the species identifications were made by analogy. Aquation, however, was much slower. An analysis carried out after 192 h of storage at pH 2 showed that 81% of the ^{51}Cr still eluted as neutral species.

The reaction of trace Cr(VI) with sulfuric acid

The results from coupled cation exchange-anion exchange determination of the products from the reaction

(1 h) of high specific activity ^{51}Cr(VI) with H_2SO_4 showed that almost 100% was an anionic species. When stored in 0.09 mol L^{-1} H_2SO_4, a slow aquation was noted, producing $Cr(H_2O)_2SO_4^+$ and $Cr(H_2O)_6^{3+}$ (Figure 3 and Table 3). The aquation of the complexes formed from the reaction with H_2SO_4 was slower than with HCl, producing about 20% each of 1+ and 3+ species after 168 h. After 3 months of storage in diluted acid, only 4% of the ^{51}Cr remained as anionic or neutral species, indicating that the initial species, produced in one hour of reaction in the ^{51}Cr(VI)-H_2SO_4 system, was $Cr(H_2O)_2(SO_4)_2^-$.[42]

The reaction of trace Cr(VI) with perchloric acid

When a high specific activity ^{51}Cr(VI) solution and concentrated perchloric acid were stirred for 25 min and an aliquot was added directly to water in the column reservoir, 82% of the ^{51}Cr was observed as hexaaquochromium(III), 14% as a 2+ species and 3% as a 1+ species. Moreover, only 0.6% of the total ^{51}Cr was as an anionic species. The identities of the lesser charged species as $Cr(ClO_4)^{2+}$ and $Cr(ClO_4)_2^+$ were made by analogy to
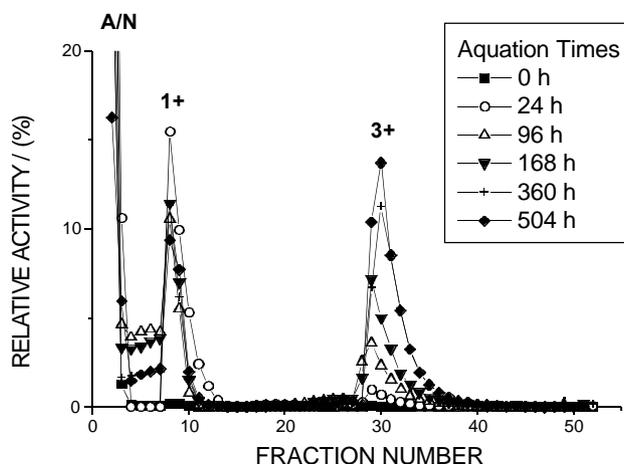
Figure 3. Cation exchange chromatograms of the products from the reaction (1h) of high specific activity ^{51}Cr(VI) and 98% H_2SO_4 after post reduction aquation.
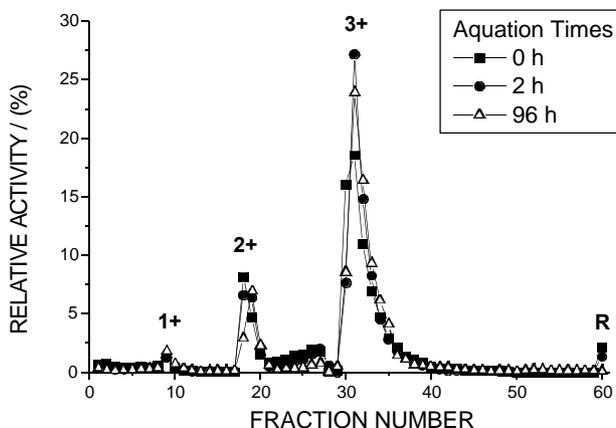
Table 3. Summary of products (%), observed after different reaction times, t(conc), and after specified aquation times, t(dil), from trace ^{51}Cr(VI) reacting with concentrated H_2SO_4

t (conc)	t (dil)	Anionic/ Neutral	Charge 1+	Charge 2+	Charge 3+	Resin
1 h	0	99.5	0.5	—	—	—-
1 h	24 h	60.0	37.0	—	3.0	—-
1 h	96 h	67	20	—	13	—-
1 h	168 h	54	23	—	23	—-
1 h	360 h	39	20	—	41	—-
1 h	504 h	29	22	—	49	—-
1 h	2200 h	4	20	—	76	
24 h	0	100	—	—	—	—-

species of similar charge found by cation exchange determinations of aqueous solutions of CrCl$_3$[36] and Cr(SCN)$_3$,[43] since no other anion is present. Charged perchlorate complexes with Cr(III) in concentrated perchloric acid have been reported,[44,45] based on spectrophotometric determinations. The results show that, in the reduction of Cr(VI) in concentrated perchloric acid, the formation of chromium-perchlorate complexes takes place and, despite moderately rapid aquation, these complexes can be characterized by chromatographic methods.

