Kinetics and Mechanisms of Redox Reactions in Aqueous Solution. Part 5.[1] Oxidation of Hypophosphorous Acid by Cerium(IV) in Aqueous Nitric Acid

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The rate of title reaction has a first-order dependence both on [Ce^{IV}] and [H^+], and an order less than unity on [H_3PO_2]. However, the observed first-order rate constant $k_{obs.}$ is dependent on the initial [Ce^{IV}], decreasing with increasing [Ce^{IV}]. The rate-limiting step is considered to be attack of a proton on the intermediate complex formed between Ce^{IV} and the active tautomer of hypophosphorous acid. The energy and entropy of activation for the rate-limiting reaction have values of 66 ± 2 kJ mol^{-1} and −88 ± 8 J K^{-1} mol^{-1} respectively. The reaction is catalysed by Ag^I and there is no change in the order of the reaction with respect to [Ce^{IV}]. The relation between $k_{obs.}$ and [Ag^I] is consistent with the equation (i) where *a* and *b* are constants.

$$k_{obs.} = a + b[Ag^I] \quad (i)$$

HYPOPHOSPHOROUS acid, H_3PO_2, in aqueous acid solution is believed to exist in two tautomeric forms and their interconversion is catalysed by hydrogen ion. The two tautomers are known as the active and inactive forms; the active form $HP(OH)_2$ has a pair of electrons available on the phosphorus atom. The existence of equilibrium (1) has been verified by measurements of the isotope-exchange rates between deuteriated [2] or tritiated [3] water and hypophosphorous acid.

$$H_2PO(OH) + H^+ \rightleftharpoons HP(OH)_2 + H^+ \quad (1)$$

The oxidation of hypophosphorous acid by Cu^{II}, halogens, and Ag^I are reported to involve the active tautomer and are characterised by a zero-order rate dependence on oxidant concentration.[4] However, the oxidations of H_3PO_2 by cerium(IV) (perchlorate [5] and sulphate [6]), vanadium(V) (perchlorate [7] and sulphate [8,9]), and chromium(VI) [10,11] exhibit a first-order dependence on oxidant concentration. Considering that the reactivity of the active tautomer $HP(OH)_2$ has been linked to a zero-order rate dependence on oxidant concentration, it was decided to investigate whether a first-order dependence in [oxidant] could be associated, in general, with the involvement of the inactive form $H_2PO(OH)$. A previous study with cerium(IV) perchlorate [5] did not offer any explanation for the retardation in the observed rate with increasing [Ce^{IV}], and left the question of the relative reactivities of the two tautomers unanswered.

While this paper awaited publication, our attention was drawn by one of the referees to the publication of the results of a reinvestigation of the kinetics of the Ce^{IV} $+H_3PO_2$ reaction in perchloric acid studied by the method of *I–t* curves at constant-potential and cyclic current-potential curves on a vibrating platinum electrode.[12] The results indicated that the redox reaction takes place in six parallel oxidation-reduction steps through intermediate complexes $[Ce(H_2PO_2)_n]^{4-n}$. It might be noted here that the mechanism proposed by us is basically the same as that proposed by Treindl and Hatala,[12] but it seems that we are able to propose a much clearer definition of the individual concentration dependences.

EXPERIMENTAL

Materials.—Cerium(IV) solutions were freshly prepared by direct dissolution of a primary standard-grade sample of ammonium cerium(IV) nitrate (G. F. Smith Chemical Co.) in a standard aqueous solution of nitric acid (Basynth's AnalaR grade). Although water slowly reduces Ce^{IV}, the rate of this reduction was too slow to affect any of our kinetic results. A stock solution of H_3PO_2 was prepared by dilution of a 50% aqueous purum grade (Fluka) sample. It was standardised iodimetrically.[13] Silver nitrate solution was prepared by direct weighing and dissolution of the sample (Sarabhai-M. Chemicals, G.R. grade) and the solution was stored in a black Polythene bottle.

