Stoicheiometry and Kinetics of the Oxidation of Hydroxylamine by Peroxomonophosphoric Acid in Acidic Perchlorate Solutions and Catalysis by Iron(III) and Iodide or Iodine

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The stoicheiometry of the reaction of H_3PO_5 and NH_3OH^+ is variable depending on the ratio of the reactants, and the products of oxidation are $H_2N_2O_2$, HNO_2, and HNO_3. When $[NH_3OH^+] > 10[H_3PO_5]$, the stoicheiometry was as in equation (i) and the kinetics were followed under this condition. The rate

$$H_3PO_5 + NH_3OH^+ \longrightarrow H_3PO_4 + \tfrac{1}{2}H_2N_2O_2 + H_3O^+ \quad \text{(i)}$$

law is as in equation (ii) with $k_1 = (1.15 \pm 0.10) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} at 45 °C. The reaction is independent

$$-d[H_3PO_5]/dt = k_1[H_3PO_5][NH_3OH^+] \quad \text{(ii)}$$

of $[H^+]$ in the range 0.1—2.0 mol dm^{-3}, but is catalysed by Fe^{II} or Fe^{III}, and iodide or iodine. The rate laws in the last two cases are as in equations (iii) and (iv) where [I] represents the concentration of

$$-d[H_3PO_5]/dt = [H_3PO_5][NH_3OH^+](k_1 + k_2[Fe^{III}]) \quad \text{(iii)}$$

$$-d[H_3PO_5]/dt = [H_3PO_5](k_1[NH_3OH^+] + k_3[I] + k_4[I][NH_3OH^+]) \quad \text{(iv)}$$

iodide, iodate, or iodine. The values of k_2, k_3, and k_4 were found to be 1.5×10^2 dm^3 mol^{-1} s^{-1}, 1.45×10^3 dm^3 mol^{-1} s^{-1}, and 1.64×10^4 dm^6 mol^{-2} s^{-1} at 45 °C.

This is the second paper in a series [1] on the mechanism of reduction of peroxomonophosphoric acid (H_3PO_5), which is conveniently obtained by the hydrolysis [2] of peroxodiphosphate in aqueous acidic solution. Oxidations [3-5] by peroxodiphosphate in general involve its hydrolysis as the rate-determining step followed by faster reactions with peroxomonophosphoric acid. However, in the oxidation of hypophosphite with peroxodiphosphate,[6] both the hydrolytic step and the redox step were found to have comparable rates. This led to the study of redox reactions starting directly from peroxomonophosphoric acid.

In the past there have been reports on the oxidation of bromide [7] and a few organic compounds [8] by peroxomonophosphate, but more thorough investigations are required. Since we have been interested in the redox chemistry of inorganic compounds of N and P, hydroxylamine seemed to be a suitable choice after the previous study [1] of the oxidation of nitrite. Studies of the oxidation of hydroxylamine by other peroxy-compounds, *e.g.* peroxodisulphate [9] and hydrogen peroxide,[10] have already been made, although these reactions were catalysed by Cu^{II}.

Experimental

Materials.—Solutions of peroxomonophosphoric acid were prepared each day whenever required, by the hydrolysis of peroxodiphosphate in 0.5 mol dm^{-3} $HClO_4$ at 45 °C for about 1.5 h. They were standardized iodometrically. Solutions of lithium perchlorate were prepared by neutralizing 70% $HClO_4$ (E. Merck) with BDH AnalaR lithium carbonate to pH 6.8. Solutions of hydroxylamine were prepared by dissolving the appropriate quantity of BDH AnalaR hydroxylamine sulphate in water and were standardized by the bromate method.[11] All other chemicals were either BDH AnalaR of E. Merck G. R. quality and were used as such. All solutions were prepared in double-distilled water, the second distillation being from potassium tetraoxomanganate(VII). All glass vessels were of Corning make.

Kinetic Procedure.—Solutions of H_3PO_5 in aqueous perchloric acid in one flask and mixtures of hydroxylamine, perchloric acid, and other required chemicals in another flask were separately equilibrated in a thermostat at 45 ± 0.1 °C unless specified otherwise. The reaction was initiated by adding the required quantity of H_3PO_5 to the second flask, and its progress followed by the disappearance of H_3PO_5. Aliquots of 5 cm^3 were withdrawn after intervals of 10 or 15 min and added to ice-cold 10% KI solution (10 cm^3). Although no further hydrolysis of peroxomonophosphoric acid to hydrogen peroxide occurs, ice-cold solutions were employed to avoid any liberation of iodine from traces of H_2O_2, if formed. Lithium perchlorate was employed to adjust the ionic strength to 0.5 mol dm^{-3}.

