Oxygen Atom Transfer by an Oxochromate (V)

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The kinetics of reaction of sodium bis (2-ethyl-2-hydroxybutyrato) oxochromate (V) with triphenylphosphine (TPP) have been studied in 100% acetone. The reaction exhibits total second order kinetics, first order with respect to each reactant. To account for the quantitative yield of triphenylphosphine oxide as one of the products of this reaction, suitable mechanistic scheme, involving a precursor complex between oxochromate (V) and TPP, with a subsequent oxygen atom transfer to TPP, has been proposed. The presence of Cu(II) salts enhances the rate of oxygen atom transfer by oxochromate (V).

In the direct epoxidation of alkenes by chromyl complexes[1], the active species considered is oxochromate (V) formed *in situ* by the prior one-electron oxidation of solvent. This observation is in accord with efficient transfer of oxygen atom from macrocyclic oxochromium (V) reported by Groves and coworkers[2]. Metalloenzymes that catalyse the incorporation of oxygen atoms derived from dioxygen into organic substrates usually contain either iron or copper. However, recently similar reactivity has also been observed with manganese and chromium porphyrins[2-4].

To demonstrate the ease with which oxochromate (V) transfers oxygen atom, we have undertaken the reaction of triphenylphosphine (TPP) with sodium bis (2-ethyl-2-hydroxybutyrato) oxochromate (V). This is in continuation of our earlier work[5] on the oxidation of nitrite ion by the same oxochromate (V) which involves transfer of an oxygen atom to the reductant.

Materials and Methods

2-Ethyl-2-hydroxybutyric acid (HEBA) and triphenylphosphine (Aldrich Chemicals, USA) were used as such. Sodium bis (2-ethyl-2-hydroxybutyrato) oxochromate (V) was prepared following the procedure of Krumpolc[6]. Solutions of Cr(V) complex [Cr(V)-HEBA] and triphenylphosphine were prepared in purified anhydrous acetone. The concentration of Cr(V) was estimated spectrophotometrically at 510 nm ($\varepsilon = 162$)[6].

The Cr(V)-TPP reaction was followed at 510 nm, i.e. the maximum due to Cr(V)[6], using a Carl-Zeiss VSU 2-P spectrophotometer. The specific rates were an average of at least 2 runs and the temperature was kept constant at 30°C. The stoichiometry of Cr(V)-TPP reaction was determined spectrophotometrically with Cr(V) in excess. After 9 half-lives, the amount of Cr(V) reacted was estimated from the decrease in absorbance at 510 nm ($\varepsilon = 162$). From the reaction mixture,

chromium (III) product was separated by pouring into water, and the precipitate filtered off and dried. Chromium (III) product remained in solution.

Results and Discussion

The IR spectrum of the precipitate exhibited a band at 1190 cm^{-1} corresponding[7] to $\nu P = O$. The IR spectrum was superimposable over that of authentic triphenylphosphine oxide. Stoichiometric data on Cr(V)-TPP reaction (Table 1) shows that one mol of Cr(V) consumes nearly 1 mol of TPP to give triphenylphosphine oxide. Under the same conditions, in the absence of oxochromate (V), the amount of triphenylphosphine oxide formed from TPP was negligible.

The Cr(III) product which remained in solution after completion of the reaction exhibited maxima at 600 ($\varepsilon = 39$) and 425 nm (55) indicating that it may be a chelated carboxylatochromium (III) compound.

The pseudo-first order specific rate is given by Eq. (1)

$$k_1 = -\frac{d \ln [Cr(V)]}{dt} \qquad \ldots (1)$$

Table 2 summarises the kinetic data for chromium (V)

Table 1—Stoichiometry of Cr(V)-TPP Reaction[a]

[TPP]₀ (moldm^{-3})	[Cr(V)]₀ mol dm^{-3}	Δ[Cr(V)][b] mol dm^{-3}	Δ[Cr(V)] : [TPP]		Ph₃-P=O (%) formed (moldm^{-3})
0.0025	0.0050	0.0026	1.0	: 0.96	—
0.0020	0.0040	0.0021	1.0	: 0.95	—
0.020	0.040	—	—	—	0.018 (90)
0.030	0.080	—	—	—	0.024 (80)

(a) Reactions were carried out at 30° ± 0.2°C in 100% acetone.
(b) After applying due corrections for the decomposition/disproportionation of Cr(V) during the reaction time, from the decrease in absorbance at 510 nm, Δ[Cr(V)] was calculated.