All the solutions were prepared in water redistilled from an all-glass unit. Other solutions were either prepared by direct weighing of samples or were analysed by standard methods. All the chemicals were used as obtained without any further purification.

Kinetic Measurements.—The reactant solutions were thermostatted in a water-bath, maintained at 19 ± 0.1 °C unless stated otherwise. The reaction was generally initiated by the rapid addition of cerium(IV) solution to solutions containing the desired concentrations of H_3PO_2 and nitric acid. The concentrations were adjusted so that [H_3PO_2] was always in excess of [Ce^{IV}]. However, it was found that the reaction system was prone to precipitation when [H_3PO_2] > 0.005 mol dm^{-3} at [H^+] = 0.4 mol dm^{-3} and 10^4[Ce^{IV}] = 5 mol dm^{-3} at I = 2 mol dm^{-3} and 22 °C. This restricts the amount of variation of the reactants.

The progress of the reaction was monitored by observing the absorbance of the cerium(IV) solution at 331 nm in a Beckman DU 2 spectrophotometer using cells of 1-cm path length. The reference solution was aqueous HNO_3 of the same concentration as that present in the reaction mixture. Sodium nitrate (B.D.H., AnalaR) was used to keep [NO_3^-] constant at 2 mol dm^{-3}. The observed first-order rate constant $k_{obs.}$ was calculated from the gradients of plots of log(absorbance) against time; these plots were linear for >80% completion of reaction. The gradients were calculated by a least-squares method. The reported $k_{obs.}$ values are averages obtained from duplicate or triplicate runs; values from repeated runs agreed to within ±2—3%. The linear correlation coefficient in all cases was better than 99%.

RESULTS

Stoicheiometry.—Several reaction mixtures having various ratios of [Ce^{IV}] and [H_3PO_2], [Ce^{IV}] being in excess, were prepared and left at room temperature (25 °C). They were analysed for Ce^{IV} from time to time. It was found that the initial rate of reduction of Ce^{IV} was fast but became sluggish when almost two equivalents of Ce^{IV} had been used up. The sluggish reduction of Ce^{IV} by phosphorous acid was independently checked in separate experiments. The stoicheiometric equation is thus written as in (2).

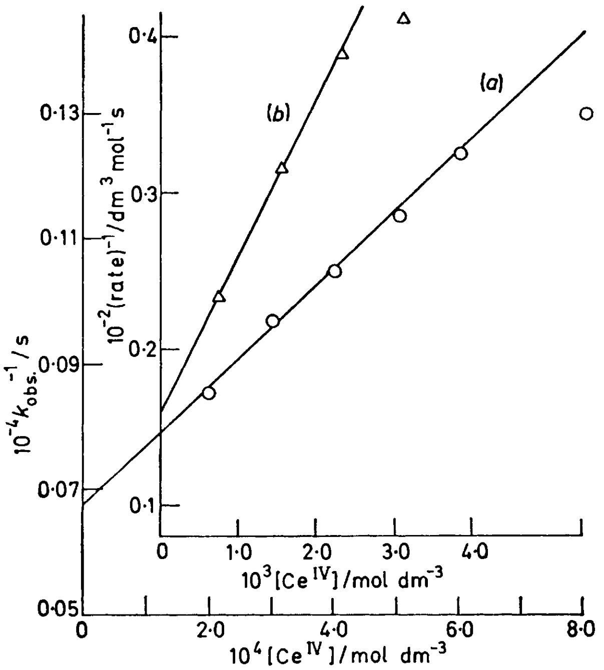

FIGURE 1 Plots of $10^{-4}\ k_{obs.}^{-1}$ (*a*, data from Table 1) and 10^{-2} (rate)$^{-1}$ (*b*, data from ref. 5) against [Ce^{IV}]$_T$

$$H_3PO_2 + 2Ce^{IV} + H_2O \longrightarrow H_3PO_3 + 2Ce^{III} + 2H^+ \quad (2)$$

