Conductometric pulse radiolysis study of the interconversion Cr(III)/Cr(VI) redox reactions in acidic solution: Atmospheric pollution relevance

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ABSTRACT

Hexavalent chromium (VI) is a potent carcinogen for humans, while trivalent chromium (III) is an important element in glucose metabolism. In atmospheric water droplets, oxidation of Cr(III) to Cr(VI) by free radicals is a major environmental issue. Laboratory simulation studies of the aqueous phase oxidation-reduction of the couple Cr(III)/Cr(VI) by OH and HO2/O2•− by applying conductometric pulse radiolysis techniques were carried out in the pH range 3.5–5.5 chosen as characteristic values of atmospheric water droplets acidity. A pKₐ of 3.9 was found for the first hydrolysis of Cr(IV). The bimolecular second-order decay of the Cr(VI) transient species shows a strong pH dependency consequence of the change of the coordination sphere of the tetrahedral Cr(VI) to the octahedral Cr(III).

1. Introduction

1.1. Biotoxicity of chromium species present in the atmosphere

Chromium heavy metal is a naturally occurring element found in soil, water, and the atmosphere, originating from both natural and human activities (Johnson et al., 2006). It is mainly present under two oxidation states: hexavalent Cr(VI) and trivalent Cr(III). Its biotoxicity depends essentially on its redox speciation. Chromium (III) is an important micronutrient essential for the human metabolism (Lau et al., 2008), while Cr(VI) is a potent human carcinogen through inhalation (Stern, 2010). Most of the Chromium (III) present in the environment come from the effluents of the leather tanning industry (Li et al., 2019). The pH of the cloud droplets, of average diameter 10–100 μm, varies between 3 and 5 (Desboeufs et al., 2003), though their acidity can attain values as low as 2 during acidic rainfall bouts in SO₂-polluted atmospheres (Salma et al., 2006).

Cloud droplets and ice crystals play a significant role in the chemical cycles of many atmospheric transition metal ions (Fe(II), Fe(III), Mn(II)). Factors such as pH, solubility, oxidation state, presence of reducing, and oxidizing-free radicals greatly affect the mass transfer of the metal ions from gas phase to-aqueous phase and hence their reactivity (Deguillaume et al., 2005). In the troposphere, hydroxyl-free radicals OH• are mainly generated by the UV photolysis of ozone in the gas phase (Monks, 2005)

\[ O_3 + h\nu_{(330\, \text{nm})} \rightarrow O_2 + O(1D) \quad (1a) \]

\[ \text{O}(1D) + H_2O \rightarrow 2 \text{OH}^* \quad (1b) \]

Other sources for OH• radicals in the tropospheric aqueous phase include processes such as the photolytic decomposition of H₂O₂. Fenton-type reactions between H₂O₂ and transition metal ions (Herrmann et al., 2010).

The main source of the perhydroxyl radical HO₂• (in equilibrium with its conjugate base Superoxide O₂•−) in the gas phase is the action of OH• on formaldehyde (HCHO) (Monks, 2005)

\[ \text{OH}^* + \text{HCHO} + O_2 \rightarrow \text{HO}_2^* + \text{CO} + H_2O \quad (2) \]

Cr(III) can be oxidized into Cr(VI) by hydroxyl-free radicals OH•, which in turn could be reduced back to Cr(III) by HO₂• or O₂•−. This interconversion in biotoxicity of chromium species can greatly impact the individuals’ health (Wang et al., 1997). In this laboratory cloud aqueous phase redox simulation, we aimed to shed further light on the Cr(III)/Cr(VI) interconversion reaction by means of conductometric pulse radiolysis in the pH range 3.5–5.5.

