Kinetics and Mechanism of the Oxidation of Iron(II) by Molecular Oxygen catalysed by Aquapalladium(II)

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Iron(II) in acid aqueous solution is rapidly oxidised by molecular oxygen in the presence of aquapalladium(II) ions. The direct reduction of Pd^{II} to Pd^0 by Fe^{II} is delayed until all the oxygen has been consumed. The rate of the catalytic reaction is a function of the concentrations of palladium(II), iron(II), acid, sulphate, and iron(III). Detailed study of these factors leads to a mechanism which accounts quantitatively for the results and involves the formation of a palladium(I) intermediate which undergoes oxidation by O_2 rather than reduction by Fe^{II}.

THE mechanism of the oxidation of iron(II) by molecular oxygen in acid aqueous solution has been the subject of many studies.[1-11] In several of these [4-7] it is reported that the reaction is catalysed by copper(II) compounds. We report here a detailed study of the catalytic effect of aquapalladium(II) on this reaction. Other examples of oxidations by molecular oxygen catalysed by palladium(II) compounds alone include those of vanadium(III),[12] alcohols,[13] and benzenediols.[14] Many examples are known of reactions in which oxidation by molecular oxygen is catalysed by copper(II) and palladium(II) compounds together.[15]

EXPERIMENTAL

Materials.—Perchloric acid, sodium sulphate, sodium perchlorate, iron(II) sulphate, and ammonium iron(III) sulphate were AnalaR chemicals (Fisons). Palladium(II) sulphate was prepared from palladium sponge (Johnson, Matthey) by the method of Rasmussen and Jørgensen.[16]

Kinetic Measurements.—Reaction mixtures were prepared from solid $Fe[SO_4]\cdot 7H_2O$ and stock solutions of the other reagents. Ionic strength was maintained constant with sodium perchlorate. The reactions were started by addition of palladium(II) sulphate solution in perchloric acid and followed by measuring the variation of absorbance with time at 300 nm (1-cm cell) in the thermostatted cell compartment (25 °C) of a Pye–Unicam SP 8000 or 450 spectrophotometer. The absorbance at 300 nm was related to the total iron(III) concentration by separate calibration experiments, at various acid and sulphate concentrations, using ammonium iron(III) sulphate. The variation of absorbance with time was almost linear up to *ca.* 20% completion of reaction. The initial reaction rates $\{v_0 = (d[Fe^{III}]/dt)_{t\rightarrow 0}\}$ given in the Tables were obtained by measuring initial gradients of absorbance–time curves and applying the calibration factor appropriate to the acid and sulphate concentrations in the reaction mixture. It was confirmed that, in the absence of palladium(II) compounds, the rate of oxidation of Fe^{II} by oxygen under our conditions was too slow to interfere with the catalytic process.

RESULTS AND DISCUSSION

When an acidic aqueous solution of iron(II) sulphate is mixed with aqueous palladium(II) sulphate (*ca.* 10^{-3} mol dm^{-3}) in the absence of dissolved oxygen, palladium metal is precipitated in the time of mixing. In the presence of dissolved oxygen the onset of palladium precipitation is delayed. Typical results of such experiments are shown in Table 1 which also gives the concentrations of iron(III) formed and the concentrations of iron(III) expected as a result of the following reactions.

$$Pd^{2+} + 2Fe^{2+} \longrightarrow Pd + 2Fe^{3+}$$

$$4Fe^{2+} + O_2 + 4H^+ \longrightarrow 4Fe^{3+} + 2H_2O$$

In the presence of small concentrations of sodium chloride (*ca.* 2×10^{-4} mol dm^{-3}), or by the use of $PdCl_2$ in place of $Pd[SO_4]$, the delay time (t) was too small to be measured by our technique. In all the kinetic experiments reported here the solutions were free from chloride and, except where indicated, contained dissolved oxygen from equilibration with air at 25 °C. Initial rates of formation of iron(III) (v_0, see Table 2) were found to depend on the concentrations of palladium(II), iron(II), acid, iron(III), and sulphate. The effects of ionic strength and the concentration of dissolved oxygen were also briefly investigated. Values of v_0 were rather insensitive to these factors. Rate measurements on mixtures saturated with oxygen gave values of v_0 *ca.* 20% greater than those reported in Table 2 when other conditions were the same.

