Do chromium(VI) complexes oxidize via a common mechanism?

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Received 20 March 2001; accepted (revised) 27 November 2001

Oxidation of 2-propanol by twelve chromium(VI) reagents exhibits identical kinetic behaviour: first order in chromium(VI) and alcohol, second order in H⁺ and inhibited by Mn(II). The activation free energies do not differ significantly. Also, the energy of activation correlates with the logarithm of frequency factor and so is the enthalpy of activation with the entropy of activation.

Kinetic studies on oxidation by chromium(VI) complexes are numerous and so are reports on the effect of substituents on the rates of oxidation of aliphatic and aromatic substrates by chromium(VI) complexes. However, literature lacks comparative reports on oxidation by chromium(VI) complexes and hence this study. Chromium(VI) oxidation of alcohols is a well studied one and 2-propanol is the model substrate for the present study.

Results

The oxidation of 2-propanol by potassium dichromate (dichromate, DC), pyridinium dichromate (PDC), quinolinium dichromate (QDC), imidazolium dichromate (IDC), nicotininium dichromate (NDC), isonicotininium dichromate (INDC), pyridinium fluorochromate (PFC), quinolinium fluorochromate (QFC), imidazolium fluorochromate (IFC), pyridinium chlorochromate (PCC), quinolinium chlorochromate (QCC) and pyridinium bromochromate (PBC) in aqueous acetic acid and in the presence of perchloric acid, studied under pseudo-first order conditions of [HClO₄] and [alcohol] >> [Cr(VI)], is first order with respect to the chromium(VI) complexes. Plots of log (absorbance) vs reaction time are straight lines, the least squares slopes yield the pseudo-first order rate constant (k’); the oxidation was followed at least up to 85% completion. The pseudo-first order rate constants decrease with increasing [Cr(VI)]°, the decrease in k’ with increasing [Cr(VI)]° is not unknown. The oxidation is first order with respect to the alcohol. Plots of k’ vs [alcohol] are linear passing through the origin. Representative rate data are given in Table 1. The reaction is strongly acid catalyzed and is second order with respect to H⁺. The variation of the oxidation rates with the concentration of the mineral acid is not linear but plots of k’ vs [HClO₄] vary yield straight lines passing through the origin. It is pertinent to note that in 10% aqueous acetic acid log [HClO₄] varies linearly with the Hammett acidity function (H₂); hence direct k’-HClO₄ correlation is more appropriate than log k’-H₂O. The oxidation is sluggish in the absence of mineral acid (pH 2.60). Added manganese(II) ion inhibits oxidation.

<table>
<thead>
<tr>
<th>[Cr(VI)]° (g atom dm⁻³)</th>
<th>[Me₂CHOH] (mol dm⁻³)</th>
<th>[HClO₄] (mol dm⁻³)</th>
<th>10⁻¹³k’ (s⁻¹)</th>
<th>10⁻¹³k’ (s⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>DC</td>
<td>PDC</td>
<td>QDC</td>
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<td></td>
</tr>
<tr>
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<td>1.0</td>
<td>0.50</td>
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<td>6.4</td>
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<td>0.50</td>
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<td>5.4</td>
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<td>0.50</td>
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<td>3.6</td>
</tr>
<tr>
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<td>0.50</td>
<td>6.7</td>
<td>6.5</td>
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<td>0.50</td>
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<td>12.1</td>
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<td>0.10</td>
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<td>0.10</td>
<td>0.70</td>
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<td>13.0</td>
</tr>
<tr>
<td>2.0</td>
<td>0.10</td>
<td>0.90</td>
<td>20.6</td>
<td>19.0</td>
</tr>
<tr>
<td>2.0</td>
<td>0.10</td>
<td>0.50</td>
<td>2.1</td>
<td>2.2</td>
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</table>

* [Mn²⁺] = 0.020 g atom dm⁻³

Note

Table 1 — Pseudo-first order rate constants for oxidation of 2-propanol by chromium(VI) complexes in 10% (v/v) aqueous acetic acid at 30°C
the oxidation. The reaction rates at 20-45°C yield the energy of activation, frequency factor, enthalpy of activation, entropy of activation and free energy of activation (Table II).