Preliminary experiments indicated that the kinetic results were unaffected by the presence of sulphate ions and trace amounts of H_2O_2. The concentration of hydroxylamine was always in ten-fold excess over peroxomonophosphoric acid for reasons stated in connection with the stoicheiometry. All reactions were carried out in the presence of 1×10^{-5} mol dm^{-3} edta (ethylenediaminetetra-acetate) since without it the results were somewhat irreproducible. The catalysis or inhibition by trace amounts of elements is known to occur [12] in oxidations of hydroxylamine. It may also be mentioned that different samples of peroxodiphosphate gave different results within a factor of 2 and hence throughout this study the same sample of peroxodiphosphate was employed. Initial rates were determined by the plane-mirror method.[13] Pseudo-first-order plots were also constructed and the second-order rate constants calculated from both methods agreed within ±10%. The pseudo-first-order rate constants are designated as k_0.

Table 1. Stoicheiometry of the reaction of H_3PO_5 with NH_3OH^+ at 25 °C, $[H^+] = 0.25$ mol dm^{-3}, and $[I^-] = 1 \times 10^{-5}$ mol dm^{-3}

$10^2[H_3PO_5]$/ mol dm^{-3}	$10^2[NH_3OH^+]$/ mol dm^{-3}	Stoicheiometry [a]	Product identified
6.00	1.00	3.01	NO_3^-
5.10	1.00	3.07	NO_3^-
4.25	1.00	2.8	NO_3^-, NO_2^-
3.40	1.00	2.6	NO_3^-, NO_2^-
0.85	4.00	1.66	NO_2^-, $H_2N_2O_2$ (?)
0.85	5.00	2.00	NO_2^-
1.70	12.0	1.24	NO_2^-, $H_2N_2O_2$ (?)
0.85	7.0	1.13	$H_2N_2O_2$, NO_2^- (?)
0.85	9.0	0.95	$H_2N_2O_2$
0.425	4.0	1.01	$H_2N_2O_2$
0.64	6.0	0.97	$H_2N_2O_2$
1.06	10.0	1.05	$H_2N_2O_2$
1.27	12.0	1.00	$H_2N_2O_2$
1.00	2.0	1.93 [b]	$N_2(NO_2^-)$
1.00	1.50	2.04 [b]	$N_2(NO_2^-)$
1.00	2.50	2.00 [b]	$N_2(NO_2^-)$

[a] Ratio of H_3PO_5 reacted to NH_3OH^+ reacted. [b] In the presence of sulphamic acid, nitrite would decompose to nitrogen.

Results

Stoicheiometry.—In the study of the stoicheiometry, solutions of H_3PO_5 and hydroxylamine of different concentrations in a suitable acidic medium were mixed. The reaction is slow, but the mixture could not be left for a long time to go to completion since H_3PO_5 is significantly hydrolysed to H_2O_2. It was found that the reaction is greatly catalysed by iodide ions and hence the determination of the stoicheiometry was made in the presence of small concentrations (1×10^{-5} mol dm^{-3}) of iodide; in this way the reaction was over in about 40 min. Excess of H_3PO_5 was determined iodometrically in ice-cold solutions and excess of hydroxylamine was determined by direct titration [14] with iodine (in KI) in the presence of MgO. Other methods of determining hydroxylamine were not suitable. The results are given in Table 1.

When $[H_3PO_5] > 5[NH_3OH^+]$, nitrate was the product and about 3 mol of H_3PO_5 were consumed by each mol of hydroxylamine, corresponding to a six-electron change for N in NH_3OH^+. For other ratios of H_3PO_5 and NH_3OH^+ (except when $[NH_3OH^+] > 10[H_3PO_5]$) the products were nitrite and nitrate, and probably $H_2N_2O_2$, also depending on the ratio of the reactants, and the stoicheiometry was variable between 3 and 1 : 1. A very small amount of a gas, which could not be identified, also formed probably as a result of the reaction [15] between HNO_2 and $H_2N_2O_2$ and this could be nitrogen. If the reactions are carried out in the presence of sulphamic acid to decompose the nitrite formed, 2 mol of H_3PO_5 are consumed in each case by 1 mol of hydroxylamine, even though $[NH_3OH^+] > [H_3PO_5]$. These results conform to equations (1) and (2).

