Kinetics and mechanism of oxidation of aliphatic aldehydes by pyridinium bromochromate

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The oxidation of six aliphatic aldehydes by pyridinium bromochromate (PBC), to the corresponding carboxylic acids, is first order each in PBC and the aldehyde. The reaction is catalysed by $H^+$; the $H^+$ dependence has the form, $k_{\text{obs}} = a + b[H^+]$. Oxidation of deuterated acetaldehyde (MeCDO) showed the presence of a substantial kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 6.40$ at 288 K). Oxidation of acetaldehyde is studied in 19 organic solvents. The solvent effect has been analysed using Taft's and Swain's multiparametric equations. The rate constants correlate well with Taft's $\sigma^*$ constants; reactions being negative. A mechanism involving transfer of a hydride ion has been suggested.

Pyridinium bromochromate (PBC) is a mild and selective oxidizing agent used in synthetic organic chemistry. Only a few reports about the kinetics and mechanisms of oxidation by PBC are available in literature. In continuation of our earlier work, we report here the kinetics and mechanism of oxidation of six aliphatic aldehydes by PBC in dimethyl sulphoxide (DMSO) as solvent. Mechanistic aspects are discussed.

Materials and Methods

PBC was prepared by reported method, and its purity was checked by iodometric determinations. Solutions of formaldehyde were prepared by heating paraformaldehyde and passing the vapours in DMSO. The amount of HCHO in DMSO was determined by chromotropic acid method. The other aldehydes were commercial products and were used as such. $p$-Toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. The solvents were purified by the usual methods.

Product analysis

In a typical reaction, acetaldehyde (4.4 g, 0.1 mol) and PBC (2.6 g, 0.01 mol) were dissolved in DMSO (100 ml) and the reaction mixture was allowed to stand for ca. 24 h to ensure completion of the reaction. The amount of acetic acid formed was determined by the procedure described earlier. Several determinations indicated a 1:1 stoichiometry (Eq. 1).

$$\text{RCHO} + \text{CrO}_2\text{BrO}_{\text{py}} \rightarrow \text{RCOOH} + \text{CrOBrO}_{\text{py}} \quad \cdots (1)$$

Results

The reactions are of first order with respect to [PBC]. Further, the pseudo-first order rate constant, $k_{\text{obs}}$, does not depend on the initial concentration of PBC. The reaction is of first order with respect to aldehydes also (Table 1). The reaction is catalysed by $H^+$. The $H^+$ dependence takes the form $k_{\text{obs}} = a + b[H^+]$.

The rates of oxidation of the six aldehydes were determined at different temperatures and the activation parameters were calculated (Table 2).

To ascertain the importance of the cleavage of the aldehydic $C-H$ bond in the rate-determining step, the oxidation of deuteriated acetaldehyde (MeCDO) was studied. The oxidation of deuterated acetaldehyde exhibited a substantial primary kinetic isotope effect (Table 2).

The oxidation of aldehydes by PBC, under a nitrogen atmosphere, failed to induce the polymerisation of acrylonitrile. Further, the addition of a radical scavenger, acrylonitrile had no effect on...
the reaction rate (Table 1). Thus a one electron oxidation, giving rise to free radicals is unlikely.

The oxidation of acetaldehyde was studied in 19 different organic solvents. There was no reaction with the solvents chosen. The kinetics was similar in all the solvents. The values of \( k_2 \) at 298 K are recorded in Table 3.

**Discussion**

The entropy and enthalpy of activation of the oxidation of six aldehydes are linearly related \((r = 0.9991)\). The value of isokinetic temperature evaluated from Exner’s plot of \( \log k_2 \) at 288 K versus \( \log k_2 \) at 318 K \((r = 0.9999)\) is 1037 ± 17 K. The linear isokinetic correlation suggests that all the aldehydes are oxidized by the same mechanism.

The observed \( H^+ \) dependence suggests that the reaction follows two mechanistic pathways, one acid-independent and the other acid-dependent. The acid catalysis can be attributed to a protonation of PBC to give a stronger oxidant and electrophile \((2)\).

\[
\text{pyHOCr}_2\text{Br}^+ + \text{H}^+ \rightarrow \text{pyHOCr(OH)}\text{OBr} \quad \ldots \quad (2)
\]

The rate constants of oxidation, \( k_2 \), is eighteen solvents (CS \(_2\) was not considered as the complete range of solvent parameters are not available) were correlated in terms of linear solvation energy relationship (Eq. 3) of Kamlet et al.\(^{12}\).

\[
\log k_2 = A_0 + p \pi^* + b \beta + a \alpha \quad \ldots \quad (3)
\]

In the equation, \( \pi^* \) represents the solvent polarity, \( \beta \) the hydrogen bond acceptor basicities and \( \alpha \) is the hydrogen bond donor acidity. \( A_0 \) is calculated from Exner’s plot of \( \log k_2 \) at 288 K versus \( \log k_2 \) at 318 K \((r = 0.9999)\) is 1037 ± 17 K.