Dependence on [Ce^{IV}].—Although the plots of log(absorbance) against time were linear for all [Ce^{IV}]$_T$ investigated, where the subscript T denotes the initial total concentration, it was found that $k_{obs.}$ values decreased with increasing [Ce^{IV}]$_T$. A perusal of Table 1 might suggest the decrease is not appreciable in relation to the change in initial [Ce^{IV}]$_T$, but nevertheless it is significant. A similar dependence of the rate constant on [Ce^{IV}]$_T$ was also observed by Carroll and Thomas.[5] It was also noted that a plot of $1/k_{obs.}$ against [Ce^{IV}]$_T$, Figure 1, was linear. Plot (*b*) in Figure 1 was obtained from the data of Carroll and Thomas.[5] A similar linear relation was also observed in the decarboxylation of aliphatic acids and in the oxidation of some diols by ammonium cerium(IV) nitrate in aqueous nitric acid solution.[14]

TABLE 1

Dependence of the observed first-order rate constant $k_{obs.}$ on [Ce^{IV}] at [H_3PO_2] = 0.003 mol dm^{-3}, [H$^+$] = 2 mol dm^{-3}, [NO_3^-] = 2.006 mol dm^{-3}, and 19 °C

10^4 [Ce^{IV}]/mol dm^{-3}	2.0	3.0	4.0	5.0	6.0	8.0
10^4 $k_{obs.}$/s^{-1}	11.7	10.3	9.5	8.8	8.1	7.7

The reduced reactivity of Ce^{IV} in solutions of higher [Ce^{IV}]$_T$ is considered to be due either to the presence of dimeric cerium(IV) species[15] which are unreactive[16] or due to the reaction of Ce^{IV} with another form of the substrate obtained in a pre-equilibrium step (1) preceding the rate-limiting reaction.

Dependence on [Ce^{III}].—The linearity of the plots of log(absorbance) against time indicated that none of the reaction products interfered with the rate profile of the reaction. It has been stated earlier that the reaction with phosphorous acid is quite slow in comparison to the present reaction. The invariance of the rate constant $k_{obs.}$ measured at different initial [Ce^{III}] and constant [NO_3^-] confirmed this view.

Dependence on [H_3PO_2].—The results of the variation of [H_3PO_2] on the rate at fixed [H$^+$] = 2 mol dm^{-3} and four different temperatures are given in Table 2. Plots of $1/k_{obs.}$ against $1/[H_3PO_2]$ were linear with an intercept on the rate axis. The plot (*a*) in Figure 2 is a typical plot obtained from data at 19 °C. This reciprocal Michaelis–Menten plot indicates the formation of intermediate complexes. The

TABLE 2

Dependence of $k_{obs.}$ on [H_3PO_2] at different temperatures with 10^4[Ce^{IV}] = 5 mol dm^{-3}, [H$^+$] = 2 mol dm^{-3}, and [NO_3^-] = 2 mol dm^{-3}

10^3 [H_3PO_2]/mol dm^{-3}	1.0	1.25	1.5	2.0	3.0	5.0
10^4 $k_{obs.}$/s^{-1} (19 °C)	3.7	4.5	5.2	6.6	8.8	11.3
(23 °C)	5.3	6.4	7.4	9.4	12.4	16.9
(27 °C)	7.4	8.8	10.2	12.8	17.4	23.6
(31 °C)	10.6	12.8	15.0	18.6	25.1	34.2

