Oxidation of 2,3-dimethylindole by peroxophosphates

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The kinetics of the oxidation of 2,3-dimethylindole 1 by peroxodiphosphoric, PDP, and peroxomonophosphoric, PMP, acids have been investigated in sulfuric acid (0.1–1 mol dm^{-3}) and 20% *v*/*v* methanol–water solutions. On the basis of the spectral and kinetic results and by analogy with the mechanism previously proposed for the oxidation of 1 by peroxomono- and peroxodi-sulfate anions, we have concluded that the reactions proceed through the following steps: an electrophilic attack of the peroxide bond at the C-3 atom of the indole ring to form an indoleninic intermediate, a second peroxo attack on the enaminic tautomer of this intermediate and the hydrolysis of the product to finally give 3-methylindole-2-carbaldehyde. The analysis of the dependence of the reaction rates with acidity shows that, under our experimental conditions, neutral $H_4P_2O_8$ and cationic $H_4PO_5^+$ are, respectively, the active species mainly involved in the oxidation processes.

Introduction

We have recently studied the kinetics and mechanisms of the oxidation of several 2,3-dialkylindoles to the corresponding 2-acyl derivatives.[1,2] In these studies, we have used two inorganic peroxo compounds, peroxodisulfate, PDS, and peroxomonosulfate, PMS, anions. These results threw new light on some interesting aspects of the mechanism of these oxidation reactions. Thus, as Scheme 1 shows, there is an initial electrophilic attack of the peroxo anion at the C-3 atom of the indole ring, with oxygen–oxygen bond fission, to give a dihydroindole† intermediate 2.

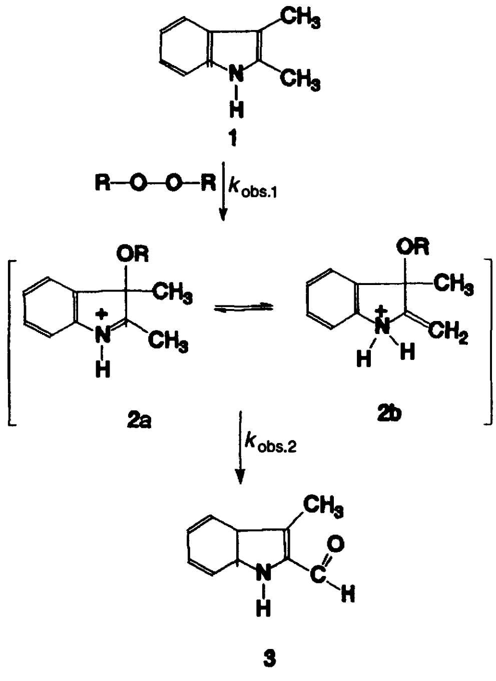
Subsequently, there is another electrophilic attack of the peroxoanion on the enaminic tautomer **2b** followed by hydrolysis of the new intermediate to give the 2-acyl derivative. The use of different substrates has allowed us to demonstrate that the presence of the short-lived enaminic tautomer **2b** is essential in accounting for the formation of this final product.[2] Furthermore, the presence of this enamine depends on the protonation state of the dihydroindole intermediate and on the structural characteristics of the substrates.

In order to analyse the generality of this reaction mechanism and to get further insight into the factors influencing the rate of these oxidation reactions, in the present work we have carried out a kinetic study of the oxidation of 2,3-dimethylindole 1 by peroxodiphosphoric, PDP, and peroxomonophosphoric, PMP, acids. These peroxo compounds which are isostructural and isoelectronic with PDS and PMS, respectively, are also known to be good electrophilic reagents capable of reacting with a variety of nucleophilic substrates.[3–5]

Experimental

Reagents

2,3-Dimethylindole 1 and potassium peroxodiphosphate $K_4P_2O_8$ (PDP) (Aldrich Quimica), were used as received. Peroxomonophosphoric acid (PMP) was prepared by acid hydrolysis of PDP according to the procedure previously described.[6] The stock solutions of PDP and PMP were prepared daily, stored in the dark at 4 °C to prevent light-induced and hydrolytic decomposition and frequently titrated by iodometry. The remaining chemicals were of analytical grade.



Scheme 1

The acidity of PMP and PDP solutions were adjusted by adding appropriate amounts of a commercial standardized solution of H_2SO_4. In all the experiments the acidity was maintained in the H_2SO_4 range 0.1–1.0 mol dm^{-3}, to ensure protonation of the dihydro indole intermediate (pK_a *ca.* 2)[1] and to avoid protonation of the indole substrate 1 (pK_a = −1.5).[7] Acidities have been expressed as hydrogen ion activities, a_H, which were calculated from the H_0 acidity function.

