SHORT PAPER

J. Chem. Research (S),
2000, 114–115

Kinetic evidence of a common mechanism in the oxidation by chromium(vi) complexes: oxidation of benzyl alcohol[†]

Chockalingam Karunakaran* and Sadasivam Suresh

Department of Chemistry, Annamalai University, Annamalainagar 608 002, India

The oxidation of benzyl alcohol by dichromate and seven chromium(VI) complexes in aqueous acetic acid in the presence of perchloric acid is first order each in the oxidants, the alcohol and the mineral acid. The oxidation conforms to the isokinetic and Exner relationships and follows a common mechanism.

Introduction

Numerous reports are available on the kinetics of oxidation of a variety of organic compounds by many chromium(VI) complexes.[1,2] So are studies which deal with the influence of substituents on the rates of oxidation by chromium(VI) complexes. However, investigations on the comparison of the rates and mechanism of oxidation of one substrate by a series of chromium(VI) complexes are rare. This communication reports that the oxidation of benzyl alcohol by dichromate and chromium(VI) complexes exhibits identical kinetic orders; the oxidation conforms to the isokinetic and Exner relationships, indicating the operation of a common mechanism.

Results and discussion

The oxidation of benzyl alcohol by potassium dichromate (dichromate), pyridinium dichromate (PDC), quinolinium dichromate (QDC), imidazolium dichromate (IDC), pyridinium fluorochromate (PFC), quinolinium fluorochromate (QFC), pyridinium chlorochromate (PCC) and quinolinium chlorochromate (QCC) in aqueous acetic acid in the presence of perchloric acid, studied under the condition: $[\mathrm{Cr(VI)}] << [\mathrm{PhCH_2OH}]$, is first order with respect to the oxidants; plots of log (absorbance) *versus* time are linear. The pseudo-first order rate constant (k') remains almost constant in the dichromate oxidation but decreases marginally with increasing $[\mathrm{Cr(VI)}]_o$ in the case of chromium(VI) complexes; for a 5-fold increase in $[\mathrm{Cr(VI)}]_o$ the decrease in k' is *ca* 12% in PDC, IDC and PCC whereas it is *ca* 40% in QCC and QFC. The oxidation is first order with respect to the substrate. Plots of k' *versus* $[\mathrm{PhCH_2OH}]$ are linear passing through the origin with correlation coefficient (r) of at least 0.99 and standard error of estimate (SD) less than 5×10^{-4}. Representative rate data are given in Table 1. The oxidation is catalysed by mineral acid and is first order with respect to $\mathrm{H^+}$. Plots of k' *versus* $[\mathrm{HClO_4}]$ yield straight lines passing through the origin ($r > 0.98$, SD < 0.7×10^{-3}). The oxidation does not occur in the absence of mineral acid. Added manganese(II) ion inhibits the oxidation. The rate measurements at 20–50°C yield the energy of activation, frequency factor, enthalpy of activation and entropy of activation. The activation energy varies linearly with the logarithm of frequency factor ($r = 0.99$, SD = 0.37) and the plot of enthalpy of activation against entropy of activation is a straight line ($r = 0.99$, SD = 0.37) indicating the existence of isokinetic relationship.[3] The linear variation of log $k'_{50°\mathrm{C}}$ with log $k'_{20°\mathrm{C}}$ (the Exner plot, $r = 0.98$, SD = 0.03) confirms the isokinetic relationship revealing the operation of a common mechanism in the oxidation by chromium(VI) complexes.[3] The isokinetic temperature is 218K.

Speciation of chromium(VI): In aqueous and partly aqueous media dichromate anion undergoes hydrolysis and in acidic solution the species of chromium(VI) present are $\mathrm{Cr_2O_7^{2-}}$, $\mathrm{HCr_2O_7^-}$, $\mathrm{H_2Cr_2O_7}$, $\mathrm{CrO_4^{2-}}$, $\mathrm{HCrO_4^-}$ and $\mathrm{H_2CrO_4}$.[4,5] Calculation of the concentration of undissociated dichromate anion reveals that *ca* 89 – 97% of the dimer is hydrolysed in the concentration range 1.0×10^{-3}–2.0×10^{-4} mol dm^{-3}. This is further confirmed by the UV–visible spectra of the oxidants. Also, the relative concentration of acid dichromate to dichromate anion ($[\mathrm{HCr_2O_7^-}] / [\mathrm{Cr_2O_7^{2-}}]$), calculated using the dissociation constant of acid dichromate, is also negligible (0.06–0.35) in the acidity range 0.05–0.30 mol dm^{-3}. $\mathrm{H_2Cr_2O_7}$ is a strong acid, dissociates to near completion making $[\mathrm{H_2Cr_2O_7}]$ in the reaction solution negligible. Calculation of the relative concentration of chromate anion to acid chromate ($[\mathrm{CrO_4^{2-}}] / [\mathrm{HCrO_4^-}] = 1.0 \times 10^{-6} - 6.0 \times 10^{-6}$) shows that chromate anion is a non-existent in the experimental acidity. The relative concentration of chromic acid ($[\mathrm{H_2CrO_4}] / [\mathrm{HCrO_4^-}]$), calculated using the reported dissociation constant, shows that it increases from 0.04 to 0.25 when the acidity is increased from 0.05 to 0.30 mol dm^{-3}; in the absence of perchloric acid the value is very low (1.5×10^{-2}). The above calculations reveal that the most abundant chromium(VI) species in the reaction solution is acid chromate. Solvents of high dielectric constant favour dissociation of ionic complexes and similar speciation is likely in PDC, QDC and IDC; the dielectric constant of the reaction medium (calculated) is 57. The UV-visible spectra of the oxidants in the presence of perchloric acid supports the same. Fluorochromate and chlorochromate anions are the probable predominant species in the case of monomers.

