

# Kinetics and mechanism of oxidation of allyl, crotyl and cinnamyl alcohol by chromium(V)

Gantla Sreelatha, Mulakaluri Prasada Rao, Bangalore Sethuram\* and Tangeda Navaneeth Rao

Department of Chemistry, Osmania University, Hyderabad 500 007, India

## Summary

The kinetics of oxidation of unsaturated alcohols *viz.* allyl, crotyl and cinnamyl alcohol by sodium bis[2-ethyl-2-hydroxy butanoato (2-)] oxochromate(V), Cr<sup>V</sup>, has been investigated in 25% (v/v) aq. HOAc:HClO<sub>4</sub>. The order in [oxidant] and [substrate] was 1.0 and 0.7 respectively. The oxidation rate increased with increase in [2-ethyl-2-hydroxybutyric acid] (EHBA) and decreased with increase in the percentage of HOAc. The rate decreases slightly with increase in [H<sup>+</sup>]. The unsaturated alcohols exhibited higher reactivity compared to their saturated analogues. A mechanism involving the formation of a complex between Cr<sup>V</sup> and alcohol which in turn disproportionates into products in a slow step is advanced to explain the kinetic results.

## Introduction

Among the series of chromium(V) (bis) chelates, the most robust is the 2-ethyl-2-hydroxybutyrato derivative<sup>(1)</sup>. This complex is stable in air and dissolves easily in polar solvents, without immediate disproportionation, in the 2–4 pH range. The facile preparation of this compound, has led to a study of the redox properties of this typical oxidation state. Chromium(V) has been extensively used as an oxidant for a variety of inorganic substrates<sup>(2)</sup> in the 2–4 pH range. However only a few references to the oxidation kinetics of organic substrates by chromium(V) have appeared. In our earlier paper<sup>(3)</sup>, results on the oxidation of benzyl alcohol and its substituted analogues by chromium(V) in the 2–4 pH range were presented and discussed. The oxidation of allyl alcohol has been reported by several workers<sup>(4–6)</sup>. Jones and Waters pointed out that allyl and crotyl alcohols were oxidised by vanadium(V) more easily than their saturated analogues due to the formation of highly reactive mesomeric intermediates<sup>(7)</sup>. It therefore seemed worthwhile to us to investigate the mechanistic aspects of oxidation of unsaturated alcohols, such as allyl, crotyl and cinnamyl alcohols by chromium(V), and to compare the reactivities of compounds with those of their saturated analogues.

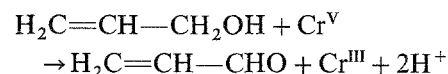
## Materials and methods

All the chemicals used were of AR grade and purified by standard methods where necessary. 2-Ethyl-2-hydroxybutyric acid (EHBA, Aldrich) was recrystallized from benzene and hexane. Allyl alcohol (AA) was purified by boiling under reflux with 2, 4-dinitrophenylhydrazine for 4–5 h followed by distillation. Sodium bis[2-ethyl-2-hydroxybutanoato(2-)] oxochromate(V) was prepared according to the literature method<sup>(1)</sup>. Stock solutions of Cr<sup>V</sup> were prepared in 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> HClO<sub>4</sub> in

the presence of 1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup> EHBA, which suppresses the decomposition of Cr<sup>V</sup>. EHBA does not undergo perceptible oxidation under the experimental conditions. Solutions were standardized iodometrically as well as spectro-photometrically using the molar extinction coefficient of Cr<sup>V</sup> complex as 1.68 × 10<sup>2</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> at 510 nm<sup>(1)</sup>. HOAc, which is a co-solvent, was also not oxidized under the experimental conditions. The reaction was initiated by adding the requisite quantities of Cr<sup>V</sup> solution to the flask containing the alcohol, HOAc and HClO<sub>4</sub> after thermostating the two solutions separately for 30 min. The reaction was monitored by noting the absorbance of the Cr<sup>V</sup> complex at 510 nm at regular intervals using a Carl-Zeiss VSU-2-p-spectrophotometer. The pH of the solution was maintained in the 2–4 range by varying the concentration of HClO<sub>4</sub>. NaClO<sub>4</sub> was used to maintain constant ionic strength.