$$3H_3PO_5 + NH_3OH^+ \longrightarrow 3H_3PO_4 + HNO_3 + H_3O^+ \quad (1)$$

$$2H_3PO_5 + NH_3OH^+ \longrightarrow 2H_3PO_4 + HNO_2 + H_3O^+ \quad (2)$$

When $[NH_3OH^+] > 10[H_3PO_5]$, no nitrite or nitrate seemed to be formed, but very small amounts of gas were evolved. The product $H_2N_2O_2$ was identified as follows. The reaction mixtures (acidic) showed an absorption peak at 207 nm which accounts for about 90% of the product ($H_2N_2O_2$) with an ε value [16] of 4.61×10^3 dm^3 mol^{-1} cm^{-1}. The same mixtures in 0.02 mol dm^{-3} NaOH showed a peak at 232 nm corresponding to $HN_2O_2^-$, and in 1.0 mol dm^{-3} NaOH showed a peak [17] at 248 nm, but the results were not quantitative. These measurements were made immediately after adding the alkali since hydroxylamine decomposes [18] in alkaline solutions yielding products which absorb. For the gas analysis the pH of the reaction mixture was brought to about 9 at which $HN_2O_2^-$ is unstable [17] and the gas was collected over water saturated with N_2O prepared [19] from concentrated solutions of nitrite and hydroxylamine hydrochloride. This gas dissolves in water, supports combustion, and is easily condensed in liquid nitrogen. After taking into account the gas dissolved in the solution, the amount accounted for 95% of the product N_2O. It is thus obvious that the stoicheiometry and the products of the reaction depend on the relative concentrations of H_3PO_5 and NH_3OH^+, as is also found in oxidations with other metal ions and oxoanions. In a recently published paper [20] on the oxidation of hydroxylamine with iodate and periodate, N_2O was reported as the major product. For kinetics studies we employed only those conditions in which $H_2N_2O_2$ is formed according to equation (3).

$$H_3PO_5 + NH_3OH^+ \longrightarrow H_3PO_4 + \tfrac{1}{2}H_2N_2O_2 + H_3O^+ \quad (3)$$

Peroxomonophosphoric Acid and Hydroxylamine Dependence.—The concentration of H_3PO_5 was varied in the range $(1.6 - 7.75) \times 10^{-3}$ mol dm^{-3} at fixed concentrations of the other reactants. Similarly, the concentration of hydroxylamine was varied in the range $(4—22) \times 10^{-2}$ mol dm^{-3}. The results are shown in Table 2. The second-order rate constant, k_1, from the pseudo-first-order plots was found to be $(1.15 \pm 0.19) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} at 45 °C, $I = 0.5$ mol dm^{-3}, and $[H^+] = 0.25$ mol dm^{-3}. The corresponding value obtained from the initial rates was $(1.15 \pm 0.10) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. The values of k_1 at 35 and 55 °C were $(0.60 \pm 0.10) \times 10^{-3}$ and $(3.6 \pm 0.2) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} under the same conditions.

Hydrogen-ion Dependence.—The hydrogen-ion concentration was varied with the help of $HClO_4$ in the range 0.1—2.0 mol dm^{-3} at three different concentrations of H_3PO_5, 3×10^{-3}, 5×10^{-3}, and 7×10^{-3} mol dm^{-3}, and at three different concentrations of hydroxylamine, 1×10^{-1}, 1.5×10^{-1}, and 2×10^{-1} mol dm^{-3}, but there was no effect on the rate.

Effect of Phosphate Ions.—The concentration of phosphate (in the form of sodium dihydrogenphosphate) was varied from 5×10^{-3} to 15×10^{-3} mol dm^{-3}, under the conditions in Table 1, but no effect was observed.