The possibility that the hydrolysis of PDP[8,9] or PMP[6] could compete with the oxidation of compound 1, has been tested by independent measurements of the rate of the hydrolytic reactions under the same acidity conditions used in the oxidation reactions. These experiments demonstrated that hydrolytic reactions are at least fifty times slower than the oxidation reactions. Interference from the reaction products of these hydrolyses was not observed. There was negligible rise in PMP concentration due to PDP hydrolysis, on the timescale of the 1-PDP reaction. Moreover, H_2O_2, the reaction product of PMP hydrolysis, does not appreciably react with compound 1

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† Dihydroindole: formerly known as indolenine

under our experimental conditions. Therefore, the oxidation rates of compound **1** by PDP and PMP can be measured without any interference from the hydrolytic decomposition of the oxidizing reagents. On the other hand, neither the presence of radical promotors nor radical traps affected the oxidation rates, which excludes the involvement of radical species in the reactions.

Instruments

Absorption measurements have been done using a UV–VIS spectrophotometer, LKB Ultrospec Plus, interfaced with an Acer computer. Whenever necessary, a rapid-mixing kinetic accessory, Photophysic Applied, was used. The evolution of the spectra of the reaction mixtures with time was recorded with a Hewlett Packard 8452A diode array spectrophotometer. In all reactions the temperature was controlled within ±0.1 °C.

Kinetic experiments

These were carried out under pseudo-first-order conditions with a large excess of PDP or PMP. The steps of the reaction were followed by monitoring the changes of absorbance at 282 and 312 nm, the wavelengths corresponding to the absorption maxima of compounds **1** and **3**, respectively. Pseudo-first-order rate constants were obtained by a non-linear square fitting of the absorbance–time data to eqn. (1).

$$A_t = A_\infty + (A_0 - A_\infty)\, e^{-k_{obs}t} \qquad (1)$$

The reactions were followed for at least two halflives. Usually, an excellent agreement between experimental and calculated A_t values was obtained. All rate constants were averaged for at least three independent runs and the standard deviations were smaller than 5%.

Results and discussion

Typical reaction mixtures of compound **1** and PDP or PMP in sulfuric acid and 20% methanol–water were monitored by UV–VIS spectroscopy. The spectral changes observed on mixing the reactants were the same for both oxidants. The spectral changes for the reaction of compound **1** and PDP as a function of time are illustrated in Fig. 1. As Fig. 1 shows, two clearly distinguishable steps can be observed in the reaction. In the first step, a decrease of the absorbance at the wavelength of maximum absorption of compound **1** is observed. Simultaneously, there is a displacement of the maximum toward 290 nm, to give a final spectrum corresponding to the well known absorption of the protonated dihydroindolic chromophore.[1,10] The clear isosbestic point in the spectra indicates the direct transformation of compound **1** into the dihydroindolic intermediate **2**.

Once the intermediate has accumulated, a new absorption band appears slowly at *ca.* 312 nm at the expense of the 290 nm peak and again with clear isosbestic points. This second step corresponds to the conversion of the dihydroindole intermediate into the final product, 3-methylindole-2-carbaldehyde **3**.[11]

These spectral changes and the yields for the conversion of **1** into **3** (*ca.* 80%) are the same as those observed previously for the reaction of compound **1** and other related 2,3-dialkylindoles with PDS and PMS.[1,2] This fact leads us to conclude that all these reactions have essentially the same mechanism. We have analysed the kinetics of the **1**–PDP and **1**–PMP reactions and discuss particular aspects of their mechanisms. We have also compared the present results with those obtained previously for the oxidation of **1** with PDS and PMS.

Oxidation of compound 1 by PDP

The values of the experimental pseudo-first-order rate constants for the first step, $k_{obs.1}$, and the second step, $k_{obs.2}$, of the **1**–PDP reaction at different PDP and sulfuric acid concentrations are reported in Tables 1 and 2, respectively. As the data in Tables 1 and 2 show, the rate constants $k_{obs.1}$ and $k_{obs.2}$ increase as the PDP concentration increases. However, whereas at fixed acidities, the plots of $k_{obs.1}$ *vs.* [PDP] are linear, the plots of $k_{obs.2}$ *vs.* [PDP] are curved.