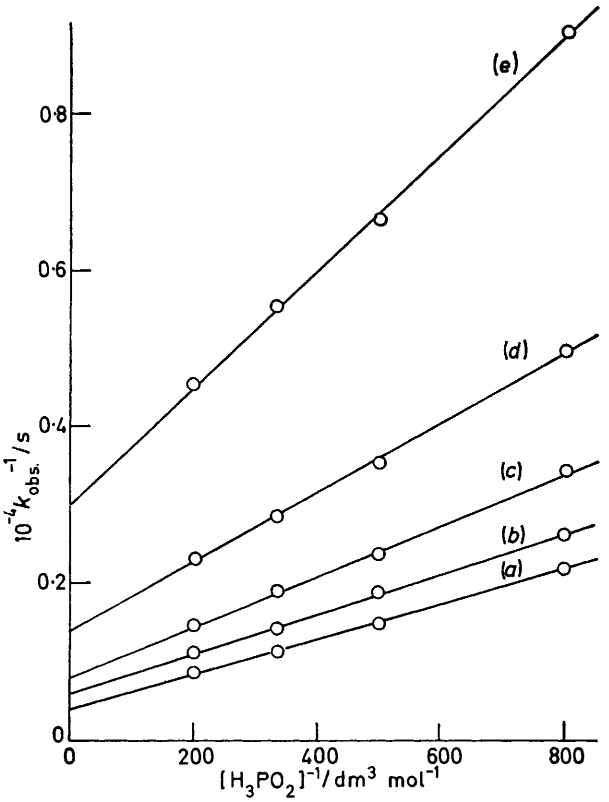

FIGURE 2 Reciprocal Michaelis–Menton plots of $10^{-4}\ k_{obs.}^{-1}$ against [H_3PO_2]$^{-1}$ at 19 °C. Plot (*a*) refers to the data in the first line of Table 2, the other plots to the data in Table 3. [H$^+$] = 2 (*a*), 1.6 (*b*), 1.2 (*c*), 0.8 (*d*), and 0.4 mol dm^{-3} (*e*)

rate-limiting constant k was evaluated at different temperatures from the values of the gradients and intercepts of similar Michaelis–Menten plots at the different temperatures. The k values are reported in Table 5 together with corresponding thermodynamic quantities.

Dependence on $[H^+]$.—The effect of $[H^+]$ on the reaction rate was investigated at different $[HNO_3]$ and $[H_3PO_2]$, each varied independently at constant concentration of the other and keeping $[NO_3^-] = 2$ mol dm^{-3}. These results are given in Table 3 (the first line of Table 2 is also part of this data). Nitric acid was considered to be completely dissociated and any contribution to $[H^+]$ from H_3PO_2 was negligible in view of the significantly small $[H_3PO_2]$ used and the low value of its K_a.[4,11,17,18] Hypophosphorous(I) acid, therefore, existed mainly in the undissociated state under our experimental conditions. Values of $k_{obs.}$ were found to increase with increasing $[H^+]$.

TABLE 3

Dependence of $k_{obs.}$ on $[H_3PO_2]$ at different $[H^+]$ with $10^4[Ce^{IV}] = 5$ mol dm^{-3}, $[NO_3^-] = 2$ mol dm^{-3}, and 19 °C

$10^3\ [H_3PO_2]$/mol dm^{-3}	1.25	2.0	3.0	5.0
$10^4\ k_{obs.}/s^{-1}$ ($[H^+] = 0.4$ mol dm^{-3})	1.1	1.5	1.8	2.2
($[H^+] = 0.8$ mol dm^{-3})	2.0	2.8	3.5	4.3
($[H^+] = 1.2$ mol dm^{-3})	2.9	4.2	5.2	6.8
($[H^+] = 1.6$ mol dm^{-3})	3.8	5.3	7.0	8.9

Some of the rate data at fixed $[H^+]$, Table 3, are illustrated in Figure 2, and the gradients and intercepts of these plots are reported in Table 5. The linear relation between $k_{obs.}$ and $[H^+]$, at fixed $[H_3PO_2]$, is shown in Figure 3 where it is to be noted that the plots pass through the origin. This indicates that reaction between Ce^{IV} and H_3PO_2 is only possible in the presence of H^+, and has led us to formulate a mechanism in which H^+ is considered to be involved in the rate-limiting step of the redox reaction.