1.2. Radiation chemistry of Cr(III) aqueous solutions

Interaction of ionizing radiation with water molecules generates highly reactive species:

\[ H_2O \rightarrow e_{aq}^- (0.28), \text{OH}^* (0.28), H^* (0.06), \text{H}_2 (0.045), \text{H}_2\text{O}_2 (0.07) \quad (3) \]

the numbers in parenthesis represent the yield in μmol/J (Buxton, 1991). In oxidizing conditions, solvated electrons are converted into OH• radicals when
solutions are saturated with nitrous oxide N₂O gas (G. V.; 1987):

$$e_{aq}^- + N₂O \rightarrow N₂ + O \quad (4a)$$

$$O + H₂OOH^+ + OH^- \quad (4b)$$

Under these conditions, the oxidation of trivalent chromium is oxidized to its tetravalent form by OH⁻:

$$Cr(III) + OH^- \rightarrow Cr(IV) + OH^- \quad (5)$$

proceeds by the formation of the [OH⁻Cr(III)] adduct with an equilibrium constant of $2.34 \times 10^4 \text{ mol}^{-1} \text{ dm}^{-3}$ then followed by an electron transfer from Cr(III) to OH⁻ within the adduct with a rate constant of $2.51 \times 10^4 \text{ s}^{-1}$ (Djouider, 2020; Djouider & Hussain, 2014).

The most convenient method of generating HO₂⁻/O₂⁻ radicals for Cr(VI) reduction is to convert in a first step, OH⁻ and H⁺ primary radicals into the same secondary reducing carboxyl radical anion radical CO₂⁻ by adding sodium formate NaHCO₃ (G. V.; 1987)

$$OH^- + HCO_2^- (HCO_2H) \rightarrow H₂O + CO_2^- \quad (6)$$

$$H^+ + HCO_2^- (HCO_2H) \rightarrow H₂ + CO_2^- \quad (7)$$

In oxygen-saturated solutions, CO₂⁻, along with the hydrated electron, are converted into O₂⁻ radical in acid-base equilibrium with its conjugate acid HO₂⁻ (Bielski et al., 1985; G. V.; 1987)

$$CO_2^- + O_2 \rightarrow O_2^- + CO_2 \quad (8a)$$

$$e_{aq}^- + O_2 \rightarrow O_2^- \quad (8b)$$

$$O_2^- + H^+ O_2^* \quad (8c)$$

$$pK_a = 4.8$$

2. Experimental

Stock solutions of Cr(III) and Cr(VI) were prepared with triply distilled and deionized water. Chrome alum KCr₂(O₄)₂·12H₂O and potassium dichromate K₂Cr₂O₇ used in this work of Analar grade were supplied by BDH and used as received. N₂O and O₂ gases were supplied by a local supplier. pHs of the aqueous solutions, measured using JENWAY 3510 pH meter from Bibby Scientific (UK), were adjusted by the addition of perchloric acid (70% assay from BDH). A 2.5 MeV van de Graaff linear accelerator generating pulses between 0.1 and 1.2 μs duration with a delivered dose between 5 and 100 Gy per pulse and equipped with optical detection system coupled with conductometric measurement arrangement, was used for pulse radiolysis purposes.

3. A.C conductivity method

Figure 1 shows a diagram of the AC method used in this work. A twin-cell arrangement consisting of an identical pair of rectangular cross-section Pyrex cells normal to the electron beam with platinum electrodes of 3 mm diameter and separated by 5 mm is made of two arms of Wheatstone bridge powered by 10 MHz a.c. sine wave from a high-frequency generator. The amplified bridge signal is mixed with a reference voltage. An oscilloscope, connected to an output of the mixer, is used to check the balancing of the bridge. The second output is connected to a signal recording apparatus.

The output signal is given by Janata et al. (1994)

$$V_{out} = k \times \Delta V \times V_{ref} \times [\cos \omega t + \cos (\omega t + \theta)] \quad (9)$$

The specific conductance, or conductivity, change $\Delta \sigma$ (in $\text{Ω}^{-1} \text{ cm}^{-1}$) which accompanies the formation or disappearance of ions, following an irradiation of an aqueous solution, is given by the Kohlrausch’s law (Janata et al., 1994):

![figure](image-url)
\[ \Delta \sigma = 0.001 \sum_j [\Delta c_j |z_j|/\Lambda_j] \]  \hspace{1cm} (10) 

where \( \Delta c_j \) is the change in molar concentration of the \( j \)th species 

\[ |z_j| \] is the net valency of the \( j \)th species 

\[ \Lambda_j = \frac{\sigma_j}{\sigma} \] is the molar conductivity in \( \Omega^{-1} \text{cm}^2 \text{mol}^{-1} \) of the \( j \)th species, \( \sigma \) being its conductivity.