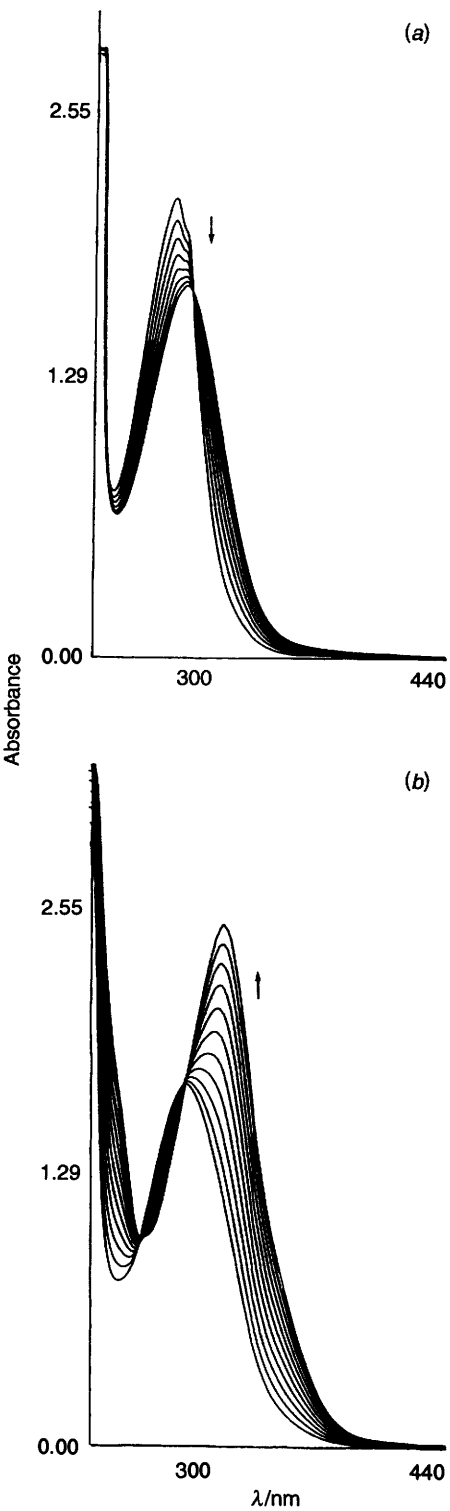


Fig. 1 Changes in UV–VIS spectra for the reaction mixture: [**1**] = 4 × 10^{-4} mol dm^{-3}, [PDP] = 2 × 10^{-3} mol dm^{-3}, [H_2SO_4] = 0.5 mol dm^{-3} at 298 K and 20% *v*/*v* methanol–water. (*a*) At 3 min intervals. (*b*) At 3 min intervals and 30 min delay time.

The influence of the temperature on the rate constants $k_{obs.1}$ and $k_{obs.2}$ is reported in Table 3. These experimental data fit the Arrhenius equation from which the activation parameters are $\Delta H^{\ddagger}_1$ = 69.06 kJ mol^{-1}, $\Delta H^{\ddagger}_2$ = 70.17 kJ mol^{-1} and $\Delta S^{\ddagger}_1$ =

Table 1 Pseudo-first-order rate constants $k_{\mathrm{obs.1}}$ for the oxidation of **1** by PDP in 20% methanol–water at 298 K. [**1**] = 4 × 10^{-4} mol dm^{-3}

[PDP]/10^{-3} mol dm^{-3}	$k_{\mathrm{obs.1}}/10^{-3}\ \mathrm{s}^{-1}$					
	a_H					
	0.754	0.873	1.011	1.259	1.355	1.568
1.608	0.99	1.21	1.12	1.27	1.19	1.39
3.218	1.78	2.25	2.35	2.57	3.16	3.16
4.830	2.37	3.18	3.24	3.74	4.15	4.88
6.435	2.95	4.10	4.63	5.32	4.76	5.96
9.653	4.34	5.71	6.41	7.35	8.29	8.81

Table 2 Pseudo-first-order rate constants $k_{\mathrm{obs.2}}$ for the oxidation of **1** by PDP in 20% methanol–water at 298 K. [**1**] = 4 × 10^{-4} mol dm^{-3}

[PDP]/10^{-3} mol dm^{-3}	$k_{\mathrm{obs.2}}/10^{-4}\ \mathrm{s}^{-1}$		
	a_H		
	0.605	0.873	1.568
2.00	4.298	4.93	3.99
3.00	—	7.15	—
4.00	6.00	8.89	—
6.00	—	11.75	—
8.00	10.51	13.13	11.70
10.00	—	14.72	13.3
12.00	14.36	—	—
16.00	—	—	16.40
20.00	—	—	20.79

