

## Electron transfer to oxochromate(V) mediated through a sulphur bond

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**Abstract.** Reduction of carboxylato bound chromium(V) by several reducing agents such as  $N_2H_4$ ,  $NH_2OH$ , Ti(III), Fe(II),  $VO^{2+}$ , U(IV) formed part of earlier studies in which electron transfer to Cr(V) seems to occur through nitrogen or by inner or outer sphere path. In the chromium(V) oxidation of lactic acid, saturation kinetics has been observed and the association constant,  $K$ , evaluated from a double reciprocal plot, indicates weak interaction between reactants. In contrast, the reduction of Cr(V) by thiolactic acid exhibits total second order kinetics – first order with respect to each reactant. Probably the  $Cr^V-S$  bond is weaker than the  $Cr^V-O$  bond and electron transfer mediated through the sulphur system is facile. Under identical conditions Cr(VI) seems to be a better oxidant for lactic than for thiolactic acid.

**Keywords.** Oxochromate(V); oxidant for lactic and thiolactic acids; Cr-S bond; facile electron transfer.

### 1. Introduction

Reduction of sodium *bis*-(2-hydroxy-2-ethyl-butanato)-oxochromate(V) monohydrate [Cr(V)-HEBA], by several reducing agents such as  $N_2H_4$  (Srinivasan and Gould 1981),  $NH_2OH$  (Rajasekar *et al* 1983), Ti(III) (Bose and Gould 1985a),  $Fe^{2+}$  (Bose and Gould 1985b),  $VO^{2+}$  (Fanchiang *et al* 1985), U(IV) (Bose and Gould 1986),  $NO_2^-$  (Rajavelu and Srinivasan 1985), has formed part of earlier studies and chromium(V) oxidation of a variety of organic compounds such as oxalic, lactic, mandelic, glycolic acids and alcohols, such as 1-propanol, 2-propanol, has been carried out by Krumpolc and Rocek (1985) in the pH range 3–4. The latter work gives a detailed stoichiometric and product analysis in each case but does not find chromium(V) as regioselective oxidant. However, the electron transfer to the chromium(V) centre mediated by a sulphur bond has not formed part of any earlier study. Hence in the present work, oxidation of thiolactic acid by oxochromate(V) has been undertaken and for comparison, under identical conditions, reduction of chromium(V) by the corresponding oxo-compound, lactic acid, has been carried out. The kinetic results of these two reactions are very much different and point to facile electron transfer to chromium(V) mediated through the sulphur bond.

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## 2. Results and discussion

Tables 1 and 2 summarise kinetic data for the chromium(V) oxidation of lactic and thiolactic acids. In both the cases the rate of disappearance of Cr(V) depends on the first power of chromium(V) concentration. The slope for a graph of logarithm of specific rate versus logarithm of lactic acid concentration is 0.81, indicating fractional order kinetics with respect to [lactic acid]. (At lower lactic acid concentrations, in the range 0.020–0.080 M, the  $k_1$  values calculated in any particular run are not constant and hence these data are not included in table 1.) Such saturation kinetics suggests the

**Table 1.** Kinetic data for chromium(V) oxidation of lactic acid<sup>a,b</sup>.

$10^3$ [lactic acid] (mol)	$10^3$ [Cr(V)] (mol)	$10^3$ [HEBA] (mol)	$10^3 k_1$ (s <sup>-1</sup> )	
			Experi- mental	Calcu- lated
1.6	1.00	—	2.6	—
1.6	2.0	—	2.6	2.5
1.6	2.5	—	2.5	—
1.6	3.0	—	2.5	—
2.0	2.0	—	2.9	2.9
2.4	2.0	—	3.2	3.2
3.2	2.0	—	3.9	3.8
1.6	2.0	2.0	5.1	—
1.6	2.0	6.0	6.0	—
1.6	2.0	10.0	7.8	—

<sup>a</sup> Reactions were carried out in 100% acetonitrile at  $28 \pm 0.2^\circ\text{C}$ .

<sup>b</sup> Under identical conditions, the specific rate for Cr(VI) oxidation of lactic acid is  $6.1 \times 10^{-3} \text{ s}^{-1}$ , when [lactic acid] = 0.16 mol and [Cr(VI)] =  $2.0 \times 10^{-4}$  mol.

