Oxidation of Formic, Acetic, Propionic, Isobutyric, Pivalic & Monochloroacetic Acids by Cerium(IV) Perchlorate

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References

The effect of various parameters such as [HClO₄], [RCOOH] and temperature at constant ionic strength on the rate and mechanism has been investigated. All kinetic experiments were performed under pseudo-first order conditions using excess of the substrate. Stoichiometries of the reaction were determined separately for the acids. Where the products are further oxidized as in the case of isobutyric and phenylacetic acids, stoichiometries are found greater than the calculated values. Experimental procedure is the same as reported earlier.

The order with respect to [Ce(IV)] is one as evidenced by the linearity of the plot of log [Ce(IV)] vs time and also by the constancy of the rate constant for different [Ce(IV)] when [RCOOH], [H⁺] and ionic strength are kept constant (Table 1). The order with respect to [RCOOH] is fractional. Plots of log k(obs) vs log [RCOOH] are linear and the slopes vary from 0.77 to 0.82 for the different aliphatic acids. On increasing [H⁺], the rate increased in all cases. The predominant species below 2.0M HCIO₄ is CeO₂⁺. Since the rate depends on [H⁺], the hydrolytic equilibrium is important

\[ Ce(OH)₂⁺ \rightarrow \left(\frac{[H₄O]_₄CeOH}{[H]⁺} + H⁺ \right) \]

and the reported equilibrium constants are between 4.8 and 7.2 (ref. 1). In a freshly electrolytically prepared cerium(IV) perchlorate in perchloric acid, only the monomeric species is present and the concentration is governed by a set of hydrolysis constants.

The plot of 1/k(obs) versus 1/[RCOOH] is linear with an intercept on 1/k(obs) at constant ionic strength, [Ce(IV)] and temperature (Table 2). The presence of the intercept and deepening of the yellow colour of Ce(IV) on the addition of the organic acid, HA indicate the formation of CeOH⁺³ or [Ce(HA)]⁺⁴ or [CA]⁺³ present.

The redox potential values of Ce(III)/Ce(IV) couple in acetic acid-perchloric acid system depends on [CH₃COOH] and on [HClO₄]. The fact that the k(obs) increases with [H⁺] indicates that [Ce(H₂O)₆]⁺⁴ is the reactive species. Hence the reaction Scheme 1 is pictured for the oxidation of acids.

\[ Ce(OH)₂⁺ \rightarrow \left(\frac{[H₄O]_₄CeOH}{[H]⁺} + H⁺ \right) \]

\[ (a) \text{Varying } [Ce⁺³]; \text{ HCIO₄ = 1M, } \mu = 1.2. \]

\[ (b) \text{Slope of log } k_{obs} \text{ vs log [RCOOH] when [Ce⁺³], } \mu \text{ and [H⁺]} \]

\[ (c) \text{90% CH₃CN.} \]

The order with respect to [Ce(IV)] is one as evidenced by the linearity of the plot of log [Ce(IV)] vs time and also by the constancy of the rate constant for different [Ce(IV)] when [RCOOH], [H⁺] and ionic strength are kept constant (Table 1). The order with respect to [RCOOH] is fractional. Plots of log k(obs) vs log [RCOOH] are linear and the slopes vary from 0.77 to 0.82 for the different aliphatic acids. On increasing [H⁺], the rate increased in all cases. The predominant species below 2.0M HCIO₄ is CeO₂⁺. Since the rate depends on [H⁺], the hydrolytic equilibrium is important [Ce(OH)₂⁺] → ([H₄O]₄CeOH)⁺³ + H⁺ and the reported equilibrium constants are between 4.8 and 7.2 (ref. 1). In a freshly electrolytically prepared cerium(IV) perchlorate in perchloric acid, only the monomeric species is present and the concentration is governed by a set of hydrolysis constants.T

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TABLE 2 — RATE CONSTANTS FOR THE OXIDATION OF THE ACIDS BY CERIUM(IV) PERCHLORATE IN PERCHLORIC ACID