For electrolyte concentrations up to 1 mmol dm\(^{-3}\), the equivalent conductance \( \Lambda_j \) can be replaced by its value for infinite dilution \( \Lambda_{\infty} \) without incurring an error of more than 2\% (Wu & Berezansky, 1995). In this work, we recorded the conductance change in the pulse-irradiated Cr(VI) and Cr(III) solutions over the time ranging from few \( \mu \)s (which is the time resolution of the conductivity method used here) to ca. 1 min after the pulse.

### 3.1. Data analysis and dosimetry

The traces obtained were analyzed using a standard basic computer code TREAT. The mathematical processes used in this program to calculate the rate constants and to determine the order of the reactions can be found elsewhere (Lloyd et al., 1994). The dose was determined by pulse-irradiating an \( \text{N}_2\text{O} \)-saturated solution of dimethyl sulfoxide (DMSO) (\( \text{CH}_3\text{S} \)) at pH 4.4, \( \Gamma \text{A} \) being equal to 1953 \( \Omega^{-1} \text{cm}^2 \text{J}^{-1} \) (Veltwisch et al., 1980).

### 4. Results and discussion

#### 4.1. Conductometric study of the Cr(III) oxidation

A typical conductivity-time curve for pulse-irradiated pH 3.5 \( \text{N}_2\text{O} \)-saturated solution of \( 4 \times 10^{-4} \) mol dm\(^{-3}\) Cr(III) is shown in Figure 2. The reaction of Cr(III) ion with OH\(^-\) (reaction 5) leads to a first order increase in conductivity after the pulse. The rate of this increase \( 3.1 \times 10^4 \text{s}^{-1} \) is in order of magnitude of its rate of oxidation, \( 2.3 \times 10^3 \text{s}^{-1} \), which takes place by an inner sphere mechanism, as determined previously (Djouider & Hussain, 2014).

The positive gain in conductivity after the pulse clearly indicates that Cr(VI) deprotonates by hydrolysis as soon as it is formed, deprotonation which must be complete within 150–200 \( \mu \)s after its formation. A number \( n \) of protons per one Cr(VI) species are released into the solution:

\[ [\text{Cr}^{IV}(\text{H}_2\text{O})_6]^{4+} = [\text{Cr}^{IV}(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{(4-n)+} + n\text{H}^+ \]  \hspace{1cm} (11)

Time-resolved conductivity measurements from Figure 2 show that a conductance \( \Gamma \Lambda = 900 \text{ J}^{-1} \Omega^{-1} \text{cm}^2 \) is obtained. Since in \( \text{N}_2\text{O} \)-saturated solution the yield of oxidizing species is 0.54 \( \mu \)mol J\(^{-1}\), a change in equivalent conductivity of \( \Delta \Lambda = 167 \Omega^{-1} \text{cm}^2 \) is derived. Since the release of one mole of protons is equivalent to the gain of 315 \( \Omega^{-1} \text{cm}^2 \), this result indicates that only a fraction, \( 167 / 315 = 0.53 \) of Cr(VI) species undergoes hydrolysis. A \( p_{k_a} \) of 3.31 is evaluated for the equilibrium (11). It should be noted that \( p_{k_a} = 4 \) was found for the hydrolysis of Cr(III) (Bokare & Choi, 2011).

\[ [\text{Cr}^{III}(\text{H}_2\text{O})_6]^{3+} = [\text{Cr}^{III}(\text{H}_2\text{O})_{6-n}(\text{OH})_n]^{3+} + \text{H}^+ \]  \hspace{1cm} (12)

Our data confirm the well-established principle that metal ions tend to be more hydrolyzed with increasing state of oxidation.

