Kinetics of Chromic Acid Oxidation of Aliphatic Acetals in Aqueous Acetic Acid Medium

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The oxidation of aliphatic acetals (prepared from aliphatic aldehydes, aliphatic alcohols, halogen substituted alcohols and aromatic alcohols) by chromic acid in aqueous acetic acid medium is first order each in [oxidant] and [acetal] and yields the corresponding ester as the main product. Substituent effect, activation parameters and salt effects suggest that the elimination of a proton from the complex species involving the acetal and chromium is the rate-determining step. The activation enthalpies and entropies of the reactions are linearly related.

In some earlier publications from our laboratory, we reported the rearrangement reactions of aromatic acetals. For instance it was reported that aromatic acetals when treated with boron trifluoride etherate give benzyl allyl ether, α, β-unsaturated aldehydes and benzaldehyde. A literature search revealed that though considerable attention has been focussed on the kinetics and mechanism of chromic acid oxidations of a variety of organic compounds similar work on chromic acid oxidation of aliphatic acetals has not been reported so far. To rectify this situation, the kinetics of oxidation of aliphatic acetals containing normal, halogen substituted and aromatic alcohols in the alcohol moiety have been studied in aqueous acetic acid medium with a view to probing the mechanism of oxidation.

Materials and Methods

All the chemicals were of AR (BDH) grade and were used either as such or purified by standard procedures. The substrates used were: acetaldehyde diethyl acetal (AEA), acetaldehyde di- n -butyl acetal (AnBA), acetaldehyde di-isobutyl acetal (AiBA), acetaldehyde di-t-butyl acetal (AtBA), acetaldehyde dibenzyl acetal (ABA), propionaldehyde diethyl acetal (PEA), propionaldehyde di-isobutyl acetal (PiBA) and propionaldehyde diethylene chlorohydrin acetal (PChA). These were prepared in the laboratory and their purities checked by the usual methods.

The reactions were studied under pseudo-first order conditions ([acetal] >> [Cr(VI)]) in acetic acid (65%, 75%, 80% and 90%, v/v) and followed iodometrically for over 60% of the reaction. The rate constants were computed from the linear \( r > 0.98 \) plots of log [oxidant] against time. The results were reproducible within ± 3%.

Chromium (VI) solution was added to solutions of the acetal in 90%, 80%, 75% and 65% (v/v) acetic acid and the reactions were allowed to proceed to completion. The solutions were diluted, excess chromic acid was neutralised with sodium bisulphite and extracted with ether. The ether extracts were dried over anhydrous sodium sulphate, solvent was removed under reduced pressure and the product mixture analysed by GLC (Toshniwal, India, 300°C, 3metre, column material SE 30). The products in each case were characterised by direct comparison with the authentic samples, as the corresponding esters (70-80% yield). Further it was found that 3 mol of chromic acid consumed 2 mol of acetal to give the product.

Results and Discussion

The kinetic results can be summarised as follows:

(i) The constancy of the first order rate coefficient at different initial \([Cr(VI)]\) and the linearity of the plots of log \( k_i \) versus log [acetal] and of \( 1/k_i \) versus 1/[acetal] with unit slopes indicate that the reaction is first order each in [oxidant] and [acetal].

(ii) At fixed ionic strength the rate decreases with increase in solvent polarity of the medium. For example under the conditions [acetal] = \( 2 \times 10^{-2}\) mol \( \text{dm}^{-3}, [Cr(VI)] = 2 \times 10^{-2}\) mol \( \text{dm}^{-3}, \) temp. = 308K and ionic strength = 0.2 mol \( \text{dm}^{-3}, 10^2 \) \( k_i \) increased from 0.5 to 11.56, 0.45 to 8.49 and 0.34 to 7.41 \( \text{dm}^{-3} \text{ mol}^{-1} \text{s}^{-1} \) for AEA, AnBA and AiBA respectively when % HOAc (v/v) was changed from 65 to 90.

(iii) The rate data have been collected in the temperature range 308K to 328K and the activation
Table I—Activation Parameters for Cr(VI) Oxidation of Aliphatic Acetals

<table>
<thead>
<tr>
<th>Acetal</th>
<th>$10^2 k_i$ (dm$^3$mol$^{-1}$s$^{-1}$)</th>
<th>$\Delta H_f$ (kJ mol$^{-1}$)</th>
<th>$-\Delta \delta f$ (JK$^{-1}$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AnBa</td>
<td>0.88</td>
<td>50.45</td>
<td>122.5</td>
</tr>
<tr>
<td>AiBA</td>
<td>0.81</td>
<td>51.30</td>
<td>120.5</td>
</tr>
<tr>
<td>AiBA</td>
<td>0.34</td>
<td>35.18</td>
<td>180.1</td>
</tr>
</tbody>
</table>

parameters calculated from the least-squares slopes of log $k_i$ versus $1/T$ (Table 1).

(iv) The rate of oxidation of AiBA with Cr(VI) does not induce polymerization of allyl acetate ruling out the possibility of a free radical mechanism.