<table>
<thead>
<tr>
<th>Acid</th>
<th>[Acid] M</th>
<th>kobs × 10^4 sec⁻¹</th>
<th>[Acid] M</th>
<th>kobs × 10^4 sec⁻¹</th>
<th>[Acid] M</th>
<th>kobs × 10^4 sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>0.025</td>
<td>3.31 ± 0.10</td>
<td>0.030</td>
<td>3.64 ± 0.06</td>
<td>0.040</td>
<td>4.25 ± 0.07</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>0.050</td>
<td>5.72 ± 0.20</td>
<td>0.060</td>
<td>6.81 ± 0.18</td>
<td>Intercept 0.535 × 10⁴</td>
<td></td>
</tr>
<tr>
<td>Isobutyric acid</td>
<td>0.0468</td>
<td>0.506 ± 0.021</td>
<td>0.0435</td>
<td>0.568 ± 0.009</td>
<td>0.0609</td>
<td>0.732 ± 0.020</td>
</tr>
</tbody>
</table>

Further insight into the nature of the reaction is obtained from a study of the products and stoichiometries. In the case of formic acid and acetic acid the stoichiometries depended on [H⁺] and temperature. The observed stoichiometries (Table 3) in the oxidation of propionic, isobutyric and pivalic acids by cerium(IV) perchlorate in perchloric acid account for the decomposition of acyloxy radicals in presence of Ce⁴⁺ to alkyl radicals or alkyl cations. Acetic acid is oxidized to formic acid and the oxidation of formic acid is much slower than that of acetic acid. Propionic acid is similarly converted to acetic acid; the oxidation of ethanol and acetaldehyde is much faster and that of acetic acid much slower than that of propionic acid. Isobutyric acid is oxidized to acetone which is identified as 2,4-dinitrophenylhydrazone and the oxidation of acetic acid is very much slower than that of isobutyric acid. Pivalic acid is converted to t-butyl alcohol.

Further analysis of the oxidation schemes (Scheme 1) for Cr(VI) and Co(III) oxidations similar schemes are postulated. The oxidation of chloroacetic acid is much slower than that of acetic acid but follows the same general course. Under pseudo-unimolecular conditions with excess of the substrate, the rates of oxidation of formic acid, acetic acid, t-butyl alcohol and benzaldehyde formed from acetic, propionic, isobutyric, pivalic and phenyl acetic acids respectively are not contributing significantly to the observed rate. This has been experimentally verified. Hence based on the reaction Scheme 1,

\[ \frac{1}{k_{obs}} = \frac{1}{n k_h} + \frac{k_h}{K n_k [RCHOH]} \]

where \( n \) = stoichiometry.

kₜ values calculated from the intercepts of the plots of 1/kₜ vs 1/[RCHOH] are presented in Table 4. Log kₜ vs 1/T plot was linear for each acid and the Arrhenius parameters were calculated (Table 5). The fact that the free energies of activation are nearly the same for these acids.
shows that these acids undergo oxidation by the same mechanism.

In the oxidation of phenylacetic and diphenylacetic acids by cerium(IV) perchlorate in perchloric acid in 30% acetonitrile solvent, the same general trend is observed. The stoichiometry of the reaction is 4 and the products are benzaldehyde and benzophenone for the oxidation of phenylacetic and diphenylacetic acids respectively. Since the intercepts of 1/kt vs 1/[RCOOH] plots are smaller, the formation constants cannot be determined with precision. $\Delta H^\ddagger$ values are related to radical stabilization.

The observed order of reactivity, monochloroacetic acid < acetic acid < propionic acid < isobutyric acid < pivalic acid and acetic acid < phenylacetic acid < diphenylacetic acid indicates that an increase in electron density at the reaction site accelerates the rate of decomposition of the complex. A plot of $\log k_t$ vs $\sigma^+$ of the substituents gives a $p$ value of -5.28 indicating a positive charge on the carbonyl carbon. The carboxylic acid which can yield a stabler cation is nitratel and the thermal decarboxylation of Ce(IV) shows that these acids undergo oxidation by the same mechanism.

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