SHORT PAPER

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First direct detection of chromium(IV) as a long lived intermediate in the oxidation of methanol by chromium(VI)†

Sanchita P. Ghosh[a,b], Manjuri Kumar[a], Aditya P. Koley[a] and Manik C. Ghosh[a*]

[a]*Chemistry and Chemical Engineering Groups, Birla Institute of Technology and Science, Pilani, Rajasthan 333 031, India*

[b]*Present address: Laboratory of Cellular Biology, NIDCD, National Institutes of Health, 5 Research Court, Room 2A-11, Rockville, MD 20850, USA*

Reduction of chromium(VI) by excess methanol in solutions buffered by 2-ethyl-2-hydroxy butanoic acid and its sodium salt proceeds through a 2-electron path to produce pink chromium(IV). With the progress of this reaction, a slow oxidation of the product chromium(IV) by reactant chromium(VI) takes place. When all the chromium(VI) is consumed, the chromium(IV) undergoes very slow disproportionation to chromium(V) and chromium(III). The formation of chromium(IV) is accelerated by both 2-ethyl-2-hydroxy butanoate ion and hydrogen ion.

Keywords: chromiun(VI), chromium(IV), alcohol oxidation

The chemistry of intermediate oxidation states of chromium lying between its stable oxidation states, +3 and +6 is receiving renewed attention because of not only their roles in inorganic reaction mechanism and organic synthesis,[1,2] but also of the carcinogenic activity involved in these less usual oxidation states.[3,4] About half a century ago Westheimer[5,6] proposed both pentavalent- and tetravalent chromium as intermediates in the oxidation of alcohols by chromium(VI). In last five decades several groups of chemists[7-11] have supported Westheimer's proposal, and have demonstrated the presence of Cr(V) as an intermediate from their EPR spectroscopic results. However, chromium(IV) has thus far escaped direct detection in the alcohol reduction of chromium(VI). In this report we characterise, for the first time, chromium(IV) as long-lived intermediate in the reaction between chromium(VI) and methanol in the presence of 2-ethyl-2-hydroxy butanoic acid.

Experimental

Materials: Sodium dichromate (Reagent Grade), acetone free methanol (Aldrich, ACS grade) and the "ligand acid", 2-ethyl-2-hydroxy butanoic acid (Aldrich) were used as received. Solutions of $NaClO_4$ were prepared by neutralising $HClO_4$ with $NaHCO_3$.

Characterisation of reaction products: The observed positive response of the final reaction solution to the 2,4-dinitro-phenylhydrazine test indicates that the oxidation product of methanol is formaldehyde. The chromium product of the first step of the reaction between 2.5×10^{-4} M chromium(VI) and 10 M methanol at 0.3 M Lig^- of pH 3.33 at 25 ^{0}C was characterized as chromium(IV) from its strong absorbance (0.45) at 510nm (molar extinction coefficient of 1800 M^{-1} cm^{-1}).[12,13] In this ligand buffer system Cr(III) has no absorbance maximum at 510 nm, and Cr(V) has a very low extinction coefficient (ε at 510 nm = 180 M^{-1} cm^{-1}).[12,13] The spectrum of the final chromium(III) product[12,13] of the overall reaction recorded after keeping a reaction mixture of 4×10^{-3} M chromium(VI), 0.2 M Lig^- of pH 3.30 and 5.0 M CH_3OH at 25 ^{0}C for 11 days [to ensure that all the Cr(V) product has also been converted to chromium(III)] shows two absoption maxima at 584 nm (ε = 87 M^{-1} cm^{-1}) and 410 nm (ε = 126 M^{-1} cm^{-1}).

Kinetic measurements: The reactions were followed by measuring the absorbance changes at 510 nm, employing either a Jasco Model V-570 or a Beckman Model 5260 spectrophotometer under pseudo-first-order conditions using a large excess of methanol over chromium(VI). Reactions were initiated by adding Cr(VI) to the buffered solutions of methanol. An exponential rise in absorbance followed by a readily separable very slow decay was observed. Rate constants associated with the rising exponential curves corresponding to the formation of pink Cr(IV) were evaluated by using either semilogarithmic plots of absorbance differences *vs* reaction time or unweighted nonlinear least squares fitting of data points to the relationship describing simple first-order transformations. Specific rates for replicate runs diverged by less than 7%. The slow formation of chromium(V) resulting from the oxidation of product Cr(IV) by reactant Cr(VI) during the progress of this first reaction was monitored from the growth of its EPR signal at g = 1.98 using a Varian E-112 X/Q-band EPR spectrometer.[14] The second order rate constants for the very slow decay pertaining to the disproportionaion of Cr(IV) to Cr(III) and Cr(V) were calculated from eqn. (1).

$$A\mathrm{t} = (A_0 + A_\infty kt[\mathrm{Cr(IV)}]_0)/(1+kt[\mathrm{Cr(IV)}_0]) \qquad (1)$$

Solutions were buffered with measured quantities of ligand acid, 2-ethyl-2-hydroxy butanoic acid (HL) and its sodium salt. Ionic strength was regulated by addition of $NaClO_4$ solution.