Mechanism: The oxidation is first order each in the oxidants, substrate and $\mathrm{H^+}$. Acid catalysis of the oxidation points out chromic acid ($\mathrm{H_2CrO_4}$) as the oxidizing species; in the case of monomers it is likely to be $\mathrm{HCrO_3X}$ where X = F or Cl. UV–visible spectral study of (1) the oxidants, (2) the oxidants with mineral acid and (3) the reaction solutions shows absence of complex formation between the substrate and chromium(VI) species. Hence the possible reaction mechanism is the rate-determining oxidation of benzyl alcohol by chromic acid or $\mathrm{HCrO_3X}$. In the rate-limiting step chromium(IV) is formed.[4,5] This is supported by the fact that manganese(II) suppresses the oxidation. Manganese(II) ion reduces chromium(IV) formed to chromium(III) and gets oxidized to manganese(IV) ($\mathrm{MnO_2}$).[4] In the absence of manganese(II) ion chromium(IV) formed reduces chromium(VI) to chromium(V); the oxidation of alcohol by chromium(V) is fast.[4,5] Although the standard reduction potentials of chromium(VI) ($\mathrm{Cr_2O_7^{2-}} / \mathrm{Cr^{3+}}$) and manganese(IV) ($\mathrm{MnO_2} / \mathrm{Mn^{2+}}$) in acidic solution are 1.33V and 1.23V separate experiment shows that reduction of chromium(VI) by manganese(II) under the experimental conditions is kinetically inert.

---

* To receive any correspondence.

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

Table 1 Oxidation of benzyl alcohol by chromium(VI) complexes 30% (v/v) aq. HOAc, 35°C

10^3 $[Cr(VI)]_o$ (g atom dm^{-3})	10 $[PhCH_2OH]_o$ (mol dm^{-3})	10 $[HClO_4]$ (mol dm^{-3})	10^3 k' (s^{-1})							
			Dichromate	PDC	QDC	IDC	PFC	QFC	PCC	QCC
0.4	1.0	3.0	9.2	7.6	5.6	7.0	6.9	4.8	7.1	5.6
0.8	1.0	3.0	8.8	7.2	5.4	6.7	6.7	4.7	6.7	5.2
1.4	1.0	3.0	9.0	6.9	4.6	6.2	5.9	3.9	6.4	4.3
2.0	1.0	3.0	9.3	6.7	4.5	6.0	5.3	3.0	6.2	3.2
2.0	0.2	3.0	1.4	1.10	0.62	1.01	0.98	0.53	0.99	0.58
2.0	0.5	3.0	3.8	3.2	2.3	3.1	2.8	1.7	2.8	1.6
2.0	1.5	3.0	12.8	10.5	6.6	9.6	8.4	4.2	8.8	5.2
2.0	1.8	3.0	14.2	12.5	6.7	11.7	10.7	4.8	9.7	5.9
2.0	1.0	0.5	1.05	0.94	0.53	0.84	0.77	0.56	0.87	0.56
2.0	1.0	1.0	2.2	1.9	1.07	1.6	1.6	1.2	1.6	0.94
2.0	1.0	1.5	3.2	2.7	1.6	2.6	2.4	1.7	2.6	1.4
2.0	1.0	2.0	4.6	3.8	2.4	3.5	3.2	2.4	3.5	2.1
2.0	1.0	2.5	6.1	5.1	3.4	4.7	4.3	2.8	4.5	2.6
2.0[a]	1.0	3.0	0.90	0.89	0.54	0.94	1.00	0.47	0.91	0.61

[a] $[Mn^{2+}] = 2.0 \times 10^{-2}$ mol dm^{-3}

Table 2 Activation and kinetic parameters

	Dichromate	PDC	QDC	IDC	PFC	QFC	PCC	QCC
E_a (kJ mol^{-1})	28.9	25.6	20.6	27.5	26.2	24.5	26.0	24.1
ln A	5.55	4.16	1.65	4.88	4.29	3.16	4.31	3.04
$\Delta H^{\neq}$ (kJ mol^{-1})	26.4	23.0	18.1	24.9	23.6	22.0	23.5	21.6
$-\Delta S^{\neq}$ (J K^{-1} mol^{-1})	207	219	240	213	218	228	218	228
$K_1 k_2$[a] (dm^6 mol^{-2} s^{-1})	0.15	0.12	0.072	0.11	0.095	0.048	0.099	0.055

[a] 35°C.

$HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4$ K_1

$H_2CrO_4 + PhCH_2OH \rightarrow PhCHO + H_2CrO_3 + H_2O$ k_2

$Cr(IV) + Cr(VI) \rightarrow 2Cr(V)$ fast[4,5]

$Cr(V) + PhCH_2OH \rightarrow PhCHO + Cr(III) + 2H^+$ fast[4,5]

Scheme 1

The rate law for the suggested mechanism is

$-d\,[Cr(VI)] / dt = 2\,K_1\,k_2\,[alcohol]\,[H^+]\,[Cr(VI)]$

with a pseudo-first order rate constant of

$k' = 2K_1\,k_2\,[alcohol]\,[H^+]$

The kinetic constants (K_1k_2) calculated are listed in Table 2. The order of reactivity is as follows: dichromate > PDC > IDC > PCC > PFC > QDC > QCC > QFC. Examination of the kinetic constants reveals that potassium dichromate is the most powerful reagent among the oxidants studied. Complexing of chromium(VI) with heterocyclic bases moderates the reactivity of chromium(VI). Among the chromium(VI) complexes, quinolinium complexes are less reactive than pyridinium complexes. The variation of oxidation rate is likely due to the degree of association of the heterocyclic bases with chromium(VI) species. This proposition also accounts for the decrease of specific rate (k') with increasing $[Cr(VI)\ complexes]_o$.

Experimental

Pyridinium dichromate (PDC),[6] quinolinium dichromate (QDC),[7] imidazolium dichromate (IDC),[8] pyridinium fluorochromate (PFC),[9] quinolinium fluorochromate (QFC),[10] pyridinium chlorochromate (PCC),[11] and quinolinium chlorochromate (QCC),[12] were prepared as reported. Benzyl alcohol was distilled before use. All chemicals used were of analytical grade. Acetic acid AR was refluxed for 6 h over chromium(VI) oxide and distilled through a column.

Rate studies at constant temperature were performed under pseudo-first order conditions with a large excess of alcohol in 30% (v/v) aqueous acetic acid. Solutions of chromium(VI) reagents were prepared and standardized iodometrically. Required volumes of the reagents of desired concentrations were mixed, and the progress of the oxidation was followed spectrophotometrically (UVIDEC-340, Jasco) at 345 nm. In kinetic runs which involve high [Cr(VI)] the absorbance measurements were restricted to the Beer–Lambert law limit. The pseudo-first order rate constants were computed from the least squares slopes of the linear plots of log (absorbance) *versus* time. Arrhenius and Eyring plots afford activation parameters.

The stoichiometry of the oxidation was determined under the condition [Cr(VI)] >> [alcohol] in 30% (v/v) aqueous acetic acid in presence of 0.30 mol dm^{-3} perchloric acid at 35°C. Iodometric estimation of chromium(VI) after 6 h as well as 24 h reveals that dichromate reacts with benzyl alcohol in the molar ratio of 1:3.

Benzaldehyde, by its 2,4-dinitrophenylhydrazone, and hexaaquachromium(III) ion, by the UV–visible spectrum of the reaction solution after completion of the reaction (578 and 397 nm), were identified as the reaction products of chromium(VI) – benzyl alcohol reaction. Hence the reaction has to be written as

$$Cr_2O_7^{2-} + 8H^+ + 3PhCH_2OH \rightarrow 3\,PhCHO + 2Cr^{3+} + 7H_2O$$

This was further confirmed by kinetic study; kinetic investigation under identical conditions with benzaldehyde as substrate reveals that chromium(VI) oxidation of benzaldehyde does not occur under the experimental conditions.

Received 17 November 1999; accepted 17 February 2000
Paper 99/70

References

1 I. Nongkynrih and M.K. Mahanti, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1403.
2 I. Nongkynrih and M.K. Mahanti, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 3325.
3 G.W. Klumpp, *Reactivity in Organic Chemistry*, Wiley, New York, 1982.
4 K.B. Wiberg. *Oxidation in Organic Chemistry*, Part A, ed. K.B. Wiberg, Academic, New York, 1965.
5 G. Cainelli, G. Cardillo: *Chromium Oxidation in Organic Chemistry*, Springer, Berlin, 1984.
6 E.J. Corey and G. Schmidt, *Tetrahedron Lett.*, 399, 1979.
7 R. Balasubramanian and V. Prathiba, *Ind. J. Chem.*, **25B**, 326, 1986.
8 S. Kim and D.C. Lhim, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3297.
9 M.N. Bhattacharjee, M.K. Chaudhuri, H.S. Dasgupta, N. Roy, and D.T. Khathing, *Synthesis*, 588, 1982.
10 V. Murugesan, A. Pandurangan: *Ind. J. Chem.*, **31B**, 377, 1992.
11 E.J. Corey and J.W. Suggs, *Tetrahedron Lett.*, 2647, 1975.
12 J. Singh, P.S., Kalsi, G.S. Jawanda and B.R. Chhabra, *Chem. Ind. (London)*, 751, 1986.