**Table 1—Rate constant for oxidation of acetaldehyde by PBC at 298 K**

<table>
<thead>
<tr>
<th>[PBC] (10^{-4}) (mol dm(^{-3}))</th>
<th>[MeCHO] (10^{-4}) (mol dm(^{-3}))</th>
<th>[TsOH] (10^{-4}) (mol dm(^{-3}))</th>
<th>(10^4 k_{2obs}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>0.0</td>
<td>7.12</td>
</tr>
<tr>
<td>1.0</td>
<td>0.20</td>
<td>0.0</td>
<td>14.3</td>
</tr>
<tr>
<td>1.0</td>
<td>0.40</td>
<td>0.0</td>
<td>29.0</td>
</tr>
<tr>
<td>1.0</td>
<td>0.60</td>
<td>0.0</td>
<td>42.8</td>
</tr>
<tr>
<td>1.0</td>
<td>0.80</td>
<td>0.0</td>
<td>57.1</td>
</tr>
<tr>
<td>1.0</td>
<td>1.00</td>
<td>0.0</td>
<td>71.0</td>
</tr>
<tr>
<td>2.0</td>
<td>0.40</td>
<td>0.0</td>
<td>28.3</td>
</tr>
<tr>
<td>4.0</td>
<td>0.40</td>
<td>0.0</td>
<td>29.0</td>
</tr>
<tr>
<td>8.0</td>
<td>0.40</td>
<td>0.0</td>
<td>29.8</td>
</tr>
<tr>
<td>1.0</td>
<td>0.40</td>
<td>0.0*</td>
<td>29.4</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>0.1</td>
<td>11.4</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>0.2</td>
<td>16.0</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>0.3</td>
<td>20.2</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>0.5</td>
<td>28.2</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>0.8</td>
<td>41.5</td>
</tr>
<tr>
<td>1.0</td>
<td>0.10</td>
<td>1.0</td>
<td>51.0</td>
</tr>
</tbody>
</table>

*contained 0.001 mol dm\(^{-3}\) acrylonitrile

**Table 2—Rate constants at different temperatures and the activation parameters of the oxidation of aldehydes by PBC**

<table>
<thead>
<tr>
<th>Subst.</th>
<th>(10^4 K) (10^{-4}) (mol dm(^{-3}) s(^{-1}))</th>
<th>(\Delta H^*) (kJ mol(^{-1}))</th>
<th>(\Delta S^*) (J mol(^{-1}) K(^{-1}))</th>
<th>(\Delta G^*) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>288 K</td>
<td>298 K</td>
<td>308 K</td>
<td>318 K</td>
</tr>
<tr>
<td>H</td>
<td>2.00</td>
<td>4.70</td>
<td>11.1</td>
<td>25.3</td>
</tr>
<tr>
<td>Me</td>
<td>34.6</td>
<td>71.3</td>
<td>149</td>
<td>305</td>
</tr>
<tr>
<td>Et</td>
<td>61.6</td>
<td>124</td>
<td>250</td>
<td>504</td>
</tr>
<tr>
<td>Pr</td>
<td>67.9</td>
<td>137</td>
<td>277</td>
<td>542</td>
</tr>
<tr>
<td>Pr(^1)</td>
<td>106</td>
<td>208</td>
<td>410</td>
<td>805</td>
</tr>
<tr>
<td>ClC(_2)</td>
<td>0.075</td>
<td>0.21</td>
<td>0.57</td>
<td>1.47</td>
</tr>
<tr>
<td>MeC(_2)O</td>
<td>5.41</td>
<td>12.5</td>
<td>27.2</td>
<td>57.8</td>
</tr>
<tr>
<td>(k_f/k_D)</td>
<td>6.40</td>
<td>5.70</td>
<td>5.48</td>
<td>5.28</td>
</tr>
</tbody>
</table>
Table 4—Temperature dependence of the reaction constant

