Kinetics and mechanism of the ruthenium(III)-catalysed oxidation of aliphatic acids by peroxodiphosphate in acetate buffers

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Summary

The kinetics of oxidation of aliphatic acids (AAs), such as propionic acid, butyric acid, isobutyric acid and valeric acids, by peroxodiphosphate (PDP) using ruthenium(III) as catalyst in aqueous H_2SO_4 at constant ionic strength and different acidities were studied. The ruthenium(III)-catalysed oxidation is first order in [PDP] and fractional order in [AA]. The order with respect to [Ru^{III}] is fractional. An analysis of the rate dependence upon [H^+] suggests that $H_3P_2O_8^-$ is the active oxidizing species in the oxidation. A mechanism consistent with the rate law is proposed.

Introduction

Several metal ions are known to oxidize dicarboxylic acids via a 1:1 complex which undergoes oxidation to the products in a rate determining step$^{(1-3)}$. However, monocarboxylic acids are oxidized at higher temperatures or only in the presence of catalyst. Thus, potassium permanganate, which oxidizes oxalic acid quantitatively, cannot oxidize acetic acid under normal conditions$^{(4)}$. Much work has been done on the oxidation of carboxylic acids by transition metal ions such as cobalt(III), vanadium(V), manganese(III), copper(III) and cerium(IV)$^{(5-9)}$. The kinetics of oxidation of inorganic and organic substrates by peroxodiphosphate have not been investigated as extensively as other oxidants, though there are a few such studies$^{(10-13)}$. Although studies using silver(I) and copper(II) as catalysts in PDP oxidations have been reported$^{(12,14)}$, catalysis involving ruthenium(III) in PDP oxidations have not. Thus, the reaction of aliphatic carboxylic acids (AAs) with peroxodiphosphate (PDP) seemed worthy of investigation.

Experimental

Materials and methods

$K_4P_2O_8$ was a gift from the FMC Corporation, USA. Solutions were prepared by dissolving a known quantity in H_2O, standardizing iodometrically$^{(15)}$ and using within 2 h. AAs (Fluka or BDH) were distilled just before use. $RuCl_3$ (John Mathey) was evaporated several times with concentrated HCl in order to remove ruthenium(IV). A stock solution, prepared in 0.3 M HCl, was standardized as described by Singh *et al.*$^{(16)}$

Peroxodiphosphate readily undergoes hydrolysis$^{(17)}$ in acidic solutions, yielding peroxomonophosphate. This conversion was avoided in our study by working in buffered systems at pH 3.4–4.5 (PDP is hydrolysed below pH 3 and a yellowish turbidity appeared above pH 4.5). The pH was varied by employing different [HOAc] at fixed [OAc^-]; [OAc^-] was varied employing a fixed [NaOAc]/[HOAc] ratio, but different overall concentrations of the two.

Kinetic measurements

All kinetic studies were made in a thermostatic bath at 313 ± 0.5 K unless stated otherwise. The reaction was initiated by addition of temperature equilibrated AA. Aliquots (5 or 10 cm^3) were withdrawn at different times and added to an iodine solution of known concentration and volume, rendering the pH between 3–4.5 by adding the required amount of NaOAc. Unreacted AA reacted with iodine and the excess of the latter was titrated against a known thiosulphate. The pH was always kept >3 in order to eliminate reaction$^{(12)}$ between PDP and iodide (present in iodine solution).

Stoichiometry and product analysis

The stoichiometry of the reaction was determined by keeping an excess of PDP with propionic acid for 24 h and estimating the remaining PDP by the iodometric procedure. One mole of propionic acid required one mole of PDP to form the products.

$$RCH_2CO_2H + H_3P_2O_8^- + H_2O \longrightarrow RCHO + CO_2 + HPO_4^{2-} + H^+ \qquad (1)$$

The products of oxidative decarboxylation of aliphatic acids were identified as $CO_2$$^{(18)}$ by a spot test, and the corresponding aldehydes$^{(19)}$ by their conversion into 2,4-dinitrophenyl hydrazone derivatives, which were subsequently identified by their m.ps. Similar products were reported in the oxidation of amino acids by PDP$^{(20)}$. The products were further qualitatively identified by g.l.c. by peak enhancement using authentic samples. The stationary phase was polyethylene glycol adipate and H_2 was used as the carrier gas. From i.r. spectral studies the observed lowering of the $\nu(C{=}O)_{assym}$ from 1380 to 1360 cm^{-1} is indicative of complex formation between ruthenium(III) and the carboxylate anion.