**Table 2.** Kinetic data for chromium(V) oxidation of thiolactic acid<sup>a</sup>.

$10^2$ [Thiolactic acid] (mol)	$10^3$ [Cr(V)] (mol)	$10^3$ [HEBA] (mol)	$10^3 k_1$ (s <sup>-1</sup> )
2.0	1.00	—	4.9
2.0	1.50	—	4.8
2.0	2.0	—	4.9
2.0	3.0	—	4.7
4.0	2.0	—	9.9
6.0	2.0	—	14.7
8.0	2.0	—	17.6
2.0	2.0	2.0	3.2
2.0	2.0	4.0	2.9
2.0	2.0	8.0	1.5

<sup>a</sup> Reactions were carried out in 100% acetonitrile at  $28 \pm 0.2^\circ\text{C}$ .

<sup>b</sup> Under identical conditions, the specific rate for Cr(VI) oxidation of thiolactic acid is  $2.2 \times 10^{-3} \text{ s}^{-1}$ , when [thiolactic acid] =  $2.0 \times 10^{-2}$  mol and [Cr(VI)] =  $2.0 \times 10^{-4}$  mol.

formation of a complex between these two reactants. Assuming this to be the 1:1 complex between Cr(V) and lactic acid, the following rate law can be deduced for the reaction,

$$\text{rate} = \frac{k_{\text{lim}}[\text{Cr(VI)}][\text{lactic acid}]}{K^{-1} + [\text{lactic acid}]}, \quad (1)$$

where  $k_{\text{lim}}$  is the limiting specific rate at higher  $[\text{lactic acid}]/[\text{Cr(V)}]$  ratios and  $K$  is the association constant for the complex between Cr(V) and lactic acid. From a linear double reciprocal plot of  $1/k_1$  versus  $1/[\text{lactic acid}]$ , values of  $k_{\text{lim}}[1/\text{intercept}] = 7.5 \times 10^{-5} \text{ s}^{-1}$ , and  $K [= \text{intercept/slope}] = 3.6 \text{ M}^{-1}$  are obtained. Using these  $K$  and  $k_{\text{lim}}$  values, the specific rates calculated agree well with those obtained experimentally (table 1). The low value of the association constant,  $K$ , between Cr(V) and lactic acid indicates weak interaction between these two reactants. This may be the reason for the complex not being detected spectrophotometrically.

In contrast to the above results, the reaction between Cr(V) and thiolactic acid exhibits second order kinetics – first order with respect to each reactant (table 2). The rate law for this reaction is

$$-\frac{d[\text{Cr(V)}]}{dt} = k_2[\text{Cr(V)}][\text{thiolactic acid}]. \quad (2)$$

Probably the interaction between Cr<sup>V</sup> and thiolactic acid is much weaker than that observed in the Cr<sup>V</sup>-lactic acid system as the Cr<sup>V</sup>-S bond is much weaker than the Cr<sup>V</sup>-O bond.

The rates of these two reactions are affected differently on adding unbound carboxylato ligand. While Cr(V) oxidation of lactic acid is marginally accelerated by the addition of unbound ligand (table 1), the rate of Cr(V) oxidation of thiolactic acid is retarded.

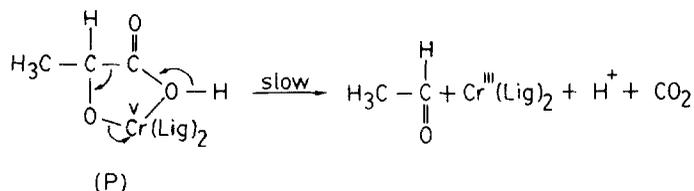
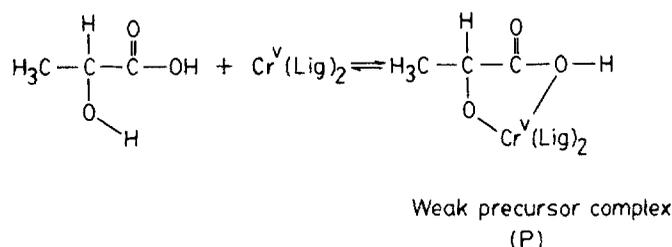
Possibly lactic acid (LA) forms complexes such as (O)Cr<sup>V</sup>(lig)(LA) and (O)Cr<sup>V</sup>(lig)<sub>2</sub>LA with mono and *bis*-chelated chromium(V). The addition of carboxylato ligand probably increases the concentration of the reactive species (O)Cr<sup>V</sup>(lig)<sub>2</sub>LA, and hence the observed increase in rate with increasing concentration of carboxylato ligand. For lactic acid of concentration 0.16 M,  $k_{\text{obs}}$  can be given as  $k_{\text{obs}} = 2.6 \times 10^{-5} + 0.0052 [\text{HEBA}]$  (approximately). As such a complex formation between Cr(V) and thiolactic acid is not observed both kinetically and spectrophotometrically, the added unbound ligand possibly favours the reversal of the equilibrium below, decreasing the concentration of mono-chelated chromium(V), which may be the more reactive species.