Table 2—Kinetic Data on Chromium (V)-TPP Reaction[a]

10^2[TPP] (moldm^{-3})	10^3[Cr(V)] (moldm^{-3})	10^3[HEBA] (moldm^{-3})	$10^3 k_1$ (s^{-1})
0.75	1.50	—	1.20
1.00	2.0	—	1.60
1.50	2.0	—	2.3
1.75	2.0	—	2.6
2.0	2.0	—	3.0
1.50	1.50	—	2.2
1.50	1.00	—	2.3
1.50	2.0	1.00	2.3
1.50	2.0	2.0	2.3
1.50	2.0	4.0	2.3

(a) Reactions were carried out at $30° \pm 0.2°$C in 100% acetone.

SCHEME 1

reaction with triphenylphosphine (TPP) in 100% acetone at $30° \pm 0.2°$C.

The reaction exhibits total second order kinetics, first order with respect to each reactant. The rate of this reaction is unaffected by the addition of unbound carboxylato ligand, HEBA, a behaviour similar to the one observed in the chromium (V) oxidation of nitrite ion[5] but contrary to the one observed in the Cr^V-$N_2^+ H_5$ (ref. 8) or Cr^V-$\overset{+}{N}H_3OH$ (ref. 9) reactions at pH 4.0, suggesting that there is loss of bound ligand in the rate-determining step. As the products of the reaction are triphenylphosphine oxide and chelated carboxylato-chromium (III), the precursor complex (P) for this reaction may involve binding between phosphorus of TPP and oxygen end of oxochromate (V) (see Scheme 1). As Cr^V-TPP reaction is very fast, no spectroscopic evidence for such precursor complex formation could be obtained. But the precursor complex of Cr^V-$N_2H_5^+$ or Cr^V-$\overset{+}{N}H_3OH$ reaction is assumed to involve a direct binding between nitrogen and chromium which results in the labilisation of carboxylato bound ligand in the slow electron transfer step of the reaction. As the chromium center is not involved in direct bond formation with phosphorus of TPP, such labilisation of bound ligand seems to be absent in the present case. Based on these observations, a mechanism shown in Scheme 1 may be proposed for the Cr(V) reaction with TPP. According to Scheme 1 the electron transfer to chromium (V) and oxygen atom transfer to phosphorus occur in a near concerted manner. Under the present reaction conditions, Cr(VI) oxidation of TPP occurs at a slower rate, ruling out Cr(VI) as an oxidant for TPP (The specific rate of Cr(VI) oxidation of TPP at $30° \pm 0.2°$C is $4.0 \times 10^{-5} s^{-1}$ with [Cr(VI)] $= 2 \times 10^{-4}$ moldm^{-3} and [TPP] $= 1.5 \times 10^{-3}$ moldm^{-3}).
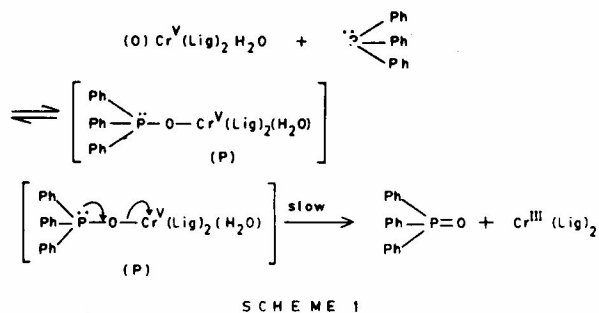
As cupric ions mediate epoxidation of olefins by dioxygen, superoxide, hydrogen peroxide and iodosylbenzene[10] in organic solvents, the influence of cupric nitrate on TPP reaction with oxochromate (V) has been attempted as this reaction seems to involve an oxygen atom transfer. The addition of cupric ion (4.0×10^{-4} moldm^{-3}) to oxochromate (V) (2.0×10^{-3} moldm^{-3}) increases the absorbance considerably with a shift in λ_{max} to 540 nm (λ_{max} for oxochromate (V) occurs at 510 nm). Probably a complex is formed between oxochromate (V) and Cu(II) which effects the facile oxygen atom transfer to TPP. Also the presence of Cu(II) along with Cr(V) and TPP increases the rate by nearly two-fold but the rate remains the same at all copper(II) concentrations (from 1.27×10^{-4} to 6.5×10^{-4} moldm^{-3}) suggesting that copper (II) does influence the oxygen atom transfer from oxochromate (V) to TPP marginally.

Further work on the epoxidation of olefins by oxochromate (V) in the presence and absence of copper (II) is in progress.

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