Results and discussion

It is worth noting that organic compounds react slowly with peroxides relative to other radical molecular processes. For instance, Edwards *et al.*$^{(21)}$ have reported that the oxidizing ability of perphosphate is several orders of magnitude lower than persulphate in the oxidation of alcohols. In our study, the reaction between PDP and AAs, when allowed to react for several hours, was also negligible.

The results for the ruthenium(III)-catalysed oxidations of propionic, butyric, isobutyric and valeric acids by PDP in H_2SO_4 are shown in the Tables 1–4.

Under the conditions [PDP] ≪ [AA] in the presence of a constant amount of ruthenium(III), the order in [PDP] was found to be unity. The pseudo-first order rate constants (k') were calculated from the slopes of the linear plots of log $(a/a-x)$ versus time ($r = 0.985$) where a and $a-x$ are the concentrations of [PDP] at zero and time t respectively. The rate dependence upon [AA] was an apparent fractional order over the concentration range studied (0.200–2.00 mol dm^{-3}), as obtained from the slopes of plots of log k' versus log [AA] ($r = 0.976$) (Table 1). The order with respect to ruthenium(III) was also fractional (ca. 0.60), as observed from the plots of log k' versus log [Ru^{III}] ($r = 0.987$).

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The reaction rate increases significantly with increase in $[H^+]$ (Table 2). A plot of k' versus $[H^+]$ passes through the origin, indicating the absence of any acid-independent path ($r = 0.987$). The order in $[H^+]$ was found to be unity from a plot of $\log k'$ versus $\log [H^+]$. The pH of the system was varied from 3.43 to 4.50 with the help of acetic acid and sodium acetate as described earlier. These results (Table 3) show that the rate decreases with the increase in pH. The oxidation was studied over the 303–318 K temperature range. Plots of $\log k$ versus $1/T$ were found to be linear ($r = 0.982$); values for the energy of activation were calculated from the slopes (Table 4).

The first and second dissociation constants of peroxodiphosphoric acid are estimated(23) to be >40 and 40, respectively, while the third and fourth dissociation constants are 6.6×10^{-6} and 2.1×10^{-8}, respectively. Hence, PDP will be present as $H_2P_2O_8^{2-}$ in aqueous solution. Further association with $[H^+]$ is also possible, depending on the pH of the medium according to Equations 1 and 2.

$$H_2P_2O_8^{2-} + H^+ \overset{K_1}{\rightleftharpoons} H_3P_2O_8^- \qquad (1)$$

$$H_3P_2O_8^- + H^+ \overset{K_2}{\rightleftharpoons} H_4P_2O_8^- \qquad (2)$$

Table 1. Effect of [AA] and $[Ru^{III}]$ on the reaction[a].

[AA] (mol dm^{-3})	$10^4 k'$ (s^{-1})	$10^4[Ru^{III}]$ (mol dm^{-3})	$10^4 k'$ (s^{-1})
0.20	2.88	5.00	10.10
0.40	3.50	4.00	8.91
0.80	4.33	3.00	7.76
1.20	4.60	2.50	6.94
1.60	5.25	2.00	6.16
2.00	10.50	1.00	4.16

[a] $[PDP] = 1.00 \times 10^{-3}$ mol dm^{-3}, pH = 3.90, I = 1.00 mol dm^{-3}, $[Ru^{III}] = 1.00 \times 10^{-4}$ mol dm^{-3}, $[AA] = 4.00 \times 10^{-1}$ mol dm^{-3}, temperature = 313 K.

Table 2. Effect of $[H^+]$ on the reaction at constant ionic strength[a].

$10^3[H^+]$ (mol dm^{-3})	$3 + \log[H^+]$	$10^4 k'$ (s^{-1})	$4 + \log k'$
3.16	0.49	2.23	0.31
3.31	0.51	2.45	0.39
6.30	0.79	4.26	0.63
12.50	1.09	8.70	0.94
19.90	1.29	12.30	1.09
22.30	1.35	14.12	1.15

[a] $[PDP] = 1.00 \times 10^{-3}$ mol dm^{-3}, $[Ru^{III}] = 1.00 \times 10^{-4}$, $[AA] = 4.00 \times 10^{-1}$ mol dm^{-3}, [I] = 1.00 mol dm^{-3}, temperature = 313 K.