#### 4.2. Pulse radiolysis study of the reduction of Cr(VI)

The rate constant of the reduction of Cr(VI) by \( \text{O}_2^- \) or/ and \( \text{HO}_2^- \)

\[ \text{Cr(VI)} + \text{HO}_2^- \rightarrow \text{Cr(V)} + \text{H}^+ + \text{O}_2 \]  \hspace{1cm} (13a)

**Figure 2.** Conductivity-time curve of a pulse-irradiated pH 3.5, \( \text{N}_2\text{O} \)-saturated solution of \( 4 \times 10^{-4} \) mol dm\(^{-3}\) of Cr(III). Dose 50 Gy.
was measured at pH 3.5 and 5.5 of an oxygen-saturated solution containing $(0.2-1) \times 10^{-3} \text{ mol dm}^{-3}$ of Cr(VI) in the presence of $1 \times 10^{-3} \text{ mol dm}^{-3}$ HCO$_2^-$, using pulse of 40 Gy dose of 0.6 µs duration. At pH range [3.5–5.5] used in this work, the ratio $[O_2^-]/[\text{HO}_2^-]$ varies between $5 \times 10^{-2}$ and 5. At pH 3.5, the conjugate acid HO$_2^-$ is the dominant species while at pH 5.5, the conjugate base O$_2^-$ anion prevails. This reduction of Cr(VI) was monitored at 350 nm and rate constants of $1.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $5.5 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ were obtained, respectively, for reaction (13a) and (13b), respectively (Figure 3). This is in agreement with the fact that reduction of metal ions by O$_2^-$ is relatively faster than their reduction by HO$_2^-$, a difference primarily due to electrostatic factors (Rush & Bielski, 1985).

\[
\text{Cr}(\text{VI}) + O_2^- \rightarrow \text{Cr}(\text{V}) + O_2 \quad (13\text{b})
\]

### 4.3. Conductometric study of the Cr(VI) reduction

A pulse radiolysis study in which changes in conductivity of O$_2$-saturated solutions, of pH 3.5, containing $4 \times 10^{-4} \text{ mol dm}^{-3}$ of HCrO$_4^-$ and $10^{-3} \text{ mol dm}^{-3}$ of HCO$_2^-$ in a cell of 2.5 cm optical path length were recorded using a single pulse of 40 Gy dose of 0.6 µs duration. Under these conditions, the OH$^-$ ions formed during the pulse, reactions (3) and (4b), are neutralized by the H$^+$ ions present in the solution in less than 0.5 µs and the conductivity signal does not appear on the µs time-scale discussed here (Schmidt, 1972). The reduction of Cr(VI) leads to the conductivity signal shown in Figure 4. This trace obeyed first-order kinetics and gave a rate constant of $2.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This decrease in conductivity is explained as follows: reaction (13b) leads to the formation of Cr(V) having

![Figure 3](image1.png)

**Figure 3.** Pseudo-first-order rate constants for reactions (13a) and (13b) at pH 3.5 (●) and 5.5 (▲) respectively, of an oxygen-saturated solution containing $(0.2-1) \times 10^{-3} \text{ mol dm}^{-3}$ of Cr(VI) in the presence of $1 \times 10^{-3} \text{ mol dm}^{-3}$ HCO$_2^-$ 40 Gy dose of 0.6 µs duration.

![Figure 4](image2.png)

**Figure 4.** Conductivity-time curve of a pulse irradiated O$_2$-saturated solution pH 3.5 of $[\text{Cr(VI)}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{HCO}_2^-] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, dose: 50 Gy, pulse duration: 0.6 µs.
a tetrahedral form, which instantaneously protonates by consuming protons from the solution according to
\[ \text{Cr(V)}_{\text{tet}} + H^+ \rightleftharpoons [\text{HCr(V)}_{\text{tet}}] \quad (14) \]

The decrease in equivalent conductivity \( \Delta \Lambda \), as calculated from the known dose \( (G \Lambda)'_{\text{dos}} = 1953 \Omega^{-1} \text{cm}^2 \) J\(^{-1} \) and \( G(\text{reducing species}) = G(\text{OH}^-) + G(H^+) + G(e_{\text{aq}}^-) = 0.62 \) (Buxton & Djouider, 1996), is \( 377 \Omega^{-1} \text{cm}^2 \) value which is higher than the conductivity value for the consumption of one proton. This clearly indicates that more than one proton with is involved in the protonation of \( \text{Cr(V)} \).

