Kinetics and mechanism of oxidation of beta benzoylpropionic acids by pyridinium fluorochromate in aqueous acetic acid medium

S Kavitha¹, A Pandurangan¹* & I Alphonse²
¹Department of Chemistry, Anna University, Chennai 600 025, India
²Department of Chemistry, St. Joseph's College, Tiruchirapalli 620 002, India
E-mail:pandurangan_a@yahoo.com

The kinetics of oxidation of beta benzoylpropionic acid and para substituted beta benzoylpropionic acids(KA) by pyridinium fluorochromate(PFC) has been studied in aqueous acetic acid medium in the presence of perchloric acid. The reaction follows first order kinetics each with respect to [PFC], [KA] and [H⁺]. Electron withdrawing substituents are found to retard the reaction and electron releasing substituents are found to increase the rate of reaction and the rate data obey the Hammett relationship. The products of the oxidation are the corresponding acids. The activation enthalpies and entropies are calculated and the possible mechanism for oxidation reaction is discussed.

IPCD Code: Int.Cl.7 C07B 33/00

A variety of compounds containing chromium (VI) have proved to be versatile reagents capable of oxidizing almost every oxidizable functional group¹. A number of new chromium(VI) containing compounds, with heterocyclic bases, like pyridinium chlorochromate (PCC)², pyridinium bromochromate (PBC)³, quinolinium fluorochromate (QFC)⁴, quinolinium bromochromate (QBC)⁵ and imidazolium fluorochromate(IFC)⁶ have been developed to improve the selectivity of oxidation of organic compounds. Among these oxidants, fluorochromates have been reported to be very stable and more reactive than other halochromates⁷.

Pyridinium fluorochromate, a mild oxidising agent gives higher yields in short reaction times. Amount of oxidant required is less compared to other similar agents (pyridinium chlorochromate) and the oxidation can be carried out in variety of solvents.

The kinetics of oxidation of phenols⁸, salicylaldehyde⁹, aliphatic alcohols¹⁰, etc have been reported. Herein we report the kinetics of oxidation of beta benzoylpropionic acids by PFC in aqueous acetic acid medium.

Experimental
All the chemicals used in the study were the purest available analar grade samples. Beta benzoylpropionic acid and p-methoxy, p-ethoxy, p-methyl, p-bromo and p-chloro substituents of beta benzoylpropionic acids were synthesized by the reaction between benzene or substituted benzene and succinic anhydride in the presence of anhydrous aluminium chloride as catalyst. Succinic anhydride was also synthesized by the dehydration of succinic acid. All the solutions used in the study were made by using distilled acetic acid and doubly distilled water.

To prepare PFC, 15 g of chromium (VI) oxide was dissolved in water in a polythene beaker and 11.5 ml of 40% hydrofluoric acid was added with stirring at room temperature. Within 5 minutes the clear solution resulted. To this solution 11.3 ml of pyridine was added slowly with stirring. The mixture was heated on a steam bath for 15 minutes and then cooled to room temperature allowed to stand for 30 - 35 min. The bright orange crystalline pyridinium fluorochromate was isolated by filtration(M.pt. = 106°-108°C, yield = 27 g).

Kinetic measurements were made by mixing appropriate volumes of thermally pre-equilibrated reactant solutions in aqueous acetic acid medium in the presence of perchloric acid. The progress of the reaction was followed by iodometric estimation of unreacted PFC. The rate constants were calculated using standard equation. The activation enthalpies and entropies were calculated.

Product study was made under mineral acid catalysed condition in beta benzoylpropionic acid. Keeping concentration of PFC in excess over beta benzoylpropionic acid, the two solutions were mixed and perchloric acid was also added. The reaction was allowed to go to completion by keeping it in a thermostat at 45°C for 3-4 h. The excess oxidant was decomposed by adding 2N sulphuric acid, potassium iodide and sodium thiosulphate solution. The solution was then shaken with ether. The two layers were separated. The ether layer was washed with water many times. The ethereal layer was kept on a water bath for the evaporation of ether and cooled in ice bath. The product was obtained which had melting point 121°C. It was dissolved in benzene and a careful TLC analysis was done with benzoic acid and beta benzoylpropionic acid as references. Only one spot corresponding to benzoic acid was obtained. Benzoic acid was
further confirmed by mixing the product obtained with pure benzoic acid and noting that there was no change in the melting point.

Keeping concentration of the oxidant in excess over the substrate, the two solutions were prepared in aqueous acetic acid. The beta benzoylpropionic acid and the oxidant were mixed in the ratio \((v/v)\) 1:5, 1:7.5 and 1:10, perchloric acid was also added to that mixture. The mixture was left at room temperature for about 24 h for the completion of the reaction. After the reaction was over, the remaining oxidant present in the mixture was estimated volumetrically. The stoichiometry of the reaction in all concentrations studied was found to be 3:2 for substrate and oxidant.

**Results and discussion**

The oxidation of beta benzoylpropionic acids by PFC in aqueous acetic acid medium in the presence of perchloric acid yields the corresponding benzoic acids.

The reaction was carried at different concentrations of pyridinium fluorochromate. The near constancy in the values of \(k_1\) irrespective of the concentration of the PFC confirms the first order dependence on PFC (Table 1). The rate of oxidation increased progressively on increasing the concentration of ketoacid, indicating first order dependence with ketoacid (Table 2). A plot of \(\log k_1\) against \(\log [KA]\) is linear with a unit slope. The second order rate constant \(k_2\) is invariant supporting the first order dependence on \([KA]\). Moreover, the plot \(\log \frac{1}{k_1}\) against \(\log [KA]\) is linear and passing through the origin. This indicates that during oxidation no complex is formed.

