

## Oxidation of Nitrite Ion by Bis(2-ethyl-2-hydroxybutyrate)oxochromate(V)

A RAJAVELU & VANGALUR S SRINIVASAN\*

Department of Chemistry, Ramakrishna Mission  
Vivekananda College, Madras 600 004

Received 15 April 1985; revised and accepted 24 July 1985

Bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) oxidises  $\text{NO}_2^-$  to  $\text{NO}_3^-$  in acetic acid-acetate buffers (pH 3.7 to 4.6) with an oxygen atom transfer in the rate-determining step. The specific rate is unaffected by the addition of unbound carboxylato ligand, suggesting the attack by  $\text{NO}^+(\text{OAc})^-$  on the oxygen end of chromium(V) complex. These results are at variance with those of earlier works [*Inorg Chem*, **20** (1981) 3176 and *Inorg Chem*, **22** (1983) 971]. The initial product of the reaction has been identified as a chelated or non-chelated monocarboxylatochromium(III) compound.

Subsequent to the preparation of several water-soluble, air-stable derivative of chromium(V) by Krumpolc and Rocěk<sup>1</sup>, redox reactions of this oxidation state with hydrazine<sup>2</sup> and hydroxylamine<sup>3</sup> have been studied by Gould and coworkers. Though the earlier works point to reversible loss of the carboxylato ligand from the Cr(V) oxidant, which then undergoes a two-electron transfer reaction with  $\text{N}_2\text{H}_4$  (ref. 2) or a four-electron transfer reaction with  $\text{NH}_2\text{OH}$  (ref. 3), the kinetic results of the present work, dealing with the oxidation of nitrite ion, under nitrogen atmosphere by bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) [Cr(V)-HEBA], are at variance with those of the earlier works.

2-Ethyl-2-hydroxybutyric acid (Aldrich) and sodium nitrite, acetic acid and sodium acetate (all BDH) were used as such. Sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) was prepared following the procedure of Krumpolc and Rocěk<sup>1</sup>. Solutions of Cr(V)-HEBA, sodium acetate, acetic acid and sodium nitrite were prepared in deoxygenated water. The concentration of Cr(V) was estimated spectrophotometrically at 510 nm ( $\epsilon = 162$ )<sup>1</sup> and periodically the  $\text{NaNO}_2$  concentration was estimated permanganometrically<sup>4</sup>. During the reaction time the change in concentration of nitrite ion (blank) was less than 5%. The Cr(V)- $\text{NO}_2^-$  reaction was followed spectrophotometrically at 510 nm, using a Carl-Zeiss VSU2-P spectrophotometer in the pH range 3.7 to 4.6 (acetate-acetic acid buffers). The decomposition/disproportionation of Cr(V)-HEBA solutions was minimised (<5%) by the addition of the unbound ligand solution ( $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>). The reactions were carried out under pseudo-first order conditions

with  $\text{NaNO}_2$  in about 20-fold excess. The specific rates were an average of at least 2 runs and the temperature was kept at 30°C.

The stoichiometry of Cr(V)- $\text{NO}_2^-$  reaction was determined both permanganometrically and spectrophotometrically, employing excess of  $\text{NO}_2^-$  and Cr(V), respectively. After about 9 half-lives,  $\text{NO}_2^-$  was estimated using standard  $\text{KMnO}_4$  solution<sup>4</sup> and the amount of Cr(V) reacted was estimated (when taken in excess) from the decrease in absorbance at 510 nm ( $\epsilon = 162$ )<sup>1</sup>. The stoichiometric data reveal that for every mol of Cr(V), one mol of  $\text{NO}_2^-$  was consumed. When Cr(V) was in excess, the loss of  $\text{NO}_2^-$  due to aerial oxidation in about 18 hr was significant (about 20% of  $[\text{NO}_2^-]$  taken). Considering the consumption of  $\text{NO}_2^-$  by air as well as the decomposition of chromium(V) in acetic acid-acetate buffers one can account for the deviation in stoichiometry from 1:1 ratio.

Table I summarises the kinetic data for the nitrite ion oxidation by Cr(V)-HEBA. The reaction exhibits total second order kinetics—first order with respect to each reactant as indicated by the linear plot of  $\log k$  versus  $\log [\text{NO}_2^-]$  passing through the origin as well as by linear plot of  $\log [\text{Cr(V)}]$  versus time. It is curious to note that in contrast to the earlier observations<sup>2,3</sup>, the rate of the reaction is least affected by the change in concentration of unbound carboxylato ligand but the rate decreases with decrease in  $[\text{H}^+]$  in a narrow pH range of 3.7 to 4.6 (beyond this pH range, Cr(V) is less stable). Quantitative interpretation of acid dependency could not be attempted with this data, as Cr(V) was

Table I—Kinetic Data for Oxidation of  $\text{NO}_2^-$  Ion by Cr(V)-HEBA<sup>a</sup>