Table 3. Effect of pH on the reaction[a].

pH	3.43	3.58	3.75	3.90	3.99	4.08	4.20	4.48
$10^4 k'$(s^{-1})	3.95	3.78	3.65	3.50	3.30	3.05	2.90	2.70

[a] $[PDP] = 1.00 \times 10^{-3}$ mol dm^{-3}, $[AA] = 4.00 \times 10^{-1}$ mol dm^{-3}, $[Ru^{III}] = 1.00 \times 10^{-4}$ mol dm^{-3}, I = 1.00 mol dm^{-3}, temperature = 313 K.

Under the present experimental conditions, $H_2P_2O_8^{2-}$, $H_3P_2O_8^-$ and $H_4P_2O_8$ may all be present in solution. The relative concentrations of the various species as a function of pH have been discussed by Crutchfield(24). Thus, the total concentration of PDP is given by

$$[PDP]_T = [H_2P_2O_8^{2-}] + [H_3P_2O_8^-] + [H_4P_2O_8] \qquad (3)$$

In Equation 3, if all three species are considered to contribute to the rate with respect to PDP, then the rate is given by Equation 4:

$$-d[PDP]_T/dt = k_1[H_2P_2O_8^{2-}] + k_2[H_3P_2O_8^-] + k_3[H_4P_2O_8] = \frac{[PDP]_T(k_1 + k_2K_1[H^+] + k_3K_1K_2[H^+]^2)}{1 + K_1[H^+] + K_1K_2[H^+]} \qquad (4)$$

where K_1 and K_2 are the equilibrium constants for the protonation of $H_2P_2O_8^{2-}$ and $H_3P_2O_8^-$, respectively, and k_1, k_2 and k_3 are the rate constants for the dissociation of the above three species. Since the least value of the second dissociation constant k'' $(1/K_1)$ is 40 mol l^{-1} and the first dissociation constant k' $(1/K_2)$ should be greater than 40 mol l^{-1}, Equation 4 reduces to the numerator term only, by neglecting the second and third terms in the denominator in comparison to unity.

The nature of the PDP species involved in the reaction may be deduced on the basis of the dependence of the reaction rates upon $[H^+]$. The first order dependence on $[H^+]$ and the absence of an intercept in the plot of $\log k'$ versus $\log[H^+]$ and decrease in rate with increase in pH leads to the conclusion that $H_3P_2O_8^-$ is the active species(13,25) involved in these oxidations.

It is worthwhile discussing the probable ruthenium(III) species before formulating the mechanism of oxidation of aliphatic acids by PDP in the presence of ruthenium(III). The deep red solution of ruthenium(III) in water blackens quickly due to hydrolysis(26). Ion exchange and spectral studies have indicated that $[Ru(H_2O)_6]^{3+}$ and $[Ru(H_2O)_5Cl]^{2+}$ are the most likely species in acid medium(27). Since it is known that aquation of $RuCl_3$ is quite fast and takes place in a matter of seconds(28), and as $[H^+]$ was kept low, aqueous ruthenium(III) is assumed to be the reactive species in the present study.

Mechanism

An apparent fractional order dependence of rate on [AA] over the concentration range studied in the presence of ruthenium(III) indicates that the AA may be involved in complex formation either with PDP or ruthenium(III). U.v. and i.r. spectral studies indicate that complexation occurs between [AA] and ruthenium(III). The λ_{max} for the AA–ruthenium(III) complex shifts on addition of PDP, indicating formation of a new species, probably ruthenium(V). The lowering of $\nu(CO_2^-)_{asym}$ from 1380 to 1360 cm^{-1} is indicative of the interaction of this group

Table 4. Activation parameters, bimolecular rate constants (k) and adduct formation constants (K)[a].