The increase in [perchloric acid] in the oxidation reaction increases the rate of the reaction and shows a direct first order dependence on \([H^+]\) (Table 3). A plot of \(\log k_1\) against \(\log [H^+]\) is linear slope shows that the order with respect to \([H^+]\) is unity. Change in ionic strength by the addition of NaClO₄ has no effect on the rate constant.

These data suggest rate law 1

\[
\text{rate} = k [KA] [PFC] [H^+] \quad \ldots (1)
\]

The rate of oxidation of beta benzoylpropionic acid is affected considerably by changing the solvent polarity of the acetic acid-water mixture. The rate of oxidation increases with the increase in the percentage of acetic acid (Table 4). From the dielectric constant values it is well known that as the polarity of the solvent decreases, the rate of oxidation increases. The plot of \(\log k_1\) against inverse of dielectric constant is linear with positive slope.

The kinetics of oxidation of a \textit{para} substituted benzoylpropionic acids were studied at different temperatures (Table 5). The second order rate constants were calculated. An examination of these data indi
Table 5—Rate constants for oxidation of substituted beta benzoylpropionic acids by PFC at different temperatures

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$10^4 \times k_1 , (\text{s}^{-1})$</th>
<th>$10^2 \times k_2 , (\text{lit} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-ethoxy</td>
<td>12.33, 16.72, 21.65, 29.82</td>
<td>8.22, 11.15, 14.43, 19.88</td>
</tr>
<tr>
<td>$p$-methyl</td>
<td>10.11, 14.70, 19.54, 24.91</td>
<td>6.74, 9.80, 13.02, 16.60</td>
</tr>
<tr>
<td>$p$-chloro</td>
<td>4.95, 6.16, 9.07, 11.99</td>
<td>3.30, 4.11, 6.05, 7.99</td>
</tr>
<tr>
<td>$p$-bromo</td>
<td>4.80, 6.07, 8.90, 11.80</td>
<td>3.20, 4.05, 5.93, 7.86</td>
</tr>
</tbody>
</table>

$[\text{PFC}] = 0.0015 \, \text{M}$ $[\text{KA}] = 0.015 \, \text{M}$ $[\text{H}] = 0.133 \, \text{M}$

Table 6—Second order rate constants and activation parameters for the oxidation of substituted beta benzoylpropionic acids by PFC

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$10^5 \times k_2 , \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</th>
<th>$E_a , \text{kcal mol}^{-1}$</th>
<th>$\Delta H^\circ , (\text{at } 308 , \text{K}), \text{ kcal mol}^{-1}$</th>
<th>$\Delta S^\circ, \text{cal deg}^{-1} \cdot \text{mol}^{-1}$</th>
<th>$\Delta G^\circ , (\text{at } 308 , \text{K}), \text{ kcal mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-chloro</td>
<td>3.30, 4.11, 6.05, 7.99</td>
<td>12.00</td>
<td>11.388</td>
<td>-24.516</td>
<td>18.938</td>
</tr>
<tr>
<td>$p$-bromo</td>
<td>3.20, 4.05, 5.93, 7.86</td>
<td>12.16</td>
<td>11.548</td>
<td>-24.048</td>
<td>18.954</td>
</tr>
</tbody>
</table>

Mechanism of oxidation beta benzoyl propionic acids by pyridinium fluorochromate

Scheme 1
The intermediate in the oxidation reaction of beta benzoyl propionic acid pyridinium fluorochromate

\[
\text{Scheme 2}
\]

cates that the oxidation is accelerated by electron-releasing substituents in the phenyl ring and electron-withdrawing substituents retard the reaction. The order of the reactivity of different substituents is as follows: \( p\)-OCH\(_3\) > \( p\)-OC\(_2\)H\(_5\) > \( p\)-CH\(_3\) > -H > \( p\)-Cl > \( p\)-Br.

A linear plot is obtained when \( \sigma \) for different substituents were plotted against log \( k_2 \). The values of reaction constant \( (p) \) were calculated to be -0.784, -0.657, -0.576 and -0.489 at 308, 313, 318 and 323 K respectively.

The energy of activation, enthalpy of activation, entropy of activation and free energy of activation were calculated (Table 6). A linear relationship between enthalpy of activation \( (\Delta H^*) \) and entropy of activation \( (\Delta S^*) \) has been observed for the oxidation of beta benzoylpropionic acids. The isokinetic temperature computed from the plot of \( (\Delta H^*) \) and \( (\Delta S^*) \) is 344 K.

Based on the results obtained and in analogy with the oxidation of keto acids by chromic acid species, the mechanism (Scheme 1) may be proposed, according to the mechanism which was proposed by Westheimer\(^{11}\) for the oxidation of alcohols by chromic acid species. The reaction follows first order kinetics each with respect to oxidant, ketoacid and acid. The decrease in rate constant with increase in dielectric constant shows the formation of a less polar transition state in the rate determining step. The absence of ionic strength on the reaction rate shows that neutral molecule is involved in the rate determining step. It is well known that pyridinium fluorochromate acts as an oxidising agent only in strong acid medium. So, the most probable oxidising species may be presumed as the protonated form of \( \text{CrO}_3\text{F}^+ \).

In the absence of any evidence for this species and from the first order dependence of the reaction on \( \text{H}^+ \) ion, the rate determining step III has been proposed. This agrees with the Westheimer scheme of oxidation of alcohols. The reaction constant \( (p) \) has a small value. As the oxidation involves the loss electrons, the negative value of the reaction constant is acceptable. The intermediate may be envisaged as in (Scheme 2).

References