Preceding the electron transfer, a reorganization of the coordination sphere of \( \text{Cr(V)}_{\text{tet}} \) is necessary (Djouider, 2020; Djouider & Hussain, 2014). The coordination sphere of \( \text{Cr(V)}_{\text{tet}} \) rearranges to \( \text{Cr(V)}_{\text{oct}} \) to match the octahedral coordination of \( \text{Cr(III)} \) (McClevery & Meyer, 2004). The electron transfer then takes place instantaneously compared with the time required for atomic positions to change. Successive protonation of \( \text{Cr(V)} \) may result in the following sequence of coordination changes: tetrahedral \( \rightarrow \) intermediate coordination sphere \( \rightarrow \) octahedral.

\[ \text{Cr(V)}_{\text{tet}} + O_2^- \rightarrow \text{Cr(V)}_{\text{tet}} + O_2 \quad (15) \]
\[ \text{Cr(V)}_{\text{tet}} + H^+ \rightarrow [\text{HCr(V)}_{\text{tet}}] \quad (16) \]
\[ [\text{HCr(V)}_{\text{tet}}] + H^+ \rightarrow [\text{H}_2\text{Cr(V)}_{\text{oct}}] \quad (17) \]
\[ \text{Cr(V)}_{\text{tet}} + [\text{H}_2\text{Cr(V)}_{\text{oct}}] \rightarrow \text{Cr(V)}_{\text{tet}} + [\text{H}_2\text{Cr(V)}_{\text{oct}}] \quad (18) \]
\[ [\text{H}_2\text{Cr(V)}_{\text{oct}}] + \text{Cr(V)}_{\text{tet}} \rightarrow [\text{H}_2\text{Cr(III)}_{\text{oct}}] + \text{Cr(V)}_{\text{tet}} \quad (19) \]

\[ K_{16} = \frac{[\text{HCr(V)}_{\text{tet}}]}{[\text{Cr(V)}_{\text{tet}}][H^+]} \quad (20) \]

\[ K_{17} = \frac{[\text{H}_2\text{Cr(V)}_{\text{oct}}]}{[\text{HCr(V)}_{\text{tet}}][H^+]^2} \quad (21) \]

The rate of recovery of \( \text{Cr(V)} \) is
\[ \frac{d[\text{Cr(V)}_{\text{tet}}]}{dt} = k_{18}[\text{Cr(V)}_{\text{tet}}][\text{H}_2\text{Cr(V)}_{\text{oct}}] + k_{19}[\text{H}_2\text{Cr(V)}_{\text{oct}}][\text{Cr(V)}_{\text{tet}}] \quad (22) \]

Application of the steady-state approximation to \( [\text{H}_2\text{Cr(V)}_{\text{oct}}] \) gives
\[ \frac{d[\text{H}_2\text{Cr(V)}_{\text{oct}}]}{dt} = k_{18}[\text{Cr(V)}_{\text{tet}}][\text{H}_2\text{Cr(V)}_{\text{oct}}] - k_{19}[\text{H}_2\text{Cr(V)}_{\text{oct}}][\text{Cr(V)}_{\text{tet}}] = 0 \]
\[ k_{18}[\text{Cr(V)}_{\text{tet}}][\text{H}_2\text{Cr(V)}_{\text{oct}}] = k_{19}[\text{H}_2\text{Cr(V)}_{\text{oct}}][\text{Cr(V)}_{\text{tet}}] \quad (23) \]

Hence, Eq. 22 becomes
\[ \frac{d[\text{Cr(V)}_{\text{tet}}]}{dt} = 2k_{18}[\text{Cr(V)}_{\text{tet}}][\text{H}_2\text{Cr(V)}_{\text{oct}}] \quad (24) \]

The occurrence of equilibria (16) and (17) does not affect the total amount of \( \text{Cr(V)} \) in the solution, that is
\[ [\text{Cr(V)}_{\text{tot}}] = [\text{Cr(V)}_{\text{tet}}] + [\text{HCr(V)}_{\text{tet}}] + [\text{H}_2\text{Cr(V)}_{\text{oct}}] \quad (25) \]