Table 3 Pseudo-first-order rate constants $k_{\mathrm{obs.1}}$ and $k_{\mathrm{obs.2}}$ for the oxidation of **1** by PDP in 20% methanol–water at different temperatures. [**1**] = 2.0 × 10^{-4} mol dm^{-3}, [PDP] = 1.6 × 10^{-3} mol dm^{-3} and [H_2SO_4] = 0.5 mol dm^{-3}

T/K	293	298	303	308	413
$k_{\mathrm{obs.1}}/10^{-3}\ \mathrm{dm}^3\ \mathrm{s}^{-1}\ \mathrm{mol}^{-1}$	—	1.93	3.19	4.69	7.72
$k_{\mathrm{obs.2}}/10^{-4}\ \mathrm{dm}^3\ \mathrm{s}^{-1}\ \mathrm{mol}^{-1}$	2.23	4.89	7.23	11.2	—

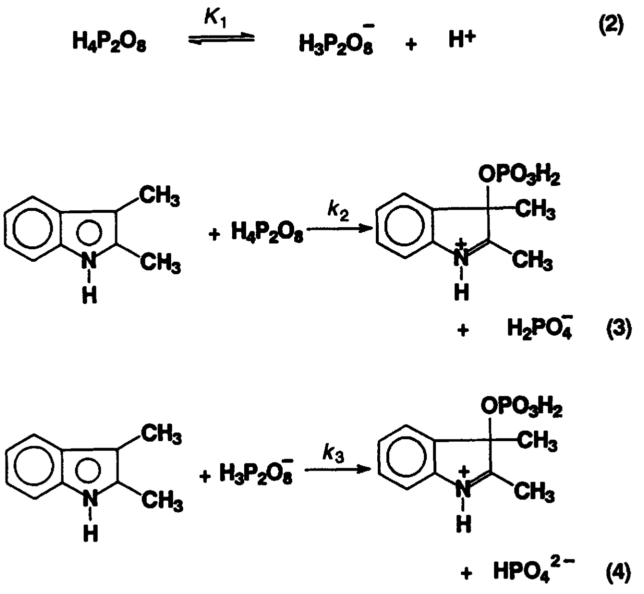
-11.87 J mol^{-1} K^{-1}, $\Delta S^{\ddagger}_2 = -19.85$ J mol^{-1} K^{-1}. Note, the close correspondence between the activation parameters for both steps of the reaction, which indicates that they involve similar transition states. On the other hand, both steps of the reaction are characterized by a low enthalpy and appreciable negative entropy of activation which is consistent with the polar mechanism reported in Scheme 1.[3,4]

The variation of ionic strength, using Na_2SO_4 as an inert salt, was found to have a negligible effect on both rate constants $k_{\mathrm{obs.1}}$ and $k_{\mathrm{obs.2}}$. Therefore, the rate-determining step of these reactions would involve at least one neutral molecule. This information is of special interest, since, under our acidic experimental conditions, PDP species of different charge can participate in the reaction.

The nature of the active PDP species involved in the reaction may be better arrived at on the basis of the dependence of the reaction rates $k_{\mathrm{obs.1}}$ and $k_{\mathrm{obs.2}}$ on hydrogen ion activity. In both cases, the rate constants increase with increasing hydrogen ion activity, but the plots show significant curvature tending to decrease the slope at the highest acidities.

At this point, two essential differences between the kinetics of the **1**–PDP and **1**–PDS reactions are apparent: (*a*) the first step of the **1**–PDP reaction is acid catalysed while that of **1**–PDS is not; (*b*) the salt effect is negligible in the second step of the **1**–PDP reaction, while it is positive in the **1**–PDS reaction. These differences probably arise from the different protonation state of the PDP and PDS species involved in the reactions.

In the acidity range in which the oxidations of **1** by PDS and PDP have been studied, PDS exists only as monoanionic $HS_2O_8^-$ species,[12] whereas PDP can exist, at least, as $H_4P_2O_8$ and $H_3P_2O_8^-$ species.[13,14] Therefore, assuming that both PDP species contribute to the rate of the reaction, the mechanism for the first step of the **1**–PDP oxidation can be expressed as in Scheme 2.