## Products and stoichiometry

Under the conditions: [Cr<sup>V</sup>] ≫ [alcohol] in 25% (v/v) acetic acid medium, Cr<sup>V</sup>, was allowed to react with unsaturated alcohol for a sufficiently long time and later the excess oxidant was estimated. Values of Δ[Cr<sup>V</sup>]/Δ[alcohol] under different concentration ranges revealed a 1:1 stoichiometry. Acrolein was characterised as the oxidation product by g.l.c.. Acrolein was not oxidised under these experimental conditions.



No polymerisation occurred when acrylonitrile was added to the reaction mixture under a N<sub>2</sub> atmosphere, indicating absence of free radical formation during the course of the reaction.

## Results and discussion

Under the conditions: [alcohol] ≫ [Cr<sup>V</sup>], plots of log (a/a-x) versus time [where 'a' and '(a-x)' are initial and final concentrations at time 't' of Cr<sup>V</sup>] were linear, indicating a first order dependence in [Cr<sup>V</sup>]. From the slopes of such plots the pseudo-first order rate constants (k<sub>obs</sub>) were evaluated at different [Cr<sup>V</sup>] and found to be the same (Table 1). The order in [alcohol], as obtained from the slope of the linear plot of log(k<sub>obs</sub>) versus log[alcohol] (Figure 1A), was 0.70 within the concentration range of alcohol (0.06–0.6 mol. dm<sup>-3</sup>) studied. At fixed [Cr<sup>V</sup>], [alcohol] and [H<sup>+</sup>], an increase in [EHBA] led to an increase in the oxidation rate (Table 1). This rate decreased slightly with increase in [H<sup>+</sup>] in the 2–4 pH range (Table 1). The rate also decreased with increase in HOAc percentage (Figure 1C). Addition of salts such as NaCl or NaClO<sub>4</sub> had a negligible effect on the reaction rate.

The chromium(V) complex, [Cr<sup>V</sup>O(EHBA)<sub>2</sub>]<sup>-</sup>, was

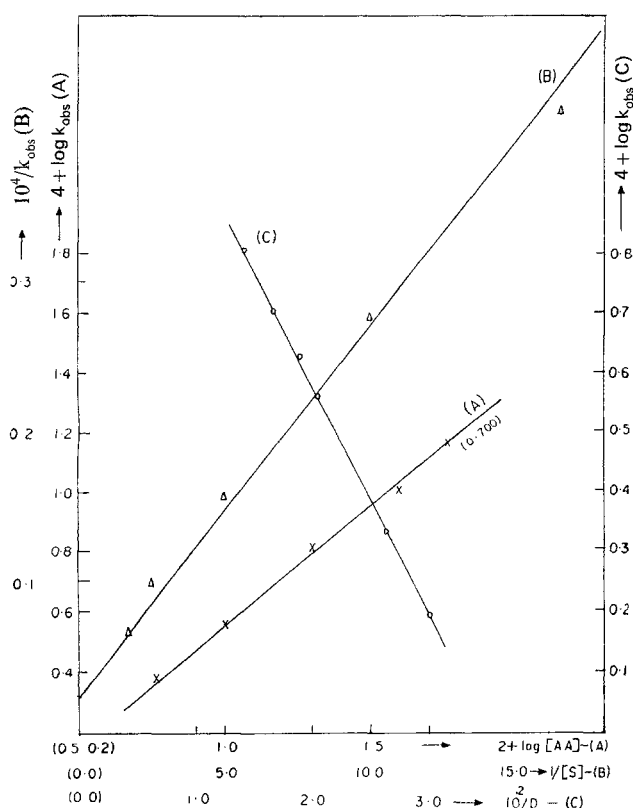
\* Author to whom all correspondence should be directed.

