

## Reduction of carboxylato-bound chromium(IV) by hydrazine

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Aqueous chromium(IV), stabilised through ligation by 2-ethyl-2-hydroxybutanoate ion, undergoes facile reduction with hydrazine, and this electron transfer process is inhibited by excess ligand anion, as well as by hydrogen ion.

Immediately after the report<sup>1,2</sup> of the stabilisation of aqueous chromium(IV) by chelation with buffers derived from  $\alpha$ -hydroxy acids, the chemistry of this unusual oxidation state has become the subject of recent interest.<sup>1–9</sup> The redox properties of this stabilised Cr(IV) with a wide range of metallic reagents have been studied<sup>1–6,8</sup> but no report exists in the literature on its redox reactions with nonmetallic substrates. We report here the kinetics of reduction of carboxylato chromium(IV) with hydrazine

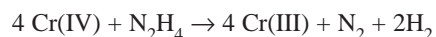
### Experimental

**Materials:** Sodium dichromate (Reagent Grade) and the “ligand acid”, 2-ethyl-2-hydroxybutanoic acid (Aldrich) were used as received. As(III) solution was made by dissolving  $As_2O_3$  (reagent grade) in aqueous NaOH. The ionic strength of the reaction mixture was adjusted with NaCl (Aldrich). Hydrazinium chloride (Alfa) was used without further purification.

**Kinetic measurements:** Pink solutions of chromium(IV) were prepared<sup>2</sup> by reducing known deficiencies of  $HCrO_4^-$  ( $2 \times 10^{-4}$  M) with an excess of (0.01 M)  $H_3AsO_3$  in presence of the buffer derived from 2-ethyl-2-hydroxybutanoic acid (LH) and its anion ( $L^-$ ), and were characterized<sup>2</sup> by its strong absorbance at 510 nm ( $\epsilon_{max} = 2500 \text{ M}^{-1} \text{ cm}^{-1}$  at  $[LH] = [L^-] = 0.10 \text{ M}$ , pH = 3.37). The generated Cr(IV) solutions were found to undergo facile reduction with hydrazine. For kinetic measurements the reaction was monitored spectrophotometrically by measuring absorbance changes at 510 nm in a Beckman Model 5260 or a Jasco Model V-570 spectrophotometer under pseudo-first-order conditions using an excess of  $[N_2H_4]$ . Conversions were followed for at least four half-lives. Rate constants for each of the exponential profiles were evaluated from semilogarithmic plots of absorbance differences vs. reaction times. Specific rates for replicate runs agreed to within 7%.

### Results and discussion

The observed stoichiometry corresponds to the following reaction.

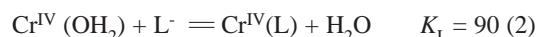


The chromium product was characterized as Cr(III) species from the observed spectrum of the final reaction mix ( $\lambda_{max} = 586 \text{ nm}$ ,  $\epsilon_{max} = 49 \text{ M}^{-1} \text{ cm}^{-1}$ ;  $\lambda_{max} = 412 \text{ nm}$ ,  $\epsilon_{max} = 65 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>1–6</sup> Kinetic data for the reaction are presented in Table 1.

The reaction, which was followed at high range of  $[N_2H_4]$  in order to minimize the disturbance arising from the disproportionation<sup>4</sup> of Cr(IV), is seen to be first-order dependent on  $[N_2H_4]$  with no hint of kinetic saturation within the range of concentrations of reductant taken. This indicates the formation of neither any Cr(IV)– $N_2H_4$  precursor complex nor any ion-pair between them under the reaction conditions, and is consistent with the uncharged nature<sup>6,8</sup> of the Cr(IV) compound under investigation. Marked inhibition of rate observed by the presence of excess ligand anion may be attributed to partial conversion of Cr(IV) to very less reactive or unreactive extraligated form  $Cr^{IV}(L)$ . Observed increase in the rate of reaction with increase in pH indicates the involvement of protonation-deprotonation equilibria in one or both the reactants. Since the reported<sup>10–12</sup>  $pK_{HA}$  values of hydrazine are 8.07 and  $-0.88$ , the only reactive hydrazine species in the pH range covered in this study is  $N_2H_5^+$  indicating that the protonated form of Cr(IV) is less reactive. Previous studies<sup>2,5</sup> have presented evidence that chelated Cr(IV) in our buffer system undergoes partial deprotonation



as well as partition between ligation levels



Considering equilibria (1) and (2), and assuming that both the protonated ( $Cr^{IV}(OH_2)$ ) and the deprotonated ( $Cr^{IV}(OH)$ ) forms, but not the extraligated species ( $Cr^{IV}(L)$ ) contribute towards oxidation process, the rate law (3) can be derived