Scheme 2

The mechanism in Scheme 2 leads to rate eqn. (5).

$$v = -\frac{\mathrm{d}[\mathrm{PDP}]_t}{\mathrm{d}t} = (k_2[H_4P_2O_8] + k_3[H_3P_2O_8^-])\,[\mathbf{1}] \quad (5)$$

where $[\mathrm{PDP}]_t$ represents the total stoichiometric concentration of PDP, which can be expressed as eqn. (6).

$$[\mathrm{PDP}]_t = [H_4P_2O_8] + [H_3P_2O_8^-] \quad (6)$$

From eqns. (2) and (6) we obtain eqn. (7).

$$[H_4P_2O_8] = \frac{(a_H)[\mathrm{PDP}]_t}{K_1 + (a_H)} \quad (7)$$

and

$$[H_3P_2O_8^-] = \frac{K_1[\mathrm{PDP}]_t}{K_1 + (a_H)} \quad (8)$$

Eqn. (5), therefore, takes the form eqn. (9).

$$v = \left[\frac{k_2(a_H)}{K_1 + (a_H)} + \frac{k_3K_1}{K_1 + (a_H)}\right][\mathbf{1}]\,[\mathrm{PDP}]_t \quad (9)$$

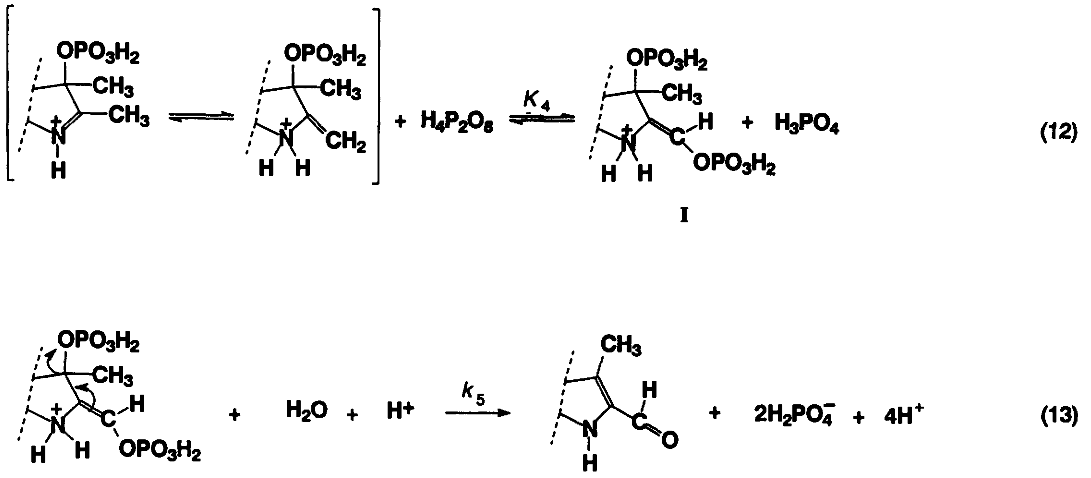
from which eqn. (10) can be obtained.

$$k_{\mathrm{obs.1}} = \frac{k_2(a_H) + k_3K_1}{K_1 + (a_H)}[\mathrm{PDP}]_t \quad (10)$$

Attempts to calculate k_2 and k_3 by a non-linear least-squares fitting using eqn. (10) gave small and negative values for k_3, and hence, this rate constant could be approximated to zero. Therefore, assuming that under our experimental conditions $k_3K_1 \ll k_2(a_H)$, eqn. (11) holds.

$$k'_{\mathrm{PDP}} = \frac{k_2(a_H)}{K_1 + (a_H)} \quad (11)$$

where k'_{PDP} represents the second-order rate constant.



Scheme 3

According to this equation the plot of $(k'_{PDP})^{-1}$ *vs.* $(a_H)^{-1}$ should be linear with slope and intercept K_1/k_2 and $1/k_2$, respectively, see Fig. 2. The parameters obtained allow us to calculate the following values for $K_1 = 5.6 \pm 0.23$ mol dm^{-3} and $k_2 = 4.25 \pm 0.26$ mol^{-1} dm^{-3} s^{-1} at 298 K.

The lack of experimental data for K_1 precludes direct comparison with the obtained K_1 value. However, this value is in reasonable agreement with that of 2 mol dm^{-3} estimated by Crutchfield *et al.*[13] by extrapolating the corresponding values for $H_4P_2O_7$ and $H_4P_2O_6$ acids, but it differs greatly from that estimated by Gupta *et al.*[14] using kinetic data (>40). The corresponding k_2 value for the 1–PDP reaction[2] previously obtained was 0.107 mol^{-1} dm^3 s^{-1}. Although the different charge of the active PDP and PDS species involved in the reactions does not allow a straightforward comparison, these data indicate that $H_4P_2O_8$ is a better electrophile than $HS_2O_8^-$.

Going now to the second step of the 1–PDP reaction, if we rule out the path involving $H_3P_2O_8^-$, its mechanism can be written as in Scheme 3.