**Table 1.** Effect of  $[\text{Cr}^{\text{V}}]$ ,  $[\text{EHBA}]$ ,  $[\text{H}^+]$  on the rate constant,  $k_{\text{obs}}$ , in the  $\text{Cr}^{\text{V}}$ -allyl alcohol reaction<sup>a</sup>.

$10^3 [\text{Cr}^{\text{V}}]$ (mol dm <sup>-3</sup> )	$10^2 [\text{EHBA}]$ (mol dm <sup>-3</sup> )	$10^3 [\text{H}^+]$ (mol dm <sup>-3</sup> )	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> )
2.00	1.00	1.00	4.60
3.00	1.00	1.00	4.50
4.00	1.00	1.00	4.40
5.00	1.00	1.00	4.60
6.00	1.00	1.00	4.30
3.00	0.500	1.00	4.00
3.00	1.00	1.00	4.50
3.00	2.00	1.00	4.80
3.00	5.00	1.00	5.30
3.00	1.00	0.300	4.81
3.00	1.00	0.500	4.70
3.00	1.00	1.00	4.50
3.00	1.00	2.00	4.40
3.00	1.00	3.00	4.20

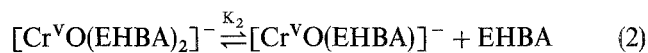
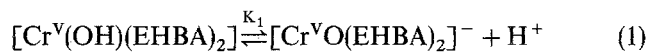
<sup>a</sup>[A.A.] =  $2.00 \times 10^{-1}$  mol dm<sup>-3</sup>; HOAC = 25% (v/v); Temp = 303 K.

found to be stable with the 2–4 pH limits, but outside this range decomposition occurred. The possible chromium(V) species present in the above pH range as suggested by Krumpolc and Rocek<sup>(8)</sup> are  $[\text{Cr}^{\text{V}}(\text{OH})(\text{EHBA})_2]$  (neutral),  $[\text{Cr}^{\text{V}}\text{O}(\text{EHBA})_2]^-$  (monoanionic) and another species containing only one EHBA



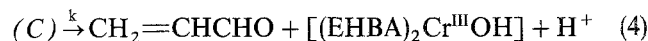
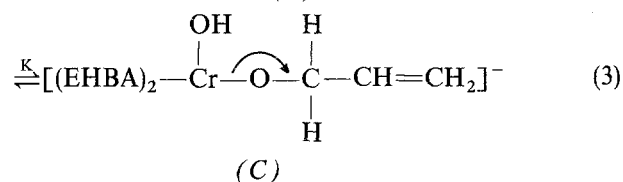
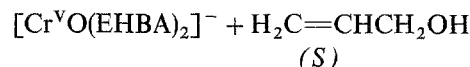
**Figure 1.** (A). Plot of  $\log k_{\text{obs}}$  versus  $\log [\text{A.A.}]$  ( $[\text{Cr}^{\text{V}}] = 3.00 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[\text{EHBA}] = 1.00 \times 10^{-2}$  mol dm<sup>-3</sup>,  $[\text{H}^+] = 1.00 \times 10^{-3}$  mol dm<sup>-3</sup>, AcOH = 25.0% (v/v); Temp = 303 K) (B). Plot of  $10^4/k_{\text{obs}}$  versus  $1/[\text{S}]$  where  $[\text{S}] = [\text{A.A.}]$  ( $[\text{Cr}^{\text{V}}] = 3.00 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[\text{EHBA}] = 1.00 \times 10^{-2}$  mol dm<sup>-3</sup>,  $[\text{H}^+] = 1.00 \times 10^{-3}$  mol dm<sup>-3</sup>; AcOH = 25.0% (v/v); Temp = 303 K) (C). Plot of  $\log k_{\text{obs}}$  versus  $10^2/D$  ( $[\text{Cr}^{\text{V}}] = 3.00 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[\text{A.A.}] = 2.00 \times 10^{-1}$  mol dm<sup>-3</sup>,  $[\text{H}^+] = 1.00 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[\text{EHBA}] = 1.00 \times 10^{-2}$  mol dm<sup>-3</sup> Temp = 303 K).

molecule, the complex  $[\text{Cr}^{\text{V}}\text{O}(\text{EHBA})^-]$ , which exists as shown in the following equilibria.