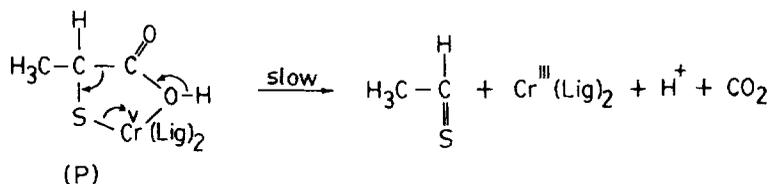
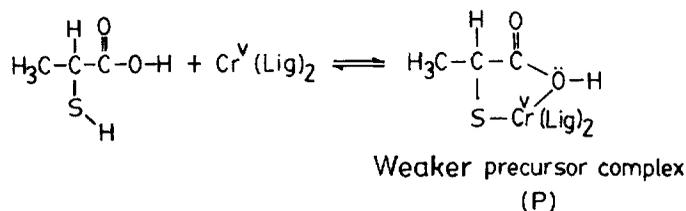
To account for these experimental results, the following mechanistic scheme 1 is proposed for the Cr(V) oxidation of lactic acid.

According to scheme 1, in the precursor complex formed between Cr<sup>V</sup> and lactic acid, a nearly synchronous C–C fission and electron transfer to Cr<sup>V</sup> occur in the slow step yielding acetaldehyde and a *bis*-chelated chromium(III) product.

Though chromium(V) does not seem to form such a complex with thiolactic acid, it is still assumed in the scheme 2 (similar to scheme 1) to illustrate the electron transfer



Scheme 1.



Scheme 2.

to Cr(V). The mechanistic scheme 2 proposed for Cr(V) oxidation of thiolactic acid is in keeping with most of the observed results. The higher absorption maxima obtained for the chromium(III) product of chromium(V) reaction with thiolactic acid, suggest a *bis*-chelated carboxylato(III) product while the effect of unbound carboxylato ligand on the rates of these reactions seems to favour a mono-chelated chromium(V). The authors are puzzled over these results. As these reaction mixtures do not initiate acrylonitrile polymerisation, radical intermediates are not considered in both schemes 1 and 2.

The complex between Cr<sup>V</sup>-thiolactic acid possibly involves a weak Cr<sup>V</sup>-S bond which mediates electron transfer to Cr<sup>V</sup> in a more facile manner than the stronger Cr<sup>V</sup>-O bond present in the complex formed between Cr<sup>V</sup> and lactic acid. Under identical conditions, Cr(VI) seems to be a better oxidant for lactic acid than for thiolactic acid. As these rates differ from those observed in Cr<sup>V</sup> reaction, with lactic and thiolactic acids, Cr(VI) may probably not be involved as an intermediate in the Cr(V) oxidation of lactic and thiolactic acids.

### 3. Experimental

Following the procedure in literature (Krumpolc and Rocek 1979), the chromium(V) complex of HEBA has been prepared. The compound was dissolved and reprecipitated several times from acetone solution using hexane till the mother liquor was colourless. Repeatable results were obtained when this sample of chromium(V) complex was used within 15 days if stored in amber-coloured bottles in a refrigerator. Lactic and thiolactic acids (Aldrich/Fluka A G) were of extra pure variety and were used as such. As the redox reactions were carried out in acetonitrile, the solvent was purified by distillation over phosphorus pentoxide at 81°C. Sodium dichromate (Analar BDH) was crystallised three or four times from water, dried at 130°C for an hour in an air oven and cooled and preserved in a desiccator.

#### 3.1 Rate measurements

Rates were estimated from absorbance changes for chromium(V) at 540 nm using a Carl Zeiss VSU2-P spectrophotometer at  $28 \pm 0.2^\circ\text{C}$ . Though the absorption maxima for chromium(V) complex in aqueous solution is 510 nm, in the solvent acetonitrile it is shifted to 540 nm. Hence the rate of Cr(V) oxidation of lactic/thiolactic acids is followed at 540 nm. The experiments were carried out under pseudo-first order conditions with the substrate in large excess. The reactions were followed for at least 4 half-lives and, from the decrease in absorbance measured at different time intervals, the specific rates were calculated using an integrated first-order equation. These agreed within  $\pm 5\%$  with those obtained from a linear graph of logarithm of change in absorbance versus time. The experiments were carried out in duplicate and the velocity constants obtained were reproducible within  $\pm 7\%$ .