Catalysis by Iron(III).—Since trace amounts of iron(II) or iron(III) are always present in the reagents and they have some role in influencing the rate of oxidation of hydroxylamine, a few experiments were studied in the presence of iron(II) and iron(III) sulphate. The results (Table 3) were similar in both cases, obviously because such trace amounts of iron(II) would be converted into the higher oxidation state in the presence of H_3PO_5. A plot of rate *versus* $[Fe^{II}]$ or $[Fe^{III}]$ is linear with an intercept, suggesting a rate law of the form (4) where A and B are constants. Also the variation of hydroxylamine

$$-d[H_3PO_5]/dt = (A + B[Fe^{III}]) \quad (4)$$

Table 2. Initial rates (v_0), pseudo-first-order rate constants (k_0), and derived second-order rate constants (k_1) in the H_3PO_5–NH_3OH^+ reaction. $[H^+] = 0.25$ mol dm^{-3}, $I = 0.5$ mol dm^{-3}, [edta] $= 1 \times 10^{-5}$ mol dm^{-3}, 45 °C

$10^3[H_3PO_5]$	$10^2[NH_3OH^+]$	10^6v_0	10^3k_1 [a]	10^3k_0	10^3k_1 [b]
mol dm^{-3}		mol dm^{-3} s^{-1}	dm^3 mol^{-1} s^{-1}	s^{-1}	dm^3 mol^{-1} s^{-1}
1.60	10.0	0.19	1.18	0.105	1.05
2.33	10.0	0.26	1.13	0.110	1.10
3.20	10.0	0.35	1.08	0.110	1.10
4.00	10.0	0.44	1.11	0.125	1.25
4.62	10.0	0.49	1.06	0.120	1.20
5.27	10.0	0.595	1.13	0.130	1.30
6.24	10.0	0.65	1.05	0.102	1.02
7.75	10.0	0.77	1.00	0.096	0.96
4.10	4.0	0.20	1.26	0.0383	0.95
4.10	6.0	0.29	1.18	0.058	0.98
4.10	8.0	0.38	1.17	0.096	1.20
4.10	10.0	0.465	1.14	0.125	1.25
4.10	12.0	0.57	1.17	0.146	1.22
4.10	14.0	0.67	1.17	0.174	1.24
4.10	16.0	0.79	1.21	0.185	1.16
4.10	18.0	0.90	1.23	0.225	1.25
4.10	20.0	1.02	1.25	0.240	1.20
4.10	22.0	1.11	1.24	0.275	1.25
		Average	1.15 ± 0.06		1.15 ± 0.10

[a] From the initial rates. [b] From the pseudo-first-order rate constants.

Table 3. Reaction of H_3PO_5 and NH_3OH^+ in the presence of Fe^{II} and Fe^{III}. $[H_3PO_5] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[NH_3OH^+] = 0.1$ mol dm^{-3}, $[H^+] = 0.25$ mol dm^{-3}, $I = 0.5$ mol dm^{-3}, [edta] $= 1 \times 10^{-5}$ mol dm^{-3}, 45 °C

$10^5[Fe^{II}]$/mol dm^{-3}	0.10	0.30	0.70	1.00	2.00	3.00
10^6v_0/mol dm^{-3} s^{-1}	0.69	0.78	0.95	1.23	1.6	2.4
$10^5[Fe^{III}]$/mol dm^{-3}	0.10	0.30		1.00		3.00
10^6v_0/mol dm^{-3} s^{-1}	0.68	0.80		1.10		2.4
$10^5[Fe^{II}]$/mol dm^{-3}	4.00	5.00	6.00			
10^6v_0/mol dm^{-3} s^{-1}	3.0	3.5	4.2			
$10^5[Fe^{III}]$/mol dm^{-3}		5.00				
10^6v_0/mol dm^{-3} s^{-1}		3.5				

Table 4. Effect of variation of $[NH_3OH^+]$ and $[H_3PO_5]$ in the reaction of H_3PO_5 with NH_3OH^+ in the presence of Fe^{III}. $[H^+] = 0.25$ mol dm^{-3}, $I = 0.5$ mol dm^{-3}, [edta] $= 1.0 \times 10^{-5}$ mol dm^{-3}, 45 °C

(*a*) $[H_3PO_4] = 4.04 \times 10^{-3}$, $[Fe^{III}] = 1.0 \times 10^{-5}$ mol dm^{-3}

$10^2[NH_3OH^+]$/mol dm^{-3}	2.75	4.0	5.5	6.75	8.0	9.5
10^6v_0/mol dm^{-3} s^{-1}	0.28	0.5	0.63	0.84	0.92	1.00
$10^2[NH_3OH^+]$/mol dm^{-3}	11.0	12.0				
10^6v_0/mol dm^{-3} s^{-1}	1.27	1.39				