**Table 1** Kinetic data for the Cr(IV) reaction with  $N_2H_4$  in excess<sup>a</sup>

$[N_2H_5^+]$ , M	$10^4[H^+]$ , M	$[L^-]$ , M	$10^2 \times k_{obs}$ , ( $s^{-1}$ )	$10^2 \times k_{calc}^b$ , ( $s^{-1}$ )
0.020	4.6	0.050	0.72	0.62
0.040	4.6	0.050	1.33	1.24
0.060	4.6	0.050	1.85	1.86
0.080	4.6	0.050	2.4	2.5
0.110	4.6	0.050	3.6	3.4
0.060	4.0	0.164	0.72	0.76
0.060	4.6	0.120	0.92	0.92
0.060	3.6	0.085	1.26	1.44
0.060	3.2	0.030	3.1	3.1
0.060	2.3	0.017	4.6	4.6
0.060	6.9	0.053	1.40	1.44
0.060	8.5	0.072	0.90	0.99
0.060	14.8	0.074	0.61	0.79
0.060	2.0	0.049	2.9	2.9

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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

<sup>a</sup>Reactions were run at  $25.0 \pm 0.5$  °C;  $\mu = 0.50 \text{ M}$  (NaCl); progress of the reaction was monitored at 510 nm with  $[Cr(IV)] = 2.0 \times 10^{-4} \text{ M}$ . Solutions were buffered with mixtures of 2-ethyl-2-hydroxybutanoic acid and its sodium salt.  
<sup>b</sup>Values calculated from (3), using parameters in text.

$$k_{\text{obs}} = (k_{\text{H}}[\text{H}^+] + kK_{\text{H}}[\text{N}_2\text{H}_4]) / (K_{\text{H}} + [\text{H}^+] + K_{\text{L}}[\text{H}^+][\text{L}^-]) \quad (3)$$

where  $k_{\text{H}}$  and  $k$  represent the respective rate constants for the reactions of  $\text{Cr}^{\text{IV}}(\text{OH}_2)$  and  $\text{Cr}^{\text{IV}}(\text{OH})$  with  $\text{N}_2\text{H}_5^+$ . A nonlinear least-squares fitting of our rate data with equation (3) produced  $k_{\text{H}} = 0.64 \pm 0.09 \text{ M}^{-1}\text{s}^{-1}$  and  $k = 1.57 \pm 0.08 \text{ M}^{-1}\text{s}^{-1}$ . Rates calculated from equation (3) with these parameters and the reported  $K_{\text{H}}$  and  $K_{\text{L}}$  values are also listed in Table 1 for comparison. Close agreement between the observed and calculated rates indicates the validity of our rate law.

Similar retardation of rate by excess ligand anion and high acidity has been observed for the uncatalysed and Mn(II) catalysed disproportionation<sup>4</sup> of Cr(IV), as well as for its reduction by metallic substrates.<sup>3,5</sup> The same factors, excess  $[\text{L}^-]$  and high  $[\text{H}^+]$  have been found<sup>1-3</sup> to accelerate the formation of Cr(IV) from the reduction of Cr(VI) with  $\text{H}_3\text{AsO}_3^-$ ,  $(\text{Mo}^{\text{V}})_2$  or U(IV), and thus impart more stability to this carboxylato chromium(IV). Thus, hydrazine does not differ from the metallic substrates when the effects of ligand anion and  $\text{H}^+$  on the reactivity trend of Cr(IV) is considered. These observations, along with the second-order nature of autodisproportionation<sup>4</sup> of Cr(IV) suggest that high concentrations of ligand anion and hydrogen ion, and low concentration of chromium(IV) are the best conditions for preparation of this aqueous carboxylato chromium(IV).

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