Results and discussion

The reaction under study has three components. (1). A two-electron transaction from methanol to chromium(VI) to give chromium(IV) which is characterised from its strong absorbance at 510 nm.[12,13] Possibility of the occurance of a parallel one-electron path[15-17] is excluded by the EPR observation (see later) that no initial chromium(V) is formed. (2). This chromium(IV) slowly reacts with the reactant chromium(VI) during the progress of the first reaction via comproportionation[12,13] to form chromium(V) that is characterized by its characteristic EPR spectrum (see later). (3). When no chromium(VI) reactant is left, the chromium(IV) product of reaction 1 undergoes a very slow disproportionation reaction[14] to form chromium(V) and chromium(III) that were characterized from their respective EPR[14] and UV-visible spectra.[12,13]

The absorbance rise part of the reaction corresponding to the formation of chromium(IV) was studied in detail. The formation of chromium(IV) from the reaction between 2.5×10^{-4} M chromium(VI) and 10 M methanol in a buffer of 0.30 M 2-ethyl-2-hydroxy butanoic acid and 0.30 M of its anion at pH 3.30 proceeds through two isosbestic points at 370 nm and 347 nm. Kinetic data for the reaction that was followed at high concentrations of methanol to minimise the interference arising from disproportionation of Cr(IV) are presented in Table 1. This reaction is found to be first-order at relatively lower concentrations of methanol, but the plot of observed rate constant, k_{obs} *vs* [methanol] deviates from linearity at very high methanol concentrations implying that a complex is formed between Cr(VI) and methanol before the electron transfer takes place. Rate of the

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* To receive any correspondence at Cell Biology and Metabolism Branch, NICHD, National Institutes of Health, Building 18T, Room 101, 9000. Rockville Pike, Bethesda, MD 20892, USA. E-mail: ghoshm@mail.nih.gov

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Table 1 Kinetic data for the formation of chromium(IV) from the reaction between Cr(VI) and methanol in the buffer derived from 2-ethyl-2-hydroxy butanoic acid and its anion with methanol in excess[a]

[CH_3OH] M	[L^-] M	pH	10^3xk_{obs}, (s^{-1})	10^3xk_{calc},[b] (s^{-1})
0.25	0.080	3.10	1.30	1.27
0.50	0.080	3.09	2.3	2.2
0.75	0.080	3.08	2.9	3.0
1.00	0.080	3.10	3.6	3.6
1.50	0.080	3.07	4.4	4.6
2.0	0.080	3.09	5.3	5.2
1.00	0.040	3.12	2.5	2.4
1.00	0.120	3.11	4.2	4.4
1.00	0.160	3.10	4.9	4.9
1.00	0.20	3.09	5.5	5.3
1.00	0.24	3.10	5.9	5.6
1.00	0.080	3.67	1.10	0.96
1.00	0.080	3.42	1.40	1.74
1.00	0.080	2.90	6.1	5.8
1.00	0.080	2.63	11.6	10.5

[a]Reactions were run at 25.0 ± 0.5 ^{0}C, μ = 0.25 M ($NaClO_4$); progress of the reaction was monitored at 510 nm with [Cr(VI)] = 5.0 X 10^{-4} M. [b]Values calculated from Eqn (6), using parameters in the text.

reaction is enhanced by increased ligand anion (L^-) concentration at a constant pH and constant [methanol], but exhibits kinetic saturation at high values of [L^-] indicating the participation of ligand anion in the complex formation. Marked acceleration of rate observed with the increase of acidity at a constant ligand anion concentration and constant [methanol] may be attributed to partial conversion of one of the reacting species to highly reactive protonated form. Since the pK of methanol is much higher[18] than the experimental pH range, the only reactive reductant species present in the reaction solutions is CH_3OH suggesting that the protonation–deprotonation equilibrium is associated with its reaction partner, chromium(VI). The plot of k_{obs} *vs* [H^+] yields a straight line with no positive intercept implying that only the protonated form of the chromium(VI) species is reactive. No hint of saturation in the plot of k_{obs} *vs* [H^+] at lowest pH 2.63 is in agreement with the known pK_a (2.2)[19] for the $Cr_2O_7^{2-}$–$HCrO_4^-$ equilibrium. The simplest reaction sequences that is consistent with the observed kinetic patterns can be outlined as reactions (2) – (5).