When the chromatographic analysis of high specific activity ^{51}Cr(VI) in concentrated HClO$_4$ is carried out immediately after mixing (*ca.* 5 min), the principal species was also the 3+ species (68%), with a significant amount of 2+ complex (24%) and some of 1+ complexes (3%). Here, anionic and neutral species were responsible for ~4% of the ^{51}Cr, while 2% remained on the resin. To further investigate the stability of these species, aliquots from the systems were diluted with water and analyzed after defined storage times (Figure 4). Analysis after 96 hours at pH 2 showed that the 3+ species had increased to 73%, while

the 2+ species decreased to 16%. Table 4 summarizes the results obtained in these studies. The possible neutral species (CrO$_2$(ClO$_4$)$_2$)[46] was either not formed or underwent hydrolysis before analysis could be started, forming the observed cationic species.

Figure 4. Cation exchange chromatograms of the products from the reaction (5 min) of high specific activity ^{51}Cr(VI) and 70% HClO$_4$ and after post reduction aquation.

Table 4. Summary of products (%), observed after different reaction times, t(conc), and after specified aquation times, t(dil), from trace ^{51}Cr(VI) reacting with concentrated HClO$_4$

t (conc)	t (dil)	Anionic/ Neutral	Charge 1+	Charge 2+	Charge 3+	Resin
5 min	0	3.5	2.7	23.7	68.0	2.0
5 min	0	5.1	—	20.4	71.7	2.8
5 min	2 h	2.6	2.5	21.5	72.2	1.3
5 min	96 h	1.8	4.1	16.1	75.2	2.7
25 min	0	0.6	2.9	14.0	82.5	—
+1 h	0	5.9	—	9.5	82.2	2.3

The reaction of trace Cr(VI) with trifluoromethanesulfonic acid

The results for the reaction (1 h) of high specific activity ^{51}Cr(VI) with CF$_3$SO$_3$H showed that 47% of the ^{51}Cr is observed as a 3+ species, 28% as 2+ species and 2% as 1+, while 14% was not retained on the cation column, indicating anionic and/or neutral species (Table 5 and Figure 5). Aquation studies suggest these to be Cr(III) species. These results show that the trifluoromethanesulfonate anion more readily forms complexes with Cr(III) than does perchlorate.

The reaction of trace Cr(VI) with concentrated nitric acid

The ion chromatographic analysis for the ^{51}Cr(VI) - 65% HNO$_3$ system showed that, after 60 min of reaction,
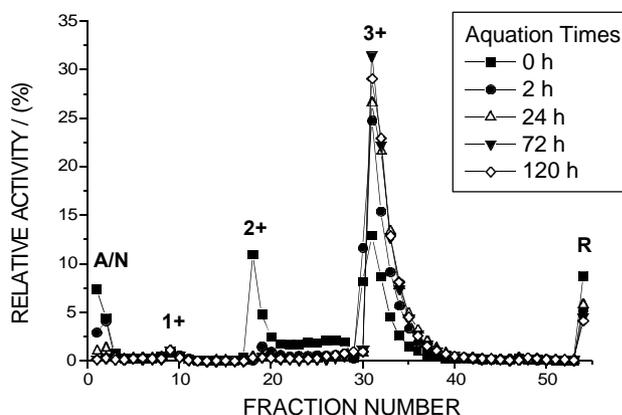
Figure 5. Cation exchange chromatograms of the products from the reaction (1 h) of high specific activity $^{51}Cr(VI)$ and 99% CF_3SO_3H and after post reduction aquation.