The rate law for this mechanism with application of the steady-state approximation to *I* is shown in eqn. (14).

$$k_{obs.2} = \frac{k_4 k_5 (a_H)[H_4P_2O_8]}{k_{-4}[H_3PO_4] + k_4[H_4P_2O_8] + k_5(a_H)} \quad (14)$$

According to eqn. (14), and assuming that under our experimental conditions $k_{-4}[H_3PO_4] \ll \{k_4[H_4P_2O_8] + k_5(a_H)\}$, a plot of $a_H/k_{obs.2}$ *vs.* a_H/[PDP] would exhibit a linear dependency, Fig. 3, from the slope and intercept of which the $k_4 = 0.24 \pm 0.14$ mol^{-1} dm^3 s^{-1} and $k_5 = 0.14 \pm 0.1$ s^{-1} values can be calculated. Although data for the second step of the 1–PDS reaction are not available, the above k_4 and k_5 values can be compared with those of 8.6×10^{-3} mol^{-1} dm^3 s^{-1} and 1.3×10^{-3} s^{-1} previously obtained for the related 3-hydroxy-3*H*-indole-PDS reaction.[1] These data reveal again that $H_4P_2O_8$ is a better electrophile than $HS_2O_8^-$ and, as expected, the phosphate ester I hydrolyses more rapidly than the corresponding sulfato ester.[15]

Oxidation of 1 by PMP

The values of the experimental pseudo-first-order rate constants $k_{obs.1}$ and $k_{obs.2}$ of the 1–PMP reaction at different PMP concentrations and hydrogen ion activities are reported in Tables 4 and 5. At fixed a_H, the plots of $k_{obs.1}$ and $k_{obs.2}$ against PMP concentration are straight lines passing through the origin. On the other hand, the change of the acidity of the media has a marked effect on $k_{obs.1}$, but it does not appreciably affect $k_{obs.2}$. The plot of $k_{obs.1}$ *vs.* a_H is curved. Attempts to fit the experimental data to different non-linear relationships were completely unsuccessful. Neither sigmoid nor double reciprocal plots adequately fit the experimental data. The deviations observed in these fits could not be imputed to an ionic strength effect, because the addition of Na_2SO_4 had negligible effect on $k_{obs.1}$.

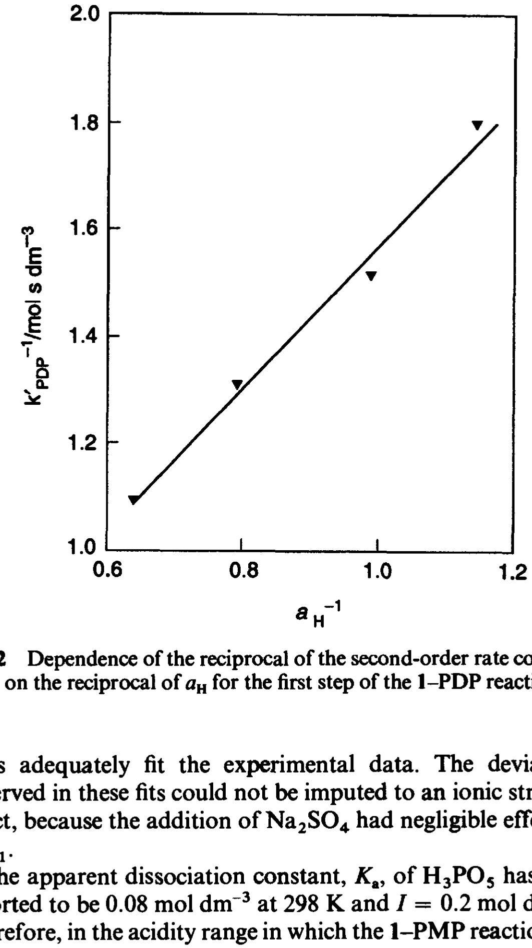


Fig. 2 Dependence of the reciprocal of the second-order rate constant k'_{PDP} on the reciprocal of a_H for the first step of the 1–PDP reaction

The apparent dissociation constant, K_a, of H_3PO_5 has been reported to be 0.08 mol dm^{-3} at 298 K and $I = 0.2$ mol dm^{-3}.[6] Therefore, in the acidity range in which the 1–PMP reaction has been studied, $a_H \gg K_a$, H_3PO_5 would largely be the predominant PMP species. In such a case, the reaction rate $k_{obs.1}$ should be independent of the acidity of the media. Thus, to explain the observed dependence of $k_{obs.1}$ with a_H, other active PMP species should be invoked.