(v) The rate of oxidation of AiBA with Cr(VI) decreases with increase in the concentration of sodium acetate. Added disodium salt of EDTA accelerates the rate of oxidation in a progressive manner. Added isobutyl acetate, an oxidation product of AiBA, in the kinetic runs with AiBA does not affect the rate.

(vi) Addition of sodium chloride retards the oxidation of AiBA by Cr(VI), The formation of less reactive chlorochromate (CrClO$_4^-$) anion in solution may possibly be inferred.

(vii) Oxidation of a mixture of AiBA and oxalic acid with Cr(VI) shows a neat first order dependence on Cr(VI) for over 50% reaction. Increase in [oxalic acid] increases the rate of oxidation in a progressive manner. For example under identical conditions as in (ii) in aqueous acetic acid (75%, v/v), $10^4 k_i$ values are found to be 1.535 s$^{-1}$ in the absence of oxalic acid and 13.71, 19.47, 33.91 and 38.70 s$^{-1}$ in the presence of 6, 9, 12 and $15\times10^{-3}$mol dm$^{-3}$ of added oxalic acid. The most likely explanation could be that the oxalic acid forms an ester by reacting with HCrO$_4^-$ and H$^+$ and this ester having a positively charged chromium can attack the acetel more easily to form the ternary complex which decomposes in a rate-determining step to give the products (Scheme 1). A similar mechanism has been proposed for the cooxidation of secondary alcohols and oxalic acid with Cr(VI).3,5

(viii) Increase in rates of AiBA and AEA oxidations by Cr(VI) is observed with increase in added [HClO$_4$] and [H$_2$SO$_4$]. The slopes of the plots of log $k_i$ versus log [H$^+$] show that the rate dependence on [H$^+$] is 0.785 in HClO$_4$ and 0.454 in H$_2$SO$_4$ for AiBA and 0.62 in HClO$_4$ and 0.30 in H$_2$SO$_4$ for AEA reactions.

For the acid catalysed oxidation, the rate law may be given as in Eq. (1).

$$-\frac{d[Cr(VI)]}{dt} = k\text{[acetal]}[Cr(VI)][H^+]$$ ...

The value of $x$ is found to be different for different mineral acids as well as for different acetals. It has been observed that concentrations being equal, increase in rate of greater in the case of HClO$_4$ than in H$_2$SO$_4$. This can be traced to the effect of the anion of these mineral acids on the chromate ion.

A plot of $1/k_i$ versus $1/[acetal]$ is linear without any intercept on the Y-axis. Therefore it can be justifiably assumed that the chromic acid oxidation of acetals proceeds through the formation of a transition state involving the acetal and HCrO$_4$ species.

It is proposed that the transition state is an entity in which the electron deficient chromium is coordinated to the oxygen atom of the alkoxy group of the acetal. In the rate-determining step such a species eliminates a protonated chromic acid through a cyclic five-centered intermediate. In the next fast step the alkyl cation is removed aided by the acetate ion to form the product ester.
Table 2—Effect of Substituents on Rate Constants

<table>
<thead>
<tr>
<th>Acetal</th>
<th>$10^2 k_2$ (dm$^3$ mol$^-1$ s$^-1$)</th>
<th>Acetal</th>
<th>$10^2 k_2$ (dm$^3$ mol$^-1$ s$^-1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEA</td>
<td>0.98</td>
<td>PiBA</td>
<td>1.08</td>
</tr>
<tr>
<td>AnBA</td>
<td>0.88</td>
<td>ABA</td>
<td>7.02</td>
</tr>
<tr>
<td>AiBA</td>
<td>0.81</td>
<td>PEA</td>
<td>1.12</td>
</tr>
<tr>
<td>ArBA</td>
<td>0.34</td>
<td>PChA</td>
<td>0.20</td>
</tr>
</tbody>
</table>

The rates of oxidation under similar experimental conditions for acetals of the same aldehyde with different alcohols are in the order ethyl > n-butyl > isobutyl > t-butyl (Table 2). This trend may be attributed to the steric hindrance offered by the alkyl groups by preventing the attainment of proper geometry for the formation of a cyclic five-centered intermediate.

The isokinetic temperature computed from the plot of $\Delta H^\ddagger$ versus $\Delta S^\ddagger$ for the oxidation of aliphatic acetals by Cr(VI) is 268K. The linear correlation between the activation enthalpies and entropies ($r = 0.9992$) shows that all the aliphatic acetals are oxidised by a similar mechanism and the changes in the rate of oxidation of aliphatic acetals by Cr(VI) are governed by changes in both enthalpy and entropy of activation.

The negative entropy of activation supports the above mechanism. Further it supports a reaction in which charge separation takes place in the transition state. The progressive lowering of the entropy of activation with increasing substitution indicates a crowded transition state in which freedom of motion of the substituent is hindered.

The effect of solvent mixtures of acetic acid and water shows that the increasing proportions of acetic acid increases the rate of oxidation. The plot of $\log k_2$ versus $1/D$ of the solvent for the oxidation of AiBA is linear with a positive slope indicating that one of the reacting species is a positive ion.

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References