(*b*) $[H_3PO_5] = 3.8 \times 10^{-3}$, $[Fe^{III}] = 2.0 \times 10^{-5}$ mol dm^{-3}

$10^2[NH_3OH^+]$/mol dm^{-3}	4.00	6.00	10.00	12.0	14.0	16.0
10^6v_0/mol dm^{-3} s^{-1}	0.69	1.14	1.70	2.1	2.45	2.7
$10^2[NH_3OH^+]$/mol dm^{-3}	18.0	20.0				
10^6v_0/mol dm^{-3} s^{-1}	3.0	3.3				

(*c*) $[NH_3OH^+] = 0.1$, $[Fe^{III}] = 1.0 \times 10^{-5}$ mol dm^{-3}

$10^3[H_3PO_5]$/mol dm^{-3}	2.0	4.0	6.0	8.0
10^6v_0/mol dm^{-3} s^{-1}	0.60	1.2	1.75	2.3

and H_3PO_5 was done in the presence of iron(III) to verify whether the rate dependence on them remains the same. The results are given in Table 4. A plot of rate *versus* $[NH_3OH^+]$ or $[H_3PO_5]$ is linear passing through the origin and hence the rate law is of the form (5).

$$-d[H_3PO_5]/dt = [H_3PO_5][NH_3OH^+](k_1 + k_2[Fe^{III}]) \quad (5)$$

Catalysis by Copper(II).—This was studied with copper(II) sulphate under the conditions in Table 2. The initial rates for 2×10^{-4}, 4×10^{-4}, and 6×10^{-4} mol dm^{-3} copper(II) were 0.64×10^{-6}, 0.68×10^{-6}, and 0.78×10^{-6} mol dm^{-3} s^{-1} respectively and hence copper(II) is not an effective catalyst for the reaction.

Catalysis by Iodide, Iodine, and Iodate.—The reaction is greatly catalysed by iodide ions as shown in Table 5. A plot of rate *versus* $[I^-]$ is linear with an intercept, suggesting a rate law similar to (4). However, variations of the concentrations of H_3PO_5 and hydroxylamine gave results (Table 6) somewhat different from those in the case of Fe^{III}. A plot of rate *versus* $[H_3PO_5]$ is linear passing through the origin, suggesting a first-order dependence on $[H_3PO_5]$. However, a plot of rate *versus* $[NH_3OH^+]$ is linear with an intercept and hence in the presence of iodide ions there should be at least one term in the rate law which is independent of $[NH_3OH^+]$. The rate law is likely to be of the form (6) where C and D are constants.

$$-d[H_3PO_5]/dt = [H_3PO_5](C[NH_3OH^+] + D[I^-]) \quad (6)$$

In the presence of aqueous iodine the results were similar to those in the case of iodide (Tables 5 and 7). The results with iodate are identical with those at the same molar concentrations of iodide (Table 5).

Discussion

In the acidic perchlorate medium employed in this investigation hydroxylamine would be completely protonated [21] and hence is shown as NH_3OH^+. Peroxomonophosphoric acid has a first acid dissociation constant of 0.08 mol dm^{-3} at 25 °C, and in 0.25 mol dm^{-3} $HClO_4$ it is likely to be present as H_3PO_5 and $H_2PO_5^-$. However, since the rate of the present reaction is unaffected by variation in $[H^+]$, both forms of

Table 5. Effect of iodide, iodine, and iodate in the reaction of H_3PO_5 with NH_3OH^+. $[H_3PO_5] = 4.00 \times 10^{-3}$ mol dm^{-3}, $[NH_3OH^+] = 0.1$ mol dm^{-3}, $[H^+] = 0.25$ mol dm^{-3}, $I = 0.5$ mol dm^{-3}, [edta] = 1.0×10^{-5} mol dm^{-3}, 45 °C