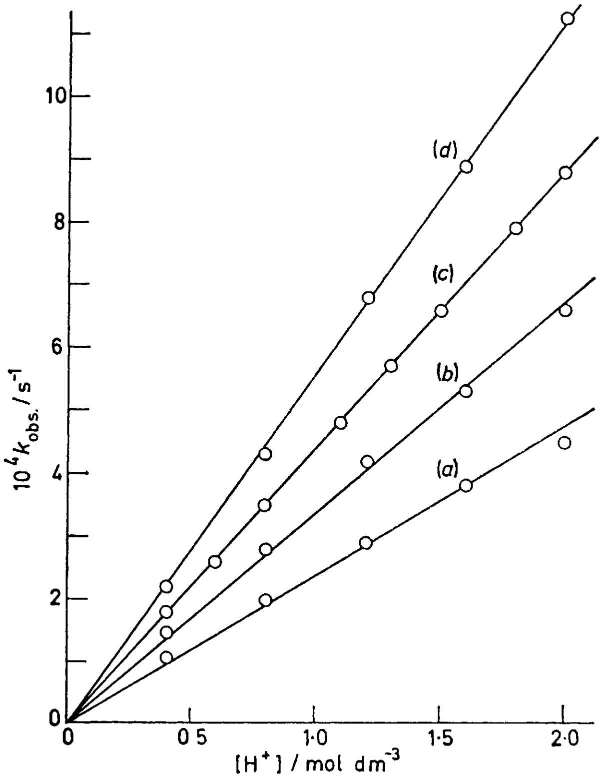

FIGURE 3 Plots of the observed rate constant $k_{obs.}$ against $[H^+]$ at 19 °C. The data illustrated are taken from Table 3. $[H_3PO_2] = 0.001\ 25$ (*a*), 0.002 (*b*), 0.003 (*c*), and 0.005 mol dm^{-3} (*d*)

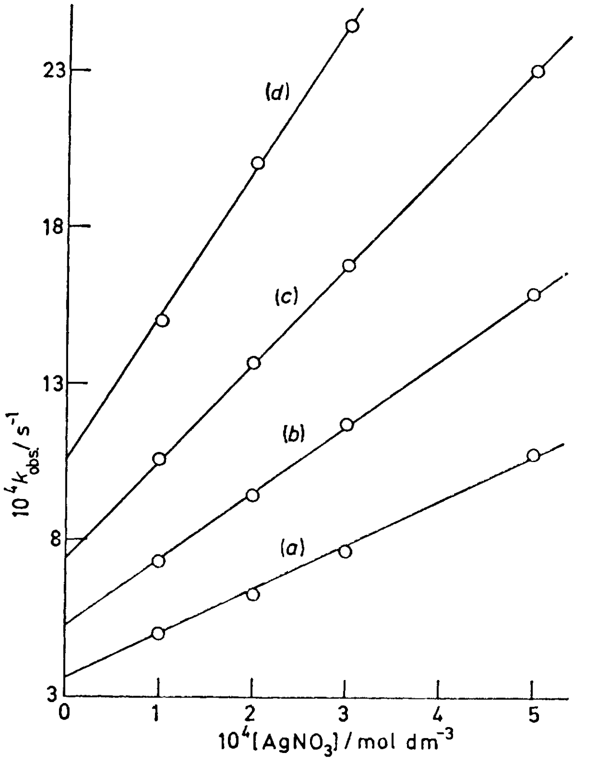

FIGURE 4 Plot of the observed rate constant $k_{obs.}$ against $[Ag^I]$, having an intercept on the rate axis consistent with equation (i); $[Ce^{IV}]_T = 0.0005$ mol dm^{-3}, $[H_3PO_2] = 0.001$ mol dm^{-3}, and $[H^+] = 2$ mol dm^{-3} with temperatures of 19, 23, 27, and 31 °C for the plots (*a*), (*b*), (*c*), and (*d*)

Dependence on $[Ag^I]$.—Silver(I) catalyses the cerium(IV) oxidations of aliphatic carboxylic acids[14] and of Hg^I.[19] Silver(I) also catalysed the oxidation of hypophosphorous acid[7] and phosphorous acid[20] by V^V and the interesting observation was made that the order of the reaction with respect to $[V^V]$ changed from one to zero in the presence of Ag^I. This prompted us to investigate the effect of Ag^I in the present reaction. The reaction was found to be catalysed by Ag^I and there was no change in the order of the reaction with respect to $[Ce^{IV}]$. The results are reported in Table 4 and a plot of $k_{obs.}$ against $[Ag^I]$, consistent with (i), is shown in Figure 4.