**Discussion**

In aqueous and partly aqueous media dichromate is hydrolyzed and in acidic solution the speciation of chromium(VI) are: \( Cr_2O_7^{2-} \), \( HCr_2O_7 \), \( Cr_2O_6^{2-} \), \( HCrO_4^{-} \) and \( H_2CrO_4 \). Calculation of the concentration of dichromate anion reveals that 95 to 99% of the dimer is hydrolyzed in the concentration range \( 4.0 \times 10^{-4} - 5.0 \times 10^{-3} \text{ mol dm}^{-3} \). The UV-visible spectra of the chromium(VI) reagents in the reaction medium but in the absence of 2-propanol confirm the same; the absorbance at 440-450 nm is insignificant. \( H_2CrO_4 \) is a strong acid and dissociates to near completion, making \( H_2CrO_4 \) in the reaction medium non-existent. Also, the relative concentration of acid dichromate to dichromate anion \( ([HCr_2O_7]/[Cr_2O_7^{2-}] = 0.12 - 1.1 \) in the acidity range \( 10^{-0} - 9.0 \text{ mol dm}^{-3} \), calculated using the dissociation constant of acid dichromate, reveals the concentration of acid dichromate also negligible. Calculation of the relative concentration of chromium to acid chromate \( ([CrO_4^{3-}]/[HCrO_4^{-}] = 3.0 \times 10^{-6} - 3.3 \times 10^{-7}) \) shows that chromate anion is a non-existent in the experimental acidity. The relative concentration of chromic acid to acid chromate \( ([H_2CrO_4]/[HCrO_4^{-}]) \), calculated using the reported dissociation constant, shows that it increases from 0.08 to 0.74 when the acidity is increased from \( 10^{-0} \) to \( 9.0 \text{ mol dm}^{-3} \); in the absence of perchloric acid the value is very low (2.1 \times 10^{-3}). The above calculations reveal that the most abundant chromium (VI) species in the reaction medium is acid chromate. However, at high acidity chromic acid is also present at comparable concentration. Solvents of high dielectric constant favour dissociation of ionic complexes and similar speciation is likely in PDC, QDC, IDC, NDC and IND; the dielectric constant of the reaction medium (calculated) is 71.3. Fluorochromate, chlorochromate and bromochromate anions \( (XCrO_4^{2-}; X= F, Cl, Br) \) are the probable predominant species in the case of monomers.

The oxidation is first order in the chromium(VI) reagents and alcohol, and second order in the mineral acid. In strongly acidic solution chromic acid is protonated and the second order dependence of the reaction rate on the concentration of the mineral acid indicates protonated chromic acid \( (H_2CrO_4^+) \) as the oxidizing species; in the case of monomers it is likely to be protonated halochromic acid \( (H_2CrO_4X^+ \text{ where } X=F \text{ or } Cl \text{ or } Br) \). The UV-visible spectra of the chromium(VI) reagents, the chromium(VI) reagents with mineral acid and the reaction solutions show absence of complex formation between the alcohol and chromium(VI) species. Hence, the possible mechanism is the rate-limiting oxidation of the alcohol by \( H_2CrO_4X^+ (X = OH, F, Cl, Br) \). In the rate-determining step chromium(VI) is formed and gets oxidized to manganese(III). In the absence of manganese(II) chromium(VI) formed reduces chromium(IV) to chromium(V) and manganese(II) chromium(IV) formed reduces chromium(VI) to chromium(V); the oxidation of alcohol by chromium(V) is fast. Although the reduction potentials of chromium(VI) \( (Cr_2O_7^{2-}/Cr_3^{+}) \) and manganese(IV) \( (MnO_2/Mn^{2+}) \) in acidic solution are 1.33V and 1.23V respectively, separate experiment shows that the reduction of chromium(VI) by manganese(II) under the experimental conditions is kinetically inert. The chromic acid oxidation of alcohols at high acidity exhibits similar kinetic results and hence the mechanism. The mechanism involving chromium(V) and chromium(IV) as the only intermediates has been preferred in the past but in recent years mechanism which involves chromium(II) also as an intermediate has been widely accepted as the correct mechanism for the chromium(VI) oxidation of many organic compounds. According to the accepted current mechanism chromium(IV) formed oxidizes the or-

<table>
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<th>Table II — Activation parameters</th>
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<tr>
<td><strong>E_a (kJ mol⁻¹)</strong></td>
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<tr>
<td>---------------------</td>
</tr>
<tr>
<td>log A</td>
</tr>
<tr>
<td>ΔH°(kJ mol⁻¹)</td>
</tr>
<tr>
<td>ΔS° (J K⁻¹ mol⁻¹)</td>
</tr>
<tr>
<td>ΔG°* (kJ mol⁻¹)</td>
</tr>
</tbody>
</table>

* 30°C
Cr(III) reduces chromium(VI) yielding chromium(II) and chromium(V) (Scheme I).