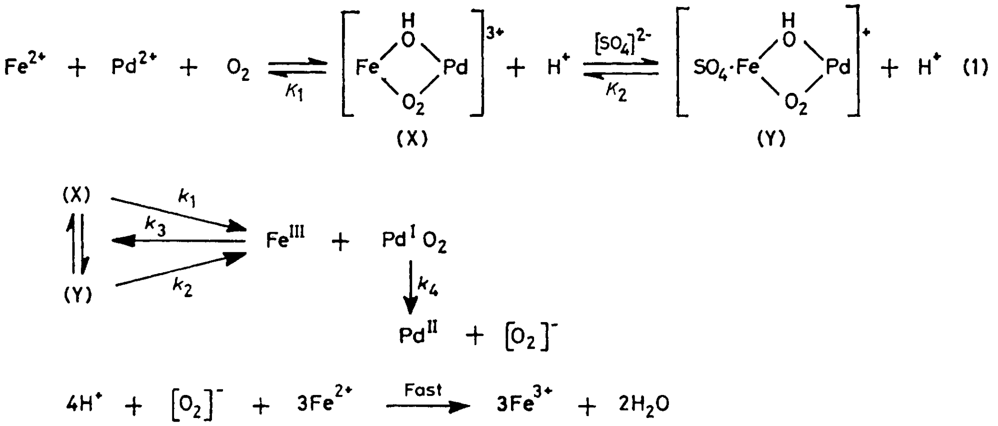
The quantitative dependence of v_0 on the concentrations of Pd^{II}, Fe^{II}, and acid appears to be fairly simple in each case. With other factors constant the initial rate is directly proportional to the stoicheiometric concentration of $Pd[SO_4]$ [Table 2(*i*)] and increases towards a limiting value with increasing $[Fe^{II}]$ [Table 2(*ii*)] and with decreasing $[H^+]$ [Table 2(*iii*)]. Plots of $1/v_0$ against $1/[Fe^{II}]$ and $1/v_0$ against $[H^+]$ are good straight lines. The relationships of v_0 with $[Fe^{III}]$ and with $[SO_4^{2-}]$ are more complicated. The effects of Fe^{III} (added to initial reaction mixtures) could not be explored beyond a concentration of *ca.* 1×10^{-3} mol dm^{-3} because initial absorbance values were then too

TABLE 1

Stoicheiometry experiments. $[FeSO_4] = 0.100$, $[HClO_4] = 0.037$ mol dm^{-3}

$10^3[PdSO_4]$ / mol dm^{-3}	t [a] / min	Absorbance [b]	$10^3[Fe^{III}]$/mol dm^{-3} Found	Calc. [c]
1.0	6	0.673	2.86	3.0
0.5	23	0.463	1.97	2.0

[a] The approximate delay time before the onset of palladium precipitation. [b] At 300 nm (1-cm cell), see Experimental section. [c] The concentration of dissolved oxyxen in the solutions is assumed to be that for air in equilibrium with water at 25 °C (*i.e.* 2.5×10^{-4} mol dm^{-3}).



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high for accurate measurement. However, it is apparent that Fe^{III} has an inhibiting effect on the reaction, and its presence also modifies the form of the dependence of v_0 on sulphate concentration. With no added iron(III), v_0 varies linearly with $[SO_4^{2-}]$ [Table 2(*iv*)(*a*)], but in the presence of added iron(III) v_0 approaches a limiting value with increasing $[SO_4^{2-}]$ [Table 2(*iv*)(*c*)]. These complications are, perhaps, not surprising in view of the fact that the sulphate ion is known[17] to co-ordinate with Fe^{2+}(aq) and Fe^{3+}(aq) to form such species as $Fe[SO_4]$, $[Fe(SO_4)]^+$, $[Fe(SO_4)_2]^-$, and there is evidence that co-ordination of $[SO_4]^{2-}$ to palladium(II) species may also occur.[18,19] In addition, both Fe^{3+}(aq) and Pd^{2+}(aq) are fairly strong acids giving rise, for example, to $[Fe(OH)]^{2+}$ and $[Pd(OH)]^+$ which might also form sulphate complexes. With these possibilities in mind we have, in proposing a mechanism, simplified the picture of the various equilibria in the initial solutions by combinining some of them to give composite constants. Our absorbance measurements are related to initial rates by using empirical absorption coefficients that cannot be attributed to specific species. We have, therefore, used the symbol Fe^{III} in the mechanistic scheme above to refer to the total of the various iron(III) species that might be present.

TABLE 2

Initial rates of formation (v_0) of iron(III) at 25 °C

(*i*) Dependence of rate on palladium(II) concentration

$10^4[PdSO_4]$/mol dm^{-3}		2.4	4.8	7.2	9.6
10^6v_0/mol dm^{-3} s^{-1}	(*a*)	0.207	0.386	0.528	0.735
	(*b*)	0.173	0.332	0.482	0.604

(*ii*) Dependence of rate on iron(II) concentration; $[SO_4^{2-}]$ = 0.200 mol dm^{-3}

$[FeSO_4]$/mol dm^{-3}		0.04	0.06	0.08	0.15	0.20
10^6v_0/mol dm^{-3} s^{-1}	(*a*)	0.486	0.720	0.929	1.30	1.73
	(*b*)	0.439		0.780	1.23	1.50
	(*c*)	0.319	0.418	0.554	0.833	0.987

(*iii*) Dependence of rate on acid concentration; $10^4[PdSO_4]$ = 9.6 mol dm^{-3}