For the chromium(VI) oxidation of these substrates under identical conditions, the specific rates were calculated from the decrease in absorbance measured from Cr(VI) at 350 nm by the above procedure.

#### 3.2 Stoichiometric studies and product analysis

Stoichiometric experiments were carried out with the oxidant in excess in 100% acetonitrile at  $28 \pm 0.2^\circ\text{C}$ . After 9 half-lives, from the change in absorbance measured for the chromium(V) complex at 540 nm, and after applying the due blank correction for the self decomposition/disproportionation of the chromium(V) complex, the amount of chromium(V) consumed by the substrate was calculated and the data concerning these are summarised in table 3. 1 mol of lactic acid/thiolactic acid needs nearly 1 mol of Cr(V) for the reaction.

After 9 half-lives, the organic product of the chromium(V) and lactic acid reaction was ether-extracted from the reaction mixture concentrate and the solvent evaporated under reduced pressure. The product gave a 2,4-dinitrophenylhydrazone derivative with m.p.  $108^\circ\text{C}$  which compares well with that of acetaldehyde 2,4-dinitrophenylhydrazone (Vogel 1978). The yield of acetaldehyde is about 90%. This experiment was performed with chromium(V) in excess. A similar procedure was followed to separate the organic product of the Cr<sup>V</sup>-thiolactic acid reaction and the IR spectrum of the product has the characteristic features of  $-\text{C}(=\text{S})-$  (broad band at  $1200-1230\text{ cm}^{-1}$ ),  $-\text{CH}$  stretching frequency of thioacetaldehyde [bands at  $2860(\text{s})$ ,

**Table 3.** Stoichiometric data for chromium(V) oxidation of lactic and thiolactic acids<sup>a</sup>.

[Substrate] (mM)	[Cr(V)] <sub>initial</sub> (mM)	[Cr(V)] <sub>final</sub> (mM)	[Cr(V)] <sup>b</sup> [substrate]
(i) <i>Lactic acid</i>			
1.00	10.0	9.1	0.90
0.75	5.0	4.3	0.93
(ii) <i>Thiolactic acid</i>			
1.13	5.0	3.9	0.97
1.00	7.5	6.5	1.00
0.75	10.0	9.3	0.93

<sup>a</sup> Reactions were carried out in 100% acetonitrile and at 28 ± 0.2 °C.

<sup>b</sup> After applying the due corrections for the decomposition/disproportionation of Cr(V) during reaction time, [Cr(V)] was calculated from the decrease in absorbance at 540 nm.

2940(s) and 2985(s)] and a sharp band at 1460 cm<sup>-1</sup> for the -CH<sub>3</sub> group (Morrill 1968). The major product of the Cr(V)-thiolactic acid reaction is thioacetaldehyde formed in 90% yield.

Taking less of chromium(V) than required, after nine half-lives the organic product was ether-extracted and the chromium(III) product left behind was dissolved in acetonitrile and was scanned from 350–600 nm. The absorption maxima for the chromium(III) product were at 420 nm ( $\epsilon \approx 72 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 560 nm ( $\epsilon \approx 50 \text{ M}^{-1} \text{ cm}^{-1}$ ). The chromium(III) product obtained from the Cr(V)-thiolactic acid reaction has absorption maxima at 415 nm ( $\epsilon \approx 80 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 560 nm ( $\epsilon \approx 68 \text{ M}^{-1} \text{ cm}^{-1}$ ). These absorption maxima and molar extinction coefficients for the chromium(III) complex are suggestive of a chelated carboxylato derivative.

## References

- Bose R N and Gould E S 1985a *Inorg. Chem.* **24** 2645  
 Bose R N and Gould E S 1985b *Inorg. Chem.* **24** 2832  
 Bose R N and Gould E S 1986 *Inorg. Chem.* **25** 94  
 Fanchiang Y-T, Bose R N, Gelerinter E and Gould E S 1985 *Inorg. Chem.* **24** 4679  
 Krumpolc M and Rocek J 1979 *Inorg. Chem.* **18** 617  
 Krumpolc M and Rocek J 1985 *J. Am. Chem. Soc.* **101** 3206  
 Morrill T C 1968 *Spectrophotometric identification of organic compounds* (New York: John Wiley) p. 95  
 Rajasekar N, Subramanian R and Gould E S 1983 *Inorg. Chem.* **22** 971  
 Rajavelu A and Srinivasan V S 1985 *Indian J. Chem.* **A24** 963  
 Srinivasan V S and Gould E S 1981 *Inorg. Chem.* **20** 3176  
 Vogel A I 1978 *Text book of practical organic chemistry* (London: Longman) p. 1111