In the hydrolysis of PMP[6] and other related phosphates,[16,17] the conjugate acids of the neutral molecules have been postulated to account for the observed rate–pH profiles of these reactions in the region of high acidity. Therefore, if we assume that neutral PMP protonates to form $H_4PO_5^+$ in a rapid equilibrium, the reaction scheme for the first step of 1–PMP reaction can be presented as eqns. (15)–(17), which leads to

$$H_4PO_5^+ \overset{K_6}{\rightleftharpoons} H_3PO_5 + H^+ \quad (15)$$

$$1 + H_4PO_5^+ \xrightarrow{k_7} 2 + H_3PO_4 \quad (16)$$

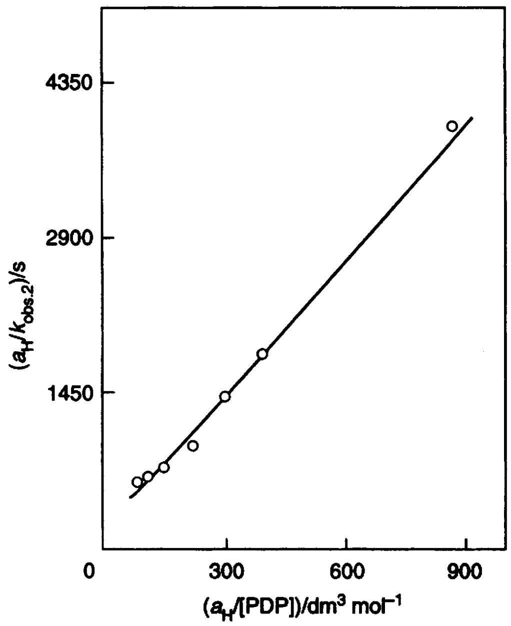


Fig. 3 Plot of $a_H/k_{obs,2}$ *vs.* $a_H/[PDP]$ for the second step of the 1–PDP reaction

Table 4 Pseudo-first-order rate constants $k_{obs,1}$ for the oxidation of **1** by PMP in 20% methanol–water at 298 K. [**1**] = 4 × 10^{-4} mol dm^{-3}

[PMP]/10^{-3} mol dm^{-3}	a_H	$k_{obs,1}/10^{-2}$ s^{-1}
1.64	0.605	1.76
3.27	0.605	3.36
4.91	0.605	5.17
6.54	0.605	6.62
1.72	0.486	1.76
1.72	0.523	2.07
1.72	0.563	2.33
1.72	0.651	2.81
1.72	0.754	3.21
1.72	0.873	3.53
1.72	1.17	4.24
1.72	1.36	4.51

Table 5 Pseudo-first-order rate constants $k_{obs,2}$ for the oxidation of **1** by PMP in 20% methanol–water at 298 K. [**1**] = 4 × 10^{-4} mol dm^{-3}

[PMP]/10^{-3} mol dm^{-3}	a_H	$k_{obs,2}/10^{-4}$ s^{-1}
1.48	0.605	4.918
2.23	0.605	9.601
2.97	0.605	15.195
4.45	0.605	27.24
1.72	0.754	5.230
1.72	0.873	5.281
1.72	1.170	4.980

$$\mathbf{1} + H_3PO_5 \xrightarrow{k_8} \mathbf{2} + H_2PO_4^- \quad (17)$$

the rate equation (18), where $[PMP]_t$ represents the total

$$v = -\frac{d[PMP]_t}{dt} = (k_7[H_4PO_5^+] + k_8[H_3PO_5])[\mathbf{1}] \quad (18)$$

concentration of PMP. Expressing $[H_4PO_5^+]$ and $[H_3PO_5]$ in terms of $[PMP]_t$, we can obtain eqn. (19) for the second-order rate constant.