$$\mathrm{Cr(VI)} + \mathrm{H}^+ \rightleftharpoons \mathrm{Cr(VI)(H^+)} \qquad K_\mathrm{H} = 10^{-2.2} \qquad (2)$$

$$\mathrm{Cr(VI)(H^+)} + \mathrm{L}^- \rightleftharpoons \mathrm{Cr(VI)(LH)} \qquad K_\mathrm{L} \qquad (3)$$

$$\mathrm{Cr(VI)(LH)} + \mathrm{CH_3OH} \rightleftharpoons \mathrm{Cr(VI)(LH)(CH_3OH)} \qquad K_\mathrm{c} \qquad (4)$$

$$\mathrm{Cr(VI)(LH)(CH_3OH)} \rightleftharpoons \mathrm{Cr(IV)(LH)} + \mathrm{HCHO} + 2\mathrm{H}^+ \quad k \qquad (5)$$

The rate law (6) which is consistent with this reaction scheme (2) – (5)

$$k_{obs} = kK_cK_L[L^-][CH_3OH][H^+]/(1+K_L[L^-]+K_cK_L\,[L^-][\,CH_3OH]) \qquad (6)$$

yields k = 11.9 ± 1.3 $M^{-1}s^{-1}$, K_c = 4.5 ± 0.8 M^{-1} and K_L = 2.1 ± 0.7 M^{-1}. Rates calculated from Eqn (6) with these parameters are also listed in Table 1 for comparison. Close agreement between the observed and calculated rates indicates the validity of the proposed reaction sequences and the rate law. Complex formation between the redox partners was also observed for the Cr(VI)–As(III) system[13] in the same ligand buffer. A much lower value of the association constant, K_c, obtained for the present reaction in comparison to that in Cr(VI)–As(III) (340 M^{-1})[13] system, is consistent with the uncharged nature of CH_3OH, the reductant under study. Enhancement of rate by excess ligand anion and high acidity was also reported for the formation of Cr(IV) from the reactions of Cr(VI) with As(III)[13] and $Mo(V)_2$.[12] However, unlike the previous two systems rate saturation observed in the present study on ligand anion concentration enables us to calculate the ligand association constant K_L.

The reaction was also followed by EPR spectroscopy monitoring the growth of Cr(V) at g=1.98[14] in order to find whether there is any initial formation of Cr(V), and to determine the rate of formation of Cr(V), if any. No initial formation of Cr(V) was observed, and the rate calculated from the initial stages of Cr(V) formation at 5.0 × 10^{-4} M chromium(VI), 1.0 M CH_3OH, 0.1 M/l and at pH 3.30 is 9.9 × 10^{-4} s^{-1}. This rate is very similar to that (1.1 × 10^{-3} s^{-1}) calculated for the formation of Cr(V) via the comproportionation reaction between the product Cr(IV) and the reactant in excess Cr(VI) at identical initial conditions for the Cr(VI)–As(III) system.[13] This observation indicates that the chromium(V) is formed from the reduction of chromium(VI) by chromium(IV), and not by methanol. Thus, methanol acts as a two-electron donor towards Cr(VI) under the reaction conditions and no parallel one-electron transfer takes place. Espenson and coworkers[20] also found that alcohols act as pure two-electron reductants towards comparatively short-lived aqueous chromium(IV).

The slow decay of chromium(IV) corresponding to its disproportionation reaction was followed with 2.5 × 10^{-4} M chromium(VI) and 10.0 M methanol in a buffer of 0.30 M 2-ethyl-2-hydroxy butanoic acid and 0.30 M of its anion at pH 3.30. The observed second-order rate (0.70 $M^{-1}s^{-1}$) is in excellent agreement with that (0.76 $M^{-1}s^{-1}$) reported[14] for the uncatalyzed disproportionation of carboxylato-bound chromium(IV) generated by treating Cr(VI) with As(III) at identical pH and [L^-], implying that methanol, like As(III) does not react with Cr(IV) in our reaction system.

The most novel facet of this study is the direct detection and stabilization of chromium(IV) in the course of oxidation of methanol by chromium(VI). Methanol, like As(III) acts as a pure two electron reductant, and does not react with Cr(IV). Thus methanol, instead of highly toxic As(III) can be used to prepare aqueous carboxylato-chromium(IV).

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