TABLE 4

Dependence of the rate constant $k_{obs.}$ on $[Ag^I]$ and values of gradient/intercept, obtained from the plot in Figure 5, at different temperatures. $10^4[Ce^{IV}] = 5$ mol dm^{-3}, $[H_3PO_2] = 0.001$ mol dm^{-3}, $[H^+] = 2$ mol dm^{-3}, and $[NO_3^-] = 2$ mol dm^{-3}

$10^4\ [AgNO_2]$/mol dm^{-3}	1.0	2.0	3.0	5.0	10^3 Gradient/intercept dm^3 mol^{-1}
$10^4\ k_{obs.}/s^{-1}$ (19 °C)	5.0	6.3	7.7	10.8	3.760
(23 °C)	7.3	9.4	11.7	15.9	3.960
(27 °C)	10.6	13.7	16.8	23.1	4.240
(31 °C)	15.0	20.1	24.5	34.1	4.430

Empirical Rate Law.—The above results, in the absence of Ag^{I}, indicate that the rate of the reaction can be represented by the empirical rate equation (3) where A, B, and C are constants and $[Ce^{IV}]_T$ is the total concentration present initially. The respective values of the constants A, B, and C are 0.589 dm^6 mol^{-2} s^{-1}, 3 290 dm^3 mol^{-1}, and 465 dm^3 mol^{-1} respectively at 19 °C as obtained from (4)—(6) which represent the intercepts and gradients of the plots in Figures 2—4.

$$k_{\text{obs.}} = \frac{A[H_3PO_2][H^+]}{1 + B[Ce^{IV}]_T + C[H_3PO_2]} \tag{3}$$

Figure	Intercept	Gradient	
2	$(1 + C[H_3PO_2])/A[H_3PO_2][H^+]$	$B/A[H_3PO_2][H^+]$	(4)
3	$C/A[H^+]$	$(1 + B[Ce^{IV}]_T)/A[H^+]$	(5)
4	Zero	$A[H_3PO_2]/(1 + B[Ce^{IV}]_T) + C[H_3PO_2])$	(6)

DISCUSSION

Carroll and Thomas [5] assumed the successive formation of a number of complexes with H_3PO_2 through a general equilibrium (7), where $n = 1$—3. The other reactions considered in the mechanism were those in equations (8) and (9) where $Ce^{4+}(aq)$ is the aquacerium(IV) ion in perchlorate solution and $(H_2PO_2)^*$ denotes an active hypophosphite group. Since the reaction proceeds through complex formation between Ce^{IV} and H_3PO_2, consistent with the reciprocal Michaelis–Menten plots shown in Figure 2, a consideration of equilibrium (7) would indicate a retarding influence of H^+ on the reaction rate, contrary to the observations made in the present study and by Carroll and Thomas.[5] Moreover, the last workers did not explain the retarding effect on the reaction rate of increasing $[Ce^{IV}]_T$. A re-analysis of their data gave a linear plot between 1/rate and $[Ce^{IV}]_T$, plot (*b*) in Figure 1. It is noted that the existence of cerium(IV) polymers in perchloric acid solution, even at high acidities, has been reported by several workers.[21-23]

$$Ce^{4+}(aq) + n\,H_3PO_2 \xrightleftharpoons{K_n} [Ce(H_2PO_2)_n]^{4-n} + nH^+ \tag{7}$$

$$[Ce(H_2PO_2)_n]^{4-n} + H^+ \xrightleftharpoons{k_{H(n)}} [Ce(H_2PO_2)^*(H_2PO_2)_{n-1}]^{4-n} + H^+ \tag{8}$$

$$[Ce(H_2PO_2)^*(H_2PO_2)_{n-1}]^{4-n} \xrightarrow{k_{d(n)}} \text{products} \tag{9}$$