The rate law for the suggested mechanism is

$$-d[Cr(VI)]/dt = 2K_1K_2k_3 [\text{alcohol}] [H^+]^2 [Cr(VI)]$$

with the pseudo-first order rate constant of

$$k_3 = 2K_1K_2k_3 [\text{alcohol}] [H^+]^2.$$

The facts that all the chromium(VI) reagents studied exhibit identical kinetic behaviour, the free energies of activation do not differ significantly and the activation energy correlates with the logarithm of frequency factor (Figure 1) and so the enthalpy of activation with the entropy of activation (Figure 2) suggest operation of a common mechanism in the oxidation by chromium(VI) complexes. The operation of the isokinetic relationship could not be further confirmed with a linear Exner plot of $\log k'_{as0}$ vs $\log k'_{as0}$ as the reactivities of the chromium(VI) reagents do not differ significantly; the variation in $k'$ with chromium(VI) reagent is not more than 30% and the error in $k'$, as in other kinetic studies, is ±4%. The observed small variation of the oxidation rate with the chromium(VI) reagent is likely due to the degree of association of the heterocyclic bases with chromium(VI) species. Although some heterocyclic bases are reported to catalyze or mediate chromium(VI) oxidation it is ruled out in the present study; the oxidation rates of chromium(VI) complexes are not significantly larger than that of potassium dichromate.
Conclusion
In aqueous acidic solution chromium(VI) complexes dissociate, the dimers undergo hydrolysis yielding chromic acid or halochromic acids thereby turning the oxidation as a chromic acid oxidation; this results in almost identical kinetic parameters.

Materials
Pyridinium dichromate (PDC)\(^{14}\), quinolinium dichromate (QDC)\(^{15}\), imidazolium dichromate (IDC)\(^{16}\), nicotinum dichromate (NDC)\(^{17}\), isonicotinum dichromate (INDC)\(^{17}\), pyridinium fluorochromate (PFC)\(^{18}\), quinolinium fluorochromate (QFC)\(^{18}\), imidazolium fluorochromate (IFC)\(^{19}\), pyridinium chlorochromate (PCC)\(^{20}\), quinolinium chlorochromate (QCC)\(^{21}\) and pyridinium bromochromate (PBC)\(^{22}\) were prepared as reported. 2-Propanol was distilled before use. All chemicals used were of analytical grade. Acetic acid, AR was refluxed for 6 hr over chromium(VI) oxide and distilled through a column.

Kinetic measurements
Kinetic studies at constant temperature were made under pseudo-first order conditions with large excess of alcohol and perchloric acid in 10% (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 (UV-Vis-DEC-340, Jasco) at 350 nm, the wavelength at which all the chromium(VI) complexes studied show maximum absorbance; the concentrations of the chromium(VI) reagents 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) vs time. Arrhenius and Eyring plots yield the activation parameters.

Stoichiometry and product analysis
The stoichiometry of the oxidation was determined under the condition: \([\text{Cr(VI)}] >> [\text{alcohol}]\) in 10% (v/v) aqueous acetic acid in the presence of perchloric acid (0.90 mol dm\(^{-3}\)) at 30°C. Iodometric estimation of chromium(VI) after 6 hr as well as 24 hr reveals that chromium(VI) reacts with 2-propanol in the ratio of 2:5. Acetone, by its bisulphite compound, and hexaaquochromium(III) ion, by the UV-visible spectrum of the reaction solution after the completion of the reaction (576 and 408 nm), were identified as the reaction products of chromium(VI) – 2-propanol reaction. Hence the reaction is represented as:

\[
2\text{Cr(VI)} + 3\text{CH}_{3}\text{CHOHCH}_{3} \rightarrow 2\text{Cr(III)} + 3\text{CH}_{3}\text{COCH}_{3} + 6\text{H}^{+}
\]

This was further confirmed by kinetic and stoichiometric studies; kinetic and stoichiometric investigations under identical conditions but with acetone as substrate reveal that chromium(VI) oxidation of acetone does not occur under the experimental conditions.

References