$$k'_{PMP} = \frac{K_6k_8 + k_7(a_H)}{K_6 + (a_H)} \quad (19)$$

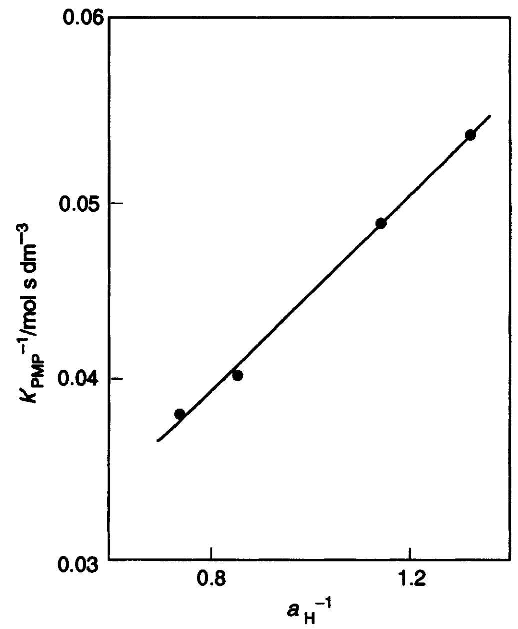
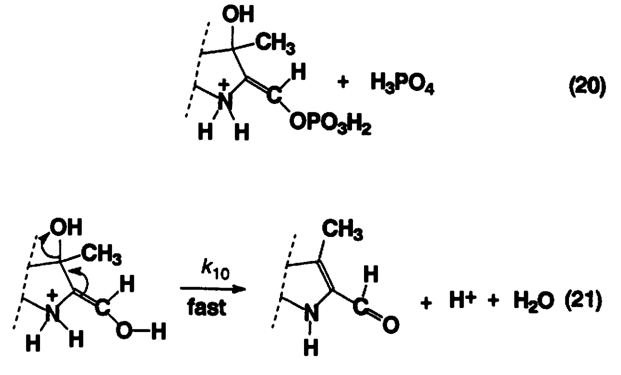


Fig. 4 Dependence of the reciprocal of the second-order rate constant k'_{PMP} on the reciprocal of a_H for the first step of the 1–PMP reaction

According to eqn. (19), at sufficiently high values of a_H, $K_6k_8 \ll k_7$ (a_H) and, therefore, the double reciprocal plot of k'_{PMP} *vs.* a_H would exhibit a linear dependence. As Fig. 4 shows, this linearity is reached for $a_H \geqslant 0.75$. From the slope and intercept of this linear plot, $k_7 = 59 \pm 14$ mol^{-1} dm^3 s^{-1} and $K_6 = 2 \pm 0.6$ values can be calculated. In comparison, the k_7 value for the 1–PMS reaction is 26 ± 2 mol^{-1} dm^3 s^{-1}.

Similarly, the second step of the 1–PMP reaction should take place through two parallel pathways involving the neutral and cationic PMP species, respectively. However, owing to the positive charge on the enaminic intermediate, the reaction pathway involving the neutral PMP species would be greatly favoured over that involving the cationic $H_4PO_5^+$ species. This would explain the negligible influence of acidity and ionic strength on the rate of this reaction. The proposed mechanism for the 2–H_3PO_5 reaction is shown in Scheme 4.



Scheme 4

The rate law for the mechanism in Scheme 4 is given in eqn. (22).

$$k_{obs.2} = k_9 \, [PMP] \qquad (22)$$

According to this equation, a plot of $k_{obs.2}$ *vs.* PMP should be linear with zero intercept. From the slope of this plot a value of $k_9 = 0.76 \pm 0.09$ dm^3 mol^{-1} s^{-1} can be obtained. This value is smaller than that of 3 dm^3 mol^{-1} s^{-1} obtained for the **1**–PMS reaction. Comparing the rate constants k_7 and k_9 for the **1**–PMP and **1**–PMS reactions reveals that HSO_5^- is a poorer electrophile than $H_4PO_5^+$, but better than H_3PO_5.

Conclusions

From this and previous studies we can conclude that the oxidation reactions of **1** by peroxophosphate and peroxosulfate species have essentially the same mechanism. There are, nevertheless, some differences between the reactions of these two types of peroxo compounds. From a kinetic point of view, the major difference is that, under our experimental conditions, the **1**–peroxophosphate reactions are acid-catalysed, while the **1**–peroxosulfate reactions are not. The dependence of the **1**–peroxophosphate reactions on hydrogen ion activity arises from the protonation equilibria experienced by the PDP and PMP species, eqns. (2) and (15), respectively.

Due to the different charges of the peroxophosphate and peroxosulfate species involved in the reactions, the factors influencing their electrophilic reactivities are more difficult to summarize. However, since $H_4P_2O_8$ is more reactive than $H_3P_2O_8^-$ and $H_4PO_5^+$ more than H_3PO_5, we can conclude that the electrophilic reactivity of the peroxo compounds increases with the number of protons bonded to them. This is probably related to the basicity of the leaving group (RO^-) in the peroxidic bond cleavage. According to the proposed polar mechanism, as the basicity of the RO^- group decreases, it becomes a better leaving group, thus increasing the reaction rate.[3,4] However, because HSO_5^- is a better electrophile than $HS_2O_8^-$, other factors, such as the polarization of the peroxidic oxygen–oxygen bond, also have influence on the electrophilic reactivity of the peroxo compounds.

Acknowledgements

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