These similarities in the dependence of the rate on $[Ce^{IV}]_T$ and the existence of dimeric cerium(IV) both in aqueous nitric acid [15] and perchloric acid [21-23] solutions could indicate that dimeric cerium(IV) species are probably not reactive in the present case since these were also considered to be inactive in the oxidation in aqueous perchloric acid solution.[5] The equilibrium constants for the formation of Ce^{IV}–Ce^{IV} and Ce^{IV}–Ce^{III} dimers from the respective monomeric species are 17 ± 2 and 2 ± 0.7 at dm^3 mol^{-1} at 30 °C and in 5.5 mol dm^{-3} HNO_3.[15] However, the exact nature of these dimeric species is not known. Similarly, the exact nature of the monomeric cerium(IV) species in aqueous nitric acid solution is also unknown. Several workers [24-26] have proposed different reactive species in the oxidations of various organic substrates, whereas others [27-29] have cautiously avoided specifying the reactive species of Ce^{IV} in the oxidation of inorganic [16] and organic substrates.[27-29]

However, if the relation between the entropy $\Delta S^\ddagger$ and the charges Z_A and Z_B of the reacting ions,[30] expressed as in equation (10) modified for S.I. units, is used to deduce information about the reacting ions, it can be shown that the reactive cerium(IV) ion is dipositively charged. However, since such an ion could be described by more than one formula, it is considered difficult to be specific about this species. Like other workers,[27-29] we also denote this species simply by Ce^{IV}.

$$\Delta S^\ddagger = -42 Z_A Z_B \quad \text{J K}^{-1}\,\text{mol}^{-1} \tag{10}$$

Mechanism.—The mechanism has been formulated to give a rate equation which is identical with that in (3) presented earlier. The existence of the free radical $H_2\dot{P}O_2$ has been reported in the oxidation of H_3PO_2 by peroxodisulphate ion.[31] The formation of the free radical was confirmed by the induced polymerisation of added acrylonitrile; neither of the solutions of Ce^{IV} or H_3PO_2, taken separately, induced the polymerisation of the monomer.

$$H_2PO(OH) + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HP(OH)_2 + H^+;\ K_1 \tag{1}$$

$$Ce^{IV} + HP(OH)_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Complex};\ K_2 \tag{11}$$

$$\text{Complex} + H^+ \xrightarrow{k} Ce^{III} + H_2\dot{P}O_2 + H^+ \tag{12}$$

$$Ce^{VI} + H_2\dot{P}O_2 + H_2O \xrightarrow{\text{fast}} Ce^{III} + H_3PO_3 + H^+ \tag{13}$$

Application of the steady-state treatment to $[HP(OH)_2]$ gives relation (14). Equation (16) follows when $[HP(OH)_2]$, as derived in (14), is substituted in (15).

$$[HP(OH)_2] = \frac{k_1[H_2PO(OH)][H^+]}{k_{-1}[H^+] + k_2[Ce^{IV}]} \tag{14}$$

$$\begin{aligned} -d[Ce^{IV}]_T/dt &= 2k[\text{Complex}][H^+] \\ &= 2kK_2[HP(OH)_2][Ce^{IV}][H^+] \end{aligned} \tag{15}$$

$$\frac{-d[Ce^{IV}]_T}{dt} = \frac{2kk_{1-}K_2[H_2PO(OH)][H^+]^2[Ce^{IV}]}{k_{-1}[H^+] + k_2[Ce^{IV}]} \tag{16}$$

$$= \frac{2kk_1K_2[H_2PO(OH)][H^+]^2[Ce^{IV}]_T}{k_{-1}[H^+](1 + K_2[HP(OH)_2]) + k_2[Ce^{IV}]_T}$$

$$= \frac{2kK_1K_2[H_2PO(OH)][H^+][Ce^{IV}]_T}{1 + K_2[HP(OH)_2] + (k_2[Ce^{IV}]_T/k_{-1}[H^+])} \tag{17}$$

$$= \frac{2kK_1K_2[H_3PO_2][H^+][Ce^{IV}]_T}{1 + K_1 + K_2[H_3PO_2] + \{k_2(1 + K_1)[Ce^{IV}]_T/k_{-1}[H^+]\}} \tag{18}$$