From Eq. (20)
\[ [\text{HCr(V)}_{\text{tot}}] = K_{16}[\text{Cr(V)}_{\text{tet}}][H^+] \quad (26) \]

From Eq. 21
\[ [\text{H}_2\text{Cr(V)}_{\text{tot}}] = K_{17}[\text{HCr(V)}_{\text{tot}}][H^+] \quad (27) \]

Eq. 24 becomes:
\[ \frac{d[\text{Cr(V)}_{\text{tet}}]}{dt} = 2k_{18}[\text{Cr(V)}_{\text{tet}}]^2K_{16}K_{17}[H^+]^2 \quad (28) \]

and the total amount of \( \text{Cr(V)} \) in the solution can be written as
\[ [\text{Cr(V)}_{\text{tot}}] = [\text{Cr(V)}_{\text{tet}}] + K_{16}[\text{Cr(V)}_{\text{tet}}][H^+] + K_{16}K_{17}[\text{Cr(V)}_{\text{tet}}][H^+]^2 \quad (29) \]

Substituting Eq. 29 in Eq. 28 gives:
\[ \frac{d[\text{Cr(V)}_{\text{tot}}]}{dt} = 2k_{18}[\text{Cr(V)}_{\text{tot}}] \left( \frac{[\text{Cr(V)}_{\text{tot}}]}{1 + K_{16}[H^+] + K_{16}K_{17}[H^+]^2} \right)^2K_{16}K_{17}[H^+]^2 \quad (30) \]

which can be arranged as:
\[ \frac{d[\text{Cr(V)}_{\text{tot}}]}{dt} = 2k_{18}K_{16}K_{17}[\text{Cr(V)}_{\text{tot}}]^2[H^+]^2 \left( \frac{1 + K_{16}[H^+] + K_{16}K_{17}[H^+]^2}{1 + K_{16}[H^+] + K_{16}K_{17}[H^+]^2} \right)^2 \quad (31) \]

Dividing both numerator and denominator by the expression \( K_{16}K_{17}[H^+]^2 \)
\[ \frac{d[\text{Cr(V)}_{\text{tot}}]}{dt} = 2k_{18} [\text{Cr(V)}_{\text{tot}}]^2 \left( \frac{1 + K_{16}[H^+] + K_{16}K_{17}[H^+]^2}{1 + K_{16}[H^+] + K_{16}K_{17}[H^+]^2} \right)^2 \quad (32) \]

Since for every 3 \( \text{Cr(V)} \) reacting, 2 \( \text{Cr(VI)} \) are reformed
\[ 3\text{Cr(V)} \rightarrow 2\text{Cr(VI)} + \text{Cr(III)} \quad (34) \]

The concentration of \( \text{Cr(VI)} \) at time \( t \) is:
\[ [\text{Cr(VI)}] = [\text{Cr(VI)}_\infty] - \frac{2}{3}[\text{Cr(V)}] \quad (35) \]

or
\[ [\text{Cr(VI)}] = \frac{3}{2} [\text{Cr(V)}] - \frac{3}{2}[\text{Cr(VI)}]_\infty \quad (36) \]

By using this equation, the rate of \( \text{Cr(VI)} \) formation is expressed as
5. Conclusion

The advanced redox-based interconversion Cr(III)/Cr(VI), presents a challenge for environmental toxicology since the former is an essential nutrient for humans and the latter being a potent carcinogen agent. In this study we shed some light on the mechanism of the interconversion Cr(III)/Cr(VI). Conductometric coupled with pulse radiolysis studies showed that at pH 3.5 Cr(III) can be oxidized by OH• to Cr(IV) which deprotonates with pK_a of 3.9. Furthermore, we showed that Cr(VI) reduction by O_2•^- leads to Cr(V), this later undergoes two successive protonations, 6.20 x 10^3 dm^3 mol^{-1} and 6.84 x 10^2 dm^3 mol^{-1}, before decaying bimolecularly with a rate constant of 3.00 x 10^8 dm^3 mol^{-1} s^{-1}.

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