Acid	k (dm^3 mol^{-1} s^{-1})	K (dm^3 mol^{-1})	E_{exp} (kJ mol^{-1})	$\Delta G^\#$ (kJ mol^{-1})	$\Delta H^\#$ (kJ mol^{-1})	$-\Delta S^\#$ (JK^{-1} mol^{-1})
Propionic	3.12	6.16	60.8	73.7	58.2	49.5
Butyric	1.14	5.24	41.5	76.4	38.9	122.0
Isobutyric	0.94	3.79	26.8	76.9	24.2	168.0
Valeric	0.82	2.13	18.8	77.2	16.1	198.0

$[PDP] = 1.00 \times 10^{-3}$ mol dm^{-3}, $[Ru^{III}] = 1.00 \times 10^{-4}$ mol dm^{-3}, pH = 3.90.

with the metal ion. Formation of such higher oxidation states of ruthenium(III) has also been proposed by earlier workers in oxidation studies with cerium(IV)(29), acid bromide(30) and periodate(31). Since PDP is a two electron oxidant, as revealed by the absence of any rate inhibition, in the presence of acrylonitrile, a two electron oxidation of the ruthenium(III)–substrate complex to form a ruthenium(V)–substrate complex is envisaged. Thus, the most probable mechanism may be written as in Scheme 1.

$$H_2P_2O_8^{2-} + H^+ \overset{K_1}{\rightleftharpoons} H_3P_2O_8^- \qquad (1)$$

$$RCH_2CO_2H + Ru^{3+} \overset{K}{\rightleftharpoons} (\text{adduct})^{3+} \qquad (5)$$

$$(\text{adduct})^{3+} + H_3P_2O_8^- \underset{\text{slow}}{\overset{k}{\rightleftharpoons}} (\text{adduct})^{5+} + H_2PO_4^- + HPO_4^- \qquad (6)$$

$$(\text{adduct})^{5+} \xrightarrow[\text{fast}]{\text{HOH}} RCHO + Ru^{3+} + 2H^+ + CO_2 \qquad (7)$$

Scheme 1

The rate law for the above mechanism can be written

$$-d[PDP]_T/dt = \frac{K_1Kk[PDP]_T[H^+][Ru^{III}][AA]}{1 + K[AA] + K[Ru^{III}]} \qquad (8)$$

Equation 8 explains first order dependence in [PDP], fractional order dependence in both [ruthenium(III)] and [AA] and first order dependence with respect to $[H^+]$.

Under the experimental conditions when [PDP] $\ll$ [AA] and [AA] was varied keeping $[H^+]$ constant, the rate law Equation 8 reduces to

$$-2.303 \log [PDP]_T/dt = k' = \frac{kK[AA][Ru^{III}]}{1 + K[AA] + K[Ru^{III}]} \qquad (9)$$

where k' is the observed pseudo-first order rate constant, k is the second order rate constant for the slow Step 6 and K is the formation constant of the adduct. Taking the reciprocal of Equation 9, we obtain

$$1/k' = \frac{1}{[AA]}\left[\frac{1}{kK[Ru^{III}]} + \frac{1}{k}\right] + \frac{1}{k[Ru^{III}]} \qquad (10)$$

From Equation 10 it is clear that a plot of $1/k'$ versus 1/[AA] at fixed [ruthenium(III)] should be linear. This proved to be correct ($r = 0.978$). From the intercept and slope the second order rate constant (k) for the slow step and formation constant (K) of the adduct were calculated; the values are recorded in Table 4.

It is observed that the rate of oxidation of AAs follows the order: propionic > butyric > isobutyric > valeric acids (Table 4). Passing from propionic to valeric acid there is an increase in the bulkiness of the molecule and this is probably the reason for the large decrease in $\Delta S^{\#}$ values. Since differences in the $\Delta S^{\#}$ values were found to be larger than the corresponding changes in E_{exp} values, these reactions may be considered to be entropy controlled. This is evident from the fact that the E_{exp} for the fastest reaction was high and *vice versa*. The decrease in reactivity from propionic to valeric acid could be due to increasing hindrance to formation of the ruthenium(III)–carboxylic acid adduct as the bulk of the acid increases. The formation constants of the adduct (K) and second order rate constant (k) obtained in the present work (Table 4) lie in this order, suggesting that the mechanism proposed is probably correct.

The activation parameters for all the acids studied may be explained on the basis of an isokinetic relationship. The $\Delta H^{\#}$ and $\Delta S^{\#}$ values are related by the equation $\Delta H^{\#} = \Delta H_0^{\#} + \beta\Delta S^{\#}$, where β is the isokinetic temperature. A plot of $\Delta H^{\#}$ versus $\Delta S^{\#}$ (Table 4) was linear with a slope equal to 290 K, which is the isokinetic temperature for this reaction series. Thus, the value is found to be much lower than that of the experimental temperature range used, indicating that the reactions are entropy controlled.

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