Here equations (17) and (18) were obtained from (16) by making appropriate substitutions for $[Ce^{IV}]_T$ and $[H_3PO_2]$. The equilibrium constant K_1 for formation of the active tautomer has been estimated[3] to be 10^{-9}—10^{-11}, so that $1 \gg K_1$ and equation (18) reduces to (19).

$$k_{\text{obs.}} = \frac{2kK_1K_2[\mathrm{H_3PO_2}][\mathrm{H^+}]}{1 + K_2[\mathrm{H_3PO_2}] + (k_2[\mathrm{Ce^{IV}}]_\mathrm{T}/k_{-1}[\mathrm{H^+}])} \quad (19)$$

This is now identical with the empirical rate equation (3) whence $A = 2kK_1K_2$, $B = k_2/k_{-1}[\mathrm{H^+}]$, and $C = K_2$. The value of B, which is 3 290 $\mathrm{dm^3\ mol^{-1}}$, thus represents the ratio k_2/k_{-1} in 2 mol $\mathrm{dm^{-3}}$ $\mathrm{HNO_3}$. The high value simply indicates that the rate of formation of the complex is much larger than the rate of reversion of the active tautomer to the inactive form. This explanation makes this scheme more acceptable than any other.

The rate acceleration by $\mathrm{H^+}$ could be explained by considering a protonated cerium(IV) species, but such an alternative to reaction (12) had to be ruled out in view of the conclusions of Blaustein and Gryder[15] that cerium(IV) species in $\mathrm{HNO_3}$ have no ionisable hydrogen ion associated with them.

Mechanism of Silver(I)-*catalysed Reaction*.—The present reaction is different from that for the vanadium(V) oxidation of $\mathrm{H_3PO_2}$ in the presence of $\mathrm{Ag^I}$ in respect of order of the reaction in the concentration of the oxidant metal ion. The order of the reaction with respect to $[\mathrm{Ce^{IV}}]$ remained unchanged, whereas it became zero order with respect to $[\mathrm{V^V}]$ in presence of $\mathrm{Ag^I}$.

The plot in Figure 4 is consistent with an empirical rate law, equation (i), which indicates that the observed rate $k_{\text{obs.}}$ is the sum of the contributions from the rates both in the presence and absence of $\mathrm{Ag^I}$. Another interesting observation is that the quotient of gradient/intercept, obtained from the plot in Figure 4, is almost constant at different temperatures (Table 5).

TABLE 5

Values of the gradient, intercept, and the rate-limiting constant $k\{= 1/2[\mathrm{H^+}](\text{intercept})\}$ as calculated from the Michaelis–Menten plots using the data in Table 2

θ_c / °C	$[\mathrm{H^+}]$ / mol $\mathrm{dm^{-3}}$	Gradient / mol $\mathrm{dm^{-3}}$	Intercept $(=1/2k[\mathrm{H^+}])$	$10^4\,k$ $\{= 1/2[\mathrm{H^+}](\text{intercept})\}$
19	2	2.3	395	6.33
23	2	1.6	265	9.43
27	2	1.2	190	13.16
31	2	0.8	130	19.23

$\Delta E^\ddagger = 66 \pm 2$ kJ $\mathrm{mol^{-1}}$; $\Delta S^\ddagger = -88 \pm 8$ J $\mathrm{K^{-1}\ mol^{-1}}$

On the basis of the present data, which are limited to fixed $[\mathrm{H^+}]$, it seems probable that the $\mathrm{Ce^{IV}}$–$\mathrm{H_3PO_2}$ complex is oxidised by $\mathrm{Ag^I}$. We defer further comment on the mechanism until the reaction is investigated in detail.*

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