If  $[\text{Cr}^{\text{V}}\text{O}(\text{EHBA})_2]^-$  is the reactive form of chromium(V), the rate should increase with decrease in  $[\text{H}^+]$  and increase in  $[\text{EHBA}]$  according to equilibria (1) and (2). This phenomenon was in fact observed, suggesting that the monoanionic species  $[\text{Cr}^{\text{V}}\text{O}(\text{EHBA})_2]^-$  could be the most probable reactive species under the experimental conditions. Complex formation between chromium(V) and alcohol was confirmed by the shift in the  $\lambda_{\text{max}}$  of chromium(V) when alcohol was added.

In view of these considerations, we propose a mechanism involving formation of a complex between a negative ion, ( $\text{Cr}^{\text{V}}$ ) and dipole (alcohol), which in turn dissociates into products by the elimination of hydride ion from the  $\alpha$ -carbon of alcohol in a slow step. This contention is supported by the effect of the dielectric constant ( $D$ ) on the reaction rate; a negative slope was obtained for a  $\log k$  plot versus  $1/D$  (Figure 1C). Scheme 1 is therefore suggested as a possible course of the reaction.



#### Scheme 1

Scheme 1 leads to the rate law (5)

$$-d[\text{Cr}(\text{V})]/dt = kK[\text{Cr}(\text{V})][\text{alcohol}] / [1 + K[\text{alcohol}]] \quad (5)$$

$$k_{\text{obs}} = \frac{kK[\text{alcohol}]}{1 + K[\text{alcohol}]} \quad (6)$$

Equation (6) predicts a first order dependence of reaction rate on alcohol at higher concentrations and zero order dependence at lower concentrations. This trend could not be observed in the present study due to experimental difficulties outside the concentration range (0.06–0.6 mol dm<sup>-3</sup>) of alcohol. Taking reciprocals of equation (6) we obtain:

$$1/k_{\text{obs}} = 1/kK[\text{alcohol}] + 1/k \quad (7)$$

According to Equation (7) a plot of  $1/k_{\text{obs}}$  versus  $1/[\text{alcohol}]$  should be linear with an intercept. This result has been obtained in the present case (Figure 1B), supporting the proposed mechanism. Similar behaviour was also observed in the ruthenium(VI)-catalysed oxidation of unsaturated alcohols by hexacyanoferrate<sup>(9)</sup>. From the slope and intercept values of these plots at different temperatures, formation ( $K$ ) and disproportionation ( $k$ ) constants of the complexes were calculated (Table 2).

**Table 2.** Formation constants, disproportionation constants, thermodynamic and activation parameters for the Cr<sup>V</sup>-unsaturated alcohol reaction<sup>a</sup>.

Alcohol	K (dm <sup>3</sup> mol <sup>-1</sup> )	10 <sup>4</sup> k (s <sup>-1</sup> )	E <sub>exp</sub> (kJ mol <sup>-1</sup> )	ΔH° (kJ mol <sup>-1</sup> )	ΔG° (kJ mol <sup>-1</sup> )	ΔS° (J K <sup>-1</sup> mol <sup>-1</sup> )
Cinnamyl	77.2	13.9	– 43.0 <sup>b</sup>	76.5 45.5 <sup>b</sup>	–11.0 67.5 <sup>b</sup>	288 –72.6 <sup>b</sup>
Crotyl	20.0	11.2	– 51.6 <sup>b</sup>	55.5 54.5 <sup>b</sup>	–7.55 68.0 <sup>b</sup>	208 –45.8 <sup>b</sup>
Allyl	1.85	7.80	– 60.5 <sup>b</sup>	34.6 63.0 <sup>b</sup>	–1.55 68.9 <sup>b</sup>	119 –19.4 <sup>b</sup>

<sup>a</sup>[Cr<sup>V</sup>] = 3.00 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>] = 1.00 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [EHBA] = 1.00 × 10<sup>-2</sup> mol dm<sup>-3</sup>; Temp = 303 K; <sup>b</sup>Activation parameters.