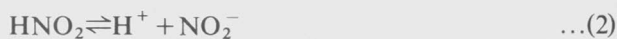
$[\text{NO}_2^-]$ mol dm <sup>-3</sup>	$10^3[\text{Cr(V)}]$ mol dm <sup>-3</sup>	$10^3[\text{lig}]$ mol dm <sup>-3</sup>	$10^3 k(\text{s}^{-1})^c$
0.080	2.0	1.0 <sup>b</sup>	2.4
0.16	2.0	1.0 <sup>b</sup>	4.7
0.24	2.0	1.0 <sup>b</sup>	6.9
0.32	2.0	1.0 <sup>b</sup>	9.0
0.48	2.0	1.0 <sup>b</sup>	13.6
0.16	1.0	1.0 <sup>b</sup>	4.6
0.16	3.0	1.0 <sup>b</sup>	4.7
0.16	2.0	1.0 <sup>c</sup>	2.4
0.16	2.0	1.0 <sup>d</sup>	1.1
0.16	2.0	0.50 <sup>b</sup>	4.1
0.16	2.0	2.0 <sup>b</sup>	4.5
0.16	2.0	4.0 <sup>b</sup>	4.5

(a) reactions were carried out in acetic acid-acetate buffers at constant ionic strength; (b) at pH = 3.7; (c) at pH = 4.4; (d) at pH = 4.6; and (e) pseudo-first order constant (in  $\text{s}^{-1}$ ) =  $-d \ln [\text{Cr(V)}]/dt$ .

unstable in other  $pH$  regions. Still the  $pH$  dependency possibly suggests the existence of an equilibrium of the type(1),



in the reaction medium, and also that the reactive species is  $(O)Cr^V(lig)_2 - (H_2O)$  which will be present in large amounts when  $[H^+]$  is more. Alternatively, as  $pK_a$  value for  $HNO_2$  is 3.37 which is close to the  $pH$  range used for this reaction, the equilibrium (2), probably with decreasing  $[H^+]$ ,



will be shifted in the forward direction thereby lowering  $[HNO_2]$ , which is probably the active species rather than  $NO_2^-$ . But there is no direct correlation between the specific rate and  $[HNO_2]$  as calculated from its  $pK_a$  at different  $pH$  values. The kinetics of  $Cr(V)$  oxidation of nitrite ion depends on  $[buffer]$  at  $pH$  3.7 (about 2-fold increase in rate for a four-fold increase in  $[buffer]$ ), indicating participation of  $OAc^-$  in the slow step of the reaction. This suggests that the reactive species may be nitrosyl acetate as nitrosation reactions are generally catalysed by  $OAc^-$ .

The addition of nitrite ion to  $Cr(V)$ -HEBA is accompanied by an initial increase in absorbance at 510 nm when the reactants are taken in equimolar concentrations (under this condition, the loss in  $[Cr(V)]$  due to the reaction with  $NO_2^-$  is less than 5%), implying the formation of a precursor complex,  $[O = N^+ : O = Cr(V)(lig)_2H_2O]$ , between  $NO^+$  ( $OAc^-$ ) and  $Cr(V)$ , probably through the oxygen end of  $(O)CrV(lig)_2H_2O$ , without the expulsion of the ligand in the slow step. Thus the mechanism of this reaction

involves nitrosation of the oxo group  $[ON^+ - : O = Cr^V]$  of  $Cr(V)$  complex, followed by an oxygen atom transfer in a slow step leading to the formation of  $NO_2^+$  and a  $Cr(III)$  species  $[(H_2O)Cr^{III}(lig)_2(H_2O)]$ . As chromium(III) is substitution-inert, the loss of the unbound ligand occurs in a fast step, probably, due to the labilising nature of  $NO_2^-$  ion<sup>5</sup> (present in excess), leading to chelated,  $[Cr^{III}(lig)]$ , or non-chelated ( $lig^-$ ) carboxylato product. This is in contrast to  $N_2H_4$  or  $NH_2OH$  reaction where the attack on chromium occurs via nitrogen end. This results in the labilisation of carboxylato ligand in the slow electron transfer step.

Under the same conditions,  $Cr(VI)$  oxidation of  $HNO_2$  occurs at a slower rate, ruling out  $Cr(VI)$  as an oxidant for  $HNO_2$  (the specific rate of  $Cr(VI)$  oxidation of  $HNO_2$  in acetic acid-acetate buffer at  $pH = 4.0$  at  $30^\circ C$  is  $2.0 \times 10^{-4} s^{-1}$  with  $[Cr(VI)] = 2.4 \times 10^{-4} mol dm^{-3}$  and  $[NO_2^-] = 0.16 mol dm^{-3}$ ).

The proposed mechanism is supported by the following experimental observation. After about 1 hr, the reaction product was chromatographed as described previously<sup>2,3</sup>. The product which eluted with  $0.20 mol dm^{-3} HClO_4$  exhibited maxima at 565 nm ( $\epsilon = 40$  approx.) and a broad band in the region 410 to 440 nm ( $\epsilon = 49$  approx.), pointing to a chelated or non-chelated monocarboxylatochromium(III) product.

## References

- 1 Krumpolc M & Rocěk J, *J Am chem Soc*, **101** (1979) 3206.
- 2 Srinivasan V S & Gould E S, *Inorg Chem*, **20** (1981) 3176.
- 3 Rajasekar N, Subramani R & Gould E S, *Inorg Chem*, **22** (1983) 971.
- 4 Vogel A I, *A text book of quantitative inorganic analysis*, (Longman, London), 1978.
- 5 Matts T C & Moore P, *J chem Soc*, (1971) 1632.