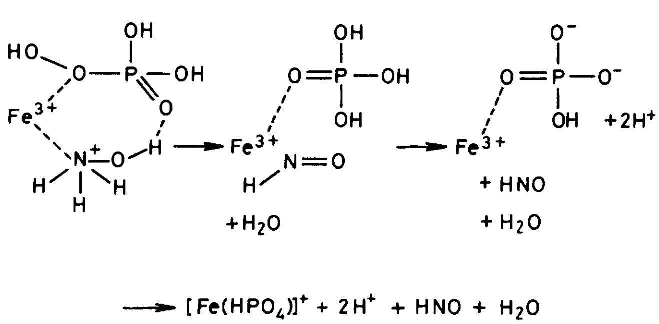
$10^7[I^-]$/mol dm^{-3}	2.00	4.00	6.00	8.00	10.0		
10^6v_0/mol dm^{-3} s^{-1}	3.2	5.5	8.1	10.4	13.0		
$10^7[I_2]$/mol dm^{-3}	0.75	1.75	3.0	4.5		6.0	6.75
10^6v_0/mol dm^{-3} s^{-1}	2.45	4.8	8.0	11.5		15.5	17.5
$10^7[IO_3^-]$/mol dm^{-3}	1.0	2.0	4.0	6.0	8.0	10.0	12.0
10^6v_0/mol dm^{-3} s^{-1}	1.75	3.3	5.6	7.7	10.2	12.5	14.5

the acid should be equally reactive towards hydroxylamine. A similar situation was found in the oxidation[22] of hypophosphite by thallium(III) wherein the reaction was independent of $[H^+]$ in the range 0.3—1.0 mol dm^{-3}, although the acid dissociation constant[23] of H_3PO_2 is 0.135 mol dm^{-3} and it would exist as H_3PO_2 and $H_2PO_2^-$. In any case the oxidation of hydroxylamine with peroxomonophosphoric acid is a simple bimolecular reaction (7) with a second-order rate constant of 1.15×10^{-3} dm^3 mol^{-1} s^{-1} at 45 °C and $I = 0.5$ mol dm^{-3}.

$$-d[H_3PO_5]/dt = k_1[H_3PO_5][NH_3OH^+] \quad (7)$$

The plot of rate *versus* [Fe^{III}] for the reactions in the presence of Fe^{III} yields an intercept equal to 0.50×10^{-6} mol dm^{-3} s^{-1} or a second-order rate constant of 1.25×10^{-3} dm^3 mol^{-1} s^{-1} which is very similar to that for the uncatalysed reaction. From the slope of this straight line, the value of k_2 was found to be 1.5×10^2 dm^6 mol^{-2} s^{-1}. The slope of a plot of rate *versus* $[NH_3OH^+]$ after division by $[H_3PO_5]$ is equal to $(k_1 + k_2[Fe^{III}])$ and this was found to be 4.4×10^{-3} and 2.6×10^{-3} dm^3 mol^{-1} s^{-1} for $[Fe^{III}] = 2 \times 10^{-5}$ and 1×10^{-5} mol dm^{-3} respectively. The calculated values were 4.25×10^{-3} and 2.75×10^{-3} dm^3 mol^{-1} s^{-1} respectively. The agreement can be regarded as satisfactory and is in conformity with equation (5).

The catalysis by Fe^{III} can be explained by its formation of a weak complex with NH_3OH^+ which may be more reactive than hydroxylamine itself. A ternary complex of H_3PO_5, NH_3OH^+, and Fe^{3+} is then likely to be formed as shown below, and as reported in the case of Cu^{2+}-catalysed oxidations with hydrogen peroxide and peroxodisulphate.[9]



Since the product of reaction (phosphate) is stabilized by strong complex formation with Fe^{3+}, a transition state with iron(III) is more facile. Moreover, ternary complexes are considered to be more stable[24] than binary complexes and hence the ternary complex seems to be a possible intermediate. Such a ternary complex has also been assumed in the Fe^{III}-catalysed oxidation[25] of hydrazine with peroxodisulphate.

The plots of rate *versus* iodide and iodine are also linear with the same intercept equal to 0.65×10^{-6} mol dm^{-3} s^{-1}. This when converted into a rate constant is equal to 1.6×10^{-3} dm^3 mol^{-1} s^{-1}. The different slopes, after dividing by $[H_3PO_5]$ and taking into account the fact that $[I_2]$ would be equivalent to $[2I^-]$ were found to yield the same value, 3.1×10^3 dm^3 mol^{-1} s^{-1}. From this it is obvious that the reaction mechanism is essentially the same in the presence of iodide or iodine. The above two sets of experiments can be considered to have been carried out under two different concentrations of iodide or iodine. The results of the variation of the hydroxylamine concentration in these cases indicate that the rate law is more complicated than shown in equation (6). The catalysis by iodide/iodine and the independence of $[NH_3OH^+]$ suggest that there is direct reaction between H_3PO_5 and iodide and that the oxidation of NH_3OH^+ probably occurs with iodine in the fast step. However, since the intercepts and slopes of the straight lines in the two cases are not equal, and also since the slopes of the lines do not yield the correct value of k_1, the rate law has a third term as shown in equation (8).

$$-d[H_3PO_5]/dt = [H_3PO_5](k_1[NH_3OH^+] + k_3[I^-] + k_4[NH_3OH^+][I^-]) \quad (8)$$

Thus catalysis by iodide occurs in a different way to that which results in the formation of iodine in a higher oxidation state.