**Table 3.** Reactivity of various organic compounds towards Cr<sup>V</sup>

Substrate	10 <sup>6</sup> k <sub>obs</sub> (s <sup>-1</sup> )
PhCH=CHCH <sub>2</sub> OH	613
Crotyl alcohol	92.0
CH <sub>2</sub> =CHCH <sub>2</sub> OH	64.1
PhCH=CHCHO	10.2
Acrolein	2.90
<i>n</i> -BuOH	1.60
<i>n</i> -PrOH	1.20

<sup>a</sup>[Cr<sup>V</sup>] = 3.00 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [EHBA] = 1.00 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [H<sup>+</sup>] = 1.00 × 10<sup>-3</sup> mol dm<sup>-3</sup>; AcOH = 50%; Temp = 303 K; [substrate] = 0.025 mol dm<sup>-3</sup>.

The order of reactivity of these three alcohols is cinnamyl > crotyl > allyl alcohol. The high reactivity of cinnamyl and crotyl alcohol is attributed to resonance stabilization and greater positive character of the transition state in these reactions compared with the allyl alcohol reaction. This conclusion receives support from the equilibrium constant data (Table 2). The unsaturated acids *viz.*, acrylic and cinnamic acid, did not undergo perceptible oxidation under the experimental conditions, indicating that C=C is unaffected by chromium(V). This result is also confirmed from the identification of the product, *viz.* acrolein, obtained from allyl alcohol. The unsaturated aldehydes undergo slow oxidation by chromium(V) (Table 3). The oxidation rates for allyl, crotyl and cinnamyl alcohol were found to be much greater than their corresponding saturated analogues *viz.*, *n*-propanol and *n*-butanol. The greater reactivity of the former is attributed to the formation of mesomeric intermediates (<sup>+</sup>CH<sub>2</sub>—CH=CH—OH,

CH<sub>2</sub>=CH—<sup>+</sup>CH—OH), which are known to be highly reactive. A similar trend was also observed by Jones and Waters<sup>(7)</sup> during their study on the oxidation of allyl and crotyl alcohol by vanadium(V).

The disproportionation constant *k* and the activation parameters, E<sub>a</sub>, ΔH<sup>‡</sup>, ΔG<sup>‡</sup> and ΔS<sup>‡</sup> are given in Table 2. An examination of the latter reveals that the fastest reaction has the lowest activation energy, indicating that the reactions are enthalpy controlled. The negative entropies of activation for crotyl and cinnamyl alcohol might be due to the formation of a more rigid complex. The formation constants, *K* and the thermodynamic parameters, ΔH°, ΔG° and ΔS° have also been calculated and are listed in Table 2.

#### Acknowledgements

One of the authors (G. S) thanks the CSIR, New Delhi, for the award of a Research Fellowship.

#### References

- (1) M. Krumpolc and J. Rocek, *J. Am. Chem. Soc.*, **101**, 3206 (1979).
- (2) S. Edwin Gould, *Acc. Chem. Res.*, **19**(3), 66 (1986).
- (3) G. Sreelatha, M. Prasada Rao, B. Sethuram and T. Navaneeth Rao, *Indian J. Chem.*, **27A**, 1031 (1988).
- (4) H. Land and W. A. Waters, *J. Chem. Soc.*, 2129 (1958).
- (5) B. Sethuram, *Curr. Sci. (India)*, **35**, 254 (1966).
- (6) K. Ganapathy and B. Vijayan, *J. Indian Chem. Soc.*, **55**, 957 (1978).
- (7) J. R. Jones and W. A. Waters, *J. Chem. Soc.*, 2068 (1962).
- (8) M. Krumpolc and J. Rocek, *Inorg. Chem.*, **24**, 617 (1985).
- (9) R. K. Dwivedi, M. Verma, P. Kumar and K. Behari, *Tetrahedron*, **39**, 815 (1983).

(Received 20 February 1989)

TMC 2036