Table 5. Summary of products (%), observed after different reaction times, t(conc), and after specified aquation times, t(dil), from trace $^{51}Cr(VI)$ reacting with concentrated CF_3SO_3H

t (conc)	t (dil)	Anionic/Neutral	Charge 1+	Charge 2+	Charge 3+	Resin
1 h	0	13.7	1.7	27.6	47.6	9.4
1 h	2 h	8.4	2.1	6.6	76.6	6.3
1 h	24 h	3.3	2.2	1.8	86.4	6.2
1 h	72 h	1.9	1.6	1.2	90.3	5.0
1 h	120 h	1.8	1.5	1.7	90.1	4.8

the major part of the ^{51}Cr (60%) was present as a 2+ species, while 34% appeared as a 3+ species and only 0.3% as anionic/neutral species. These results are consistent with an earlier study.[47] As shown in Figure 6, aquation was relatively rapid, producing 3+ species. An interesting feature was the relatively high amount (7%) of ^{51}Cr-labelled species that remains on the resin after the passage of all eluents. This species hydrolyzed only slowly when stored in 0.01 mol L^{-1} HNO$_3$ (Table 6). .

The reaction of trace Cr(VI) with aqueous solutions of nitric acid

When trace $^{51}Cr(VI)$ is placed in dilute aqueous HNO$_3$, the Cr(VI) concentrations decreased with time. Figure 7 shows the results for seven different solutions with initial concentrations of Cr(VI) of 10^{-6} mol L^{-1} and nitric acid concentrations of 2, 1, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} mol L^{-1}.

In agreement with other workers,[13,20,21] these results show that low concentrations of Cr(VI) are not stable in an acid solution, an observation which has implications with respect to the storage of Cr(VI) solutions in studies of environmental speciation. Figure 7 indicates that the reduction velocity is proportional to the nitric acid
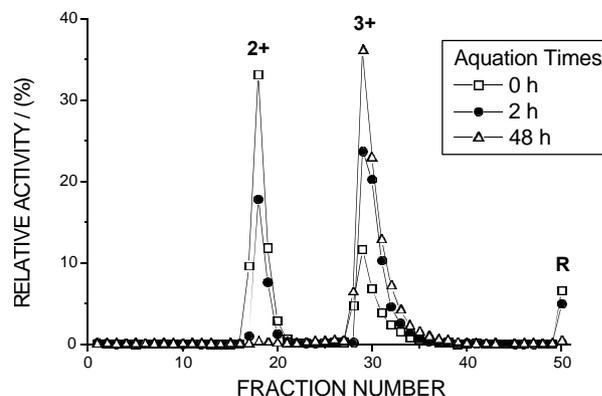
Figure 6. Cation exchange chromatograms of the products from the reaction (1 h) of high specific activity $^{51}Cr(VI)$ and 65% HNO$_3$ and after post reduction aquation.

Table 6. Summary of products (%), observed after different reaction times, t(conc), and after specified aquation times, t(dil), from trace $^{51}Cr(VI)$ reacting with concentrated HNO$_3$

t (conc)	t (dil)	Anionic/Neutral	Charge 1+	Charge 2+	Charge 3+	Resin
1 h	0	0.3	0.3	59.0	33.8	6.6
1 h	2 h	0.5	0.2	28.9	65.4	5.0
1 h	48 h	0.2	—	1.4	98.0	0.4
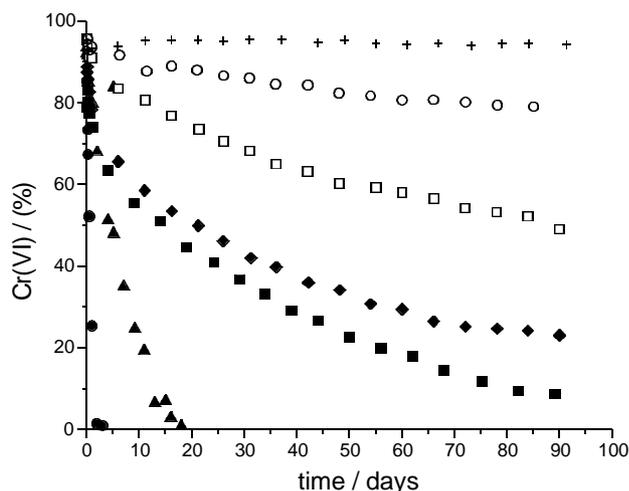
Figure 7. Reduction kinetics of 10^{-6} mol L^{-1} $^{51}Cr(VI)$ in the presence of different concentrations of HNO$_3$. ● = 2 mol L^{-1}, ▲ = 1 mol L^{-1}, ■ = 10^{-1} mol L^{-1}, ◆ = 10^{-2} mol L^{-1}, □ = 10^{-3} mol L^{-1}, ○ = 10^{-4} mol L^{-1}, + = 10^{-5} mol L^{-1}.

concentration. A similar behavior is observed for higher Cr(VI) concentrations although the relative reduction velocities decreased as the Cr(VI) concentration increased.