The slope of the linear plot of rate *versus* $[NH_3OH^+]$ is equal to $[H_3PO_5](k_1 + k_4[I^-])$. This has values of 18.5×10^{-6} and 33.6×10^{-6} s^{-1} for 2×10^{-7} mol dm^{-3} KI and 1.75×10^{-7} mol dm^{-3} I_2. If these values are divided by $[H_3PO_5]$ and k_1 ($=1.6 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}) is subtracted from them, the values of k_4 are found to be 1.65×10^4 and 1.63×10^4 dm^6 mol^{-2} s^{-1}. Since the values of k_4 are similar, the rate law (8) appears to hold. The intercepts of these lines are equal to

Table 6. Effect of variation of $[H_3PO_5]$ and $[NH_3OH^+]$ in the iodide-catalysed reaction. $[I^-] = 2.0 \times 10^{-7}$ mol dm^{-3}, $[H^+] = 0.25$ mol dm^{-3}, $I = 0.5$ mol dm^{-3}, [edta] = 1×10^{-5} mol dm^{-3}, 45 °C

(*a*) $[H_3PO_5] = 3.8 \times 10^{-3}$ mol dm^{-3}

$10^2[NH_3OH^+]$/mol dm^{-3}	4.00	6.00	8.00	10.0	12.0	14.0
10^6v_0/mol dm^{-3} s^{-1}	1.0	2.4	2.8	3.1	3.3	3.6
$10^2[NH_3OH^+]$/mol dm^{-3}	16.0	18.0	20.0			
10^6v_0/mol dm^{-3} s^{-1}	4.2	4.55	4.9			

(*b*) $[NH_3OH^+] = 0.1$ mol dm^{-3}

$10^3[H_3PO_5]$/mol dm^{-3}	0.78	1.55	2.30	3.35	3.85	5.27
10^6v_0/mol dm^{-3} s^{-1}	0.70	1.45	1.95	2.5	3.2	4.25
$10^3[H_3PO_5]$/mol dm^{-3}	6.15					
10^6v_0/mol dm^{-3} s^{-1}	4.9					

Table 7. Effect of variation of $[H_3PO_5]$ and $[NH_3OH^+]$ in the iodine-catalysed reaction. $[I_2] = 1.75 \times 10^{-7}$ mol dm^{-3}, $[H^+] = 0.25$ mol dm^{-3}, $I = 0.5$ mol dm^{-3}, [edta] = 1.0×10^{-5} mol dm^{-3}, 45 °C

(*a*) $[NH_3OH^+] = 0.1$ mol dm^{-3}

$10^3[H_3PO_5]$/mol dm^{-3}	0.74	2.24	3.32	3.82	4.5	5.2
10^6v_0/mol dm^{-3} s^{-1}	1.45	3.3	3.35	5.4	6.5	7.2
$10^3[H_3PO_5]$/mol dm^{-3}	6.0					
10^6v_0/mol dm^{-3} s^{-1}	8.3					

(*b*) $[H_3PO_5] = 4.10 \times 10^{-3}$ mol dm^{-3}

$10^2[NH_3OH^+]$/mol dm^{-3}	4.0	6.0	8.0	10.0	12.0	14.0
10^6v_0/mol dm^{-3} s^{-1}	3.6	4.2	5.0	5.5	6.1	6.7
$10^2[NH_3OH^+]$/mol dm^{-3}	16.0	18.0	20.0	22.0		
10^6v_0/mol dm^{-3} s^{-1}	7.3	7.8	8.3	9.1		