<table>
<thead>
<tr>
<th>Temp./K</th>
<th>288</th>
<th>298</th>
<th>308</th>
<th>318</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho^*$</td>
<td>$-2.54 \pm 0.01$</td>
<td>$-2.41 \pm 0.02$</td>
<td>$-2.30 \pm 0.01$</td>
<td>$-2.21 \pm 0.01$</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.9999</td>
<td>0.9999</td>
<td>0.9999</td>
<td>0.9999</td>
</tr>
<tr>
<td>$sd$</td>
<td>0.01</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
</tr>
</tbody>
</table>

log $k_2 = -4.05 + 1.66(\pm 0.20)\pi^* + 0.20(\pm 0.16)\beta - 0.33(\pm 0.15)\alpha$ ... (4)

$R^2 = 0.8782; sd = 0.18; n = 18; \psi = 0.27$

log $k_2 = -4.13 + 1.78(\pm 0.21)\pi^* + 0.09(\pm 0.17)\beta$ ... (5)

$R^2 = 0.8398; sd = 0.20; n = 18; \psi = 0.31$

log $k_2 = -4.11 + 1.80(\pm 0.20)\pi^*$ ... (6)

$r^2 = 0.8368; sd = 0.20; n = 18; \psi = 0.30$

log $k_2 = -3.09 + 0.41(\pm 0.39)\beta$ ... (7)

$r^2 = 0.0639; sd = 0.47; n = 18; \psi = 0.89$

Here $n$ is the number of data points and $\psi$ is the Exner’s statistical parameter.13

Kamlet’s12 triparametric equation explain ca. 88% of the effect of solvent on the oxidation. However, by Exner’s criterion the correlation is poor (cf. Eq. 4). The major contribution is of solvent polarity. It is alone accounted for ca. 83% of the data. Both $\beta$ and $\alpha$ play relatively minor roles.

The data on the solvent effect were also analysed in terms of Swain’s equation14 of cation- and anion-solvating concept of the solvents (Eq. 8).

log $k_2 = aA + bB + C$ ... (8)

Here $A$ represents the anion-solvating power of the solvent and $B$ the cation-solvating power. $C$ is the intercept term. $(A+B)$ is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of Eq. (8), separately with $A$ and $B$ and with $(A+B)$.

log $k_2 = 0.38(\pm 0.05)A + 1.82(\pm 0.03)B - 4.25$ ... (9)

$R^2 = 0.9948; sd = 0.04; n = 19; \psi = 0.05$

log $k_2 = 0.12(\pm 0.60)A - 3.00$ ...

$r^2 = 0.0443; sd = 0.38; n = 19; \psi = 0.91$

log $k_2 = 1.76(\pm 0.08)B - 4.12$ ...

$r^2 = 0.9662; sd = 0.09; n = 19; \psi = 0.13$

log $k_2 = 1.31(\pm 0.19)(A+B) - 4.19$ ...

$r^2 = 0.7454; sd = 0.24; n = 19; \psi = 0.38$

The rates of oxidation of acetaldehyde in different solvents show a very good correlation in Swain’s equation (Eq. 9) with the cation-solvating power playing the major role. In fact, the cation solvation alone accounts for ca. 97% of the data. The solvent polarity represented by $(A+B)$, also accounted for ca. 75% of the data.

The rates of the oxidation of the six aldehydes show excellent correlation with Taft’s $\sigma^*$ substituent constants15, the reaction constant being negative (Table 4). The negative polar reaction constant indicates an electron deficient carbon centre in the transition state of the rate-determining step.

There is no kinetic evidence for the formation of an intermediate complex in the present reaction, however, its formation in small amounts cannot be ruled out. The presence of a substantial primary kinetic isotope effect ($k_T/k_D = 6.40$ at 288 K), confirms that the aldehyde $C-H$ bond is cleaved in the rate determining step. The large negative value of the polar reaction constant together with the substantial deuterium isotope effect indicates that the transition state approaches a carbocation in character. Hence, transfer of a hydride ion from the aldehyde to the oxidant is suggested. The hydride ion transfer mechanism is also supported by the major role of cation-solvating power of the solvents. The mechanism shown in Scheme 1 accounts for all the observed data.

$$\begin{align*}
\text{O} & \\
R-C-H + O\text{CrOBrOpyH} & \xrightarrow{\text{slow}} R-C=O \\
& + (\text{HOCrOBrOpyH})^- \\
\text{R}^- + C=O + (\text{HOCrOBrOpyH})^- & \xrightarrow{\text{fast}} \text{RCOOH} + \text{O\text{CrBrOpyH}}
\end{align*}$$

\text{Scheme 1}
Acknowledgement
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References
10 Peterson R C, J org Chem, 29 (1964) 3133.
13 Exner O, Prog phy org Chem, 10 (1973) 411.