A complete chromatographic analysis on the first fraction eluted from an anion exchange analysis (containing the cationic and neutral species), showed that

the radioactivity related to Cr(III) is distributed among several species, the most prominent being the hexaaquo ion, and that this distribution changed with time. Polymeric Cr(III) species became more important as the concentration of Cr(VI) increased. These polymeric species change even more slowly with storage than do the monomeric species, in agreement with published results.[48]

Comparison of the behavior of trace Cr(VI) in different acids

The major initial reduction products from perchloric, trifluoromethanesulfonic and nitric acids were 2+ and 3+, although the analysis also indicated the presence of anionic/neutral, 1+ and higher polymeric species (Figures 4-6). On storage in 0.01 mol L^{-1} acid, the monomeric 2+ and 1+ species underwent aquation forming hexaaquochromium(III). Reduction in these concentrated acids formed small amounts (2-9%) of polymeric species which were retained by the cation resin. The product from reduction in perchloric acid was relatively resistant to depolymerization. By contrast, the higher charged species produced by reduction in 99% CF_3SO_3H or 65% HNO_3 underwent depolymerization upon aquation in 0.01 mol L^{-1} acid. It should be noted that none of the chromatograms indicated the presence of dimeric and/or trimeric species eluting with 1 mol L^{-1} $Ca(ClO_4)_2$ at pH 2, even though some species were retained by the cation exchange column.

When these results are compared to those observed with the other acids (Figures 1-3), some significant differences are noted. The major product when trace concentrations of ^{51}Cr(VI) reacts with concentrated CF_3SO_3H, HNO_3 and $HClO_4$ is the 3+ species, $Cr(H_2O)_6^{3+}$, and the smaller amounts of 1+ and 2+ species are rapidly converted to the 3+ species on aquation. By contrast, when trace ^{51}Cr(VI) reacts with HCl, HF or H_2SO_4, complexed species, $Cr(H_2O)_3Cl_3$, $Cr(H_2O)_3F_3$ and $Cr(H_2O)_2(SO_4)_2^-$, respectively, are the main initial products. As chloride, fluoride and sulfate form very much stronger complexes with Cr(III) than do trifluoromethanesulfonate, perchlorate and nitrate, this is not an unexpected result. On the other hand, even the small amounts of 2+ and 1+ species seen with the "non-complexing" anions suggests that the mechanism of the reduction reaction probably involves a ligand capture step to form complexes.

The results reported here on the reduction of Cr(VI) in solutions of several oxidizing acids, not involving a conventional reducing species such as chloride, suggest that "acid", *i.e.*, the proton, may be a defining reagent in the reduction pathway. Archundia *et al.*,[12] in discussing the reduction of Cr(VI) in formic acid, concluded that the process is promoted by H$^+$ and is perhaps independent of the nature of the acid anion, although the latter may participate to form CrL$_n$-type species. Thus, the role of the different anions present, which depend on the acid used, should contribute importantly, as they form complexes (pseudo-esters) whose stability may influence the overall kinetics of the acid-reduction process and the resulting product distributions.

Conclusions

The results indicate that low concentrations of Cr(VI) are reduced by concentrated acids forming hexaaquochromium(III) and other complexes of Cr(III), which can be separated by chromatographic methods. In any media and with any reducing agent, the overall process whereby ^{51}Cr(VI) is reduced to ^{51}Cr(III) is probably a multi-step one, since three electrons must be transferred to produce Cr(III). The appearance of Cr(III) species bonded to one, two or even three anions suggests the direct participation of the anion in the electron transfer process.

Thus, acidic Cr(VI) standard solutions and procedures for the determination of chromium in metal alloys[49] and biological materials,[50] which are based on acid dissolution of the sample in $HClO_4$ or another strong acid, followed by Cr(VI) determination using spectrophotometric or titrimetric procedures, must be used with caution due to this complicating factor of acid-induced reduction.

Acknowledgements

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