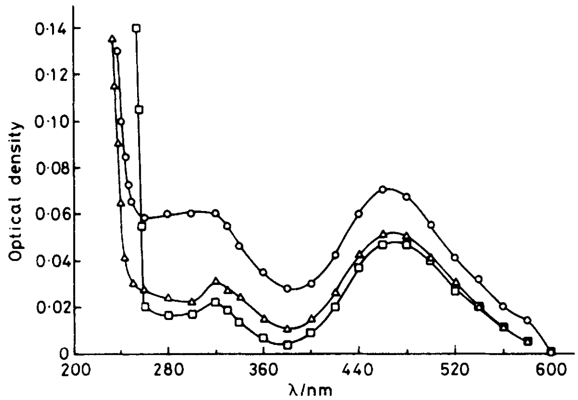


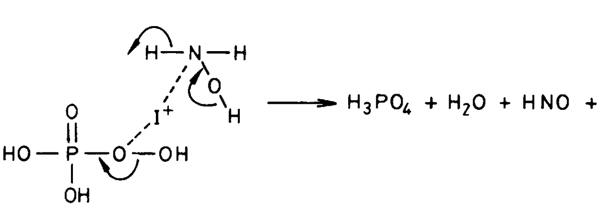
Figure. Optical densities of I_2 and mixtures of I_2 and H_3PO_5: ○, $[I_2] = 1 \times 10^{-4}$; △, $[I_2] = 1 \times 10^{-4}$ and $H_3PO_5 = 1 \times 10^{-3}$; □, $[I_2] = 1 \times 10^{-4}$ and $[H_3PO_5] = 1 \times 10^{-2}$ mol dm^{-3}

1.25×10^{-6} and 2.4×10^{-6} mol dm^{-3} s^{-1} for the above concentrations of iodide and iodine. The k_3 values calculated from these are found to be 1.65×10^3 and 1.67×10^3 dm^3 mol^{-1} s^{-1}. Again the agreement is very satisfactory.

A plot of rate *versus* $[H_3PO_5]$ is linear passing through the origin and of slope ($k_1[NH_3OH^+] + k_3[I^-] + k_4[NH_3OH^+][I^-]$). The graphical slopes are 8.0×10^{-4} and 14.2×10^{-4} s^{-1} for the above mentioned concentrations of iodide and iodine. The slopes calculated with average values of k_3 ($=1.45 \times 10^3$ dm^3 mol^{-1} s^{-1}) and k_4 (1.64×10^4 dm^6 mol^{-2} s^{-1}) are 7.8×10^{-4} and 12.5×10^{-4} s^{-1}. Again, from the plot of rate *versus* $[I^-]$ or $[I_2]$, the slope equal to ($k_3 + k_4[NH_3OH^+]$) was found to be 12.4 dm^3 mol^{-1} s^{-1} (calculated value 12.3). Thus the results have fairly good internal consistency.

The reaction of iodine with hydroxylamine is slow.[26] It is likely to be faster in the absence of trace amounts of iodide, but it does not appear to be faster than the reaction of H_3PO_5 and iodide. The I^-/IO_3^- cycle also does not seem to operate since visual observation of H_3PO_5 and aqueous iodine indicated a slow reaction. The reaction of iodine(I) with hydroxylamine is fast and hence catalysis appears to operate through the I^-/I^+ cycle. The inclusion of the second term in the rate law (8) could thus be explained.

The third term of the rate law arises out of the catalysis by I^+ which is produced by the oxidation of iodide/iodine. The iodine(I) forms a ternary complex with H_3PO_5 and hydroxylamine. This appears to be reasonable in view of the marginal evidence for a complex of H_3PO_5 and iodine in the Figure, which is in fact a complex of H_3PO_5 and iodine(I). The probable structure of the activated complex is shown below.



Edwards[27] has suggested a mechanism for oxidations by peroxides in which there is nucleophilic attack on the peroxide oxygen. In the present case the order of reactivity with H_3PO_5 is bromide,[7] nitrite,[28] hydrazine,[29] and hydroxylamine. This appears to be in accord with the nucleophilic action of these reducing substances on the peroxide oxygen, which is said to depend largely on the polarisability and less on the basicity of the nucleophiles.[26] However, this mechanism should not be considered established unless nucleophilic attack on oxygen is tenable in other redox systems of H_3PO_5. Moreover, the inclusion of hydrazine and hydroxylamine in this list is not very logical since these are generally contaminated with trace metal ions which may act as catalysts, either as such or in the form of edta complexes. There is no direct attack of the nucleophile on the oxygen in the case of catalysed reactions.

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