$[HClO_4]$/mol dm^{-3}		0.055	0.110	0.165	0.220	0.275
10^6v_0/mol dm^{-3} s^{-1}	(*a*)	1.17	0.935	0.730	0.520	0.476
	(*b*)	0.970	0.775	0.602		0.435
$[HClO_4]$/mol dm^{-3}		0.330	0.385	0.440	0.495	
10^6v_0/mol dm^{-3} s^{-1}	(*a*)			0.322	0.292	
	(*b*)	0.368	0.350		0.276	
$[HClO_4]$/mol dm^{-3}		0.066	0.121	0.231	0.341	0.451
10^6v_0/mol dm^{-3} s^{-1}	(*c*)	0.680	0.544	0.413	0.328	0.263

(*iv*) Dependence of rate on sulphate concentration; $[FeSO_4]$ = 0.04 mol dm^{-3}

$[SO_4^{2-}]$/mol dm^{-3}		0.04	0.08	0.12	0.16	0.20
10^6v_0/mol dm^{-3} s^{-1}	(*a*)	0.146	0.232	0.332	0.439	0.520
	(*c*)	0.129	0.186	0.237	0.260	0.296

All solutions contained dissolved oxygen from equilibration with air at 25 °C. Except where stated otherwise, the following conditions apply: $[PdSO_4] = 7.2 \times 10^{-4}$, $[FeSO_4] = 0.100$, $[HClO_4] = 0.165$, $[SO_4^{2-}] = 0.100$, $I = 0.965$ mol dm^{-3}. (*a*) Values of v_0 for experiments with no Fe^{III} present initially. (*b*) and (*c*) values of v_0 for experiments with $10^4[Fe^{III}]_0 = 4.4$ and 8.8 mol dm^{-3} respectively.

The initial stage is represented by the fast pre-equilibrium (1). The iron(II), palladium(II), and oxygen form a complex which loses a proton to form (X), and this can then form (Y) by addition of a sulphate ion. Both (X) and (Y) can break down to give the final product, Fe^{III}, and a stationary-state intermediate Pd^IO_2. This in turn regenerates Pd^{II} and gives $[O_2]^-$ which is rapidly reduced in the last step. The path labelled k_3 represents the sum of several possible reactions (depending on the exact form of Fe^{III}), and the rate constant k_3 may thus be a function of acid and sulphate concentrations. We also assume that the concentration of (Y) is small compared with those of (X) and Pd^{2+}. Thus, the stoicheiometric concentration of palladium is given by: $[Pd]_0 \simeq [Pd^{2+}] + [X]$. If we now use the steady-state approximation $d[Pd^IO_2]/dt = 0$, and insert the values of [X] and [Y] in terms of the equilibrium constants for reactions (1), the final rate equation derived from the mechanism is (2) where $[Fe^{III}]_0$ = concentration of iron(III) added initially.

$$\left(\frac{d[Fe^{III}]}{dt}\right)_{t\to 0} = v_0 = \frac{4k_4K_1[Fe^{2+}][O_2][Pd]_0(k_1 + k_2K_2[SO_4^{2-}])}{(k_4 + k_3[Fe^{III}]_0)([H^+] + K_1[Fe^{2+}][O_2])} \quad (2)$$

Equation (2) is of the correct form to account for most of our results and it may be tested quantitatively for consistency by comparing the gradients and intercepts of various linear plots (Table 3) with calculated values. First, consider the experiments in which $[Fe^{III}]_0 = 0$.

TABLE 3

Gradients and intercepts of linear plots

Plot [a]	Table 2 reference	Gradient (G)	Intercept [b] (I)	(I)/(G)
v_0, [$PdSO_4$]	(*i*) (*a*)	6.9×10^{-4} s^{-1}	0	
$1/v_0$, 1/[$FeSO_4$]	(*ii*) (*a*)	7.2×10^{4} s	3.5×10^{5} dm^3 mol^{-1} s	4.9 dm^3 mol^{-1}
	(*ii*) (*b*)	8.1×10^{4} s	3.8×10^{5} dm^3 mol^{-1} s	4.7 dm^3 mol^{-1}
	(*ii*) (*c*)	1.0×10^{5} s	4.8×10^{5} dm^3 mol^{-1} s	4.8 dm^3 mol^{-1}
$1/v_0$, [$HClO_4$]	(*iii*) (*a*)	5.7×10^{6} dm^6 mol^{-2} s	5.0×10^{5} dm^3 mol^{-1} s	0.088 mol dm^{-3}
	(*iii*) (*b*)	6.0×10^{6} dm^6 mol^{-2} s	7.0×10^{5} dm^3 mol^{-1} s	0.12 mol dm^{-3}
	(*iii*) (*c*)	5.9×10^{6} dm^6 mol^{-2} s	1.1×10^{6} dm^3 mol^{-1} s	0.18 mol dm^{-3}
v_0, [SO_4^{2-}]	(*iv*) (*a*)	2.3×10^{-6} s^{-1}	$(4 \pm 1) \times 10^{-8}$ mol dm^{-3} s^{-1}	1.7×10^{-2} mol dm^{-3}

[a] The first named quantity is the ordinate. [b] On the ordinate axis when abscissa is zero.

Equation (2) then becomes (3).

$$v_0 = \frac{4K_1[Fe^{2+}][O_2][Pd]_0(k_1 + k_2K_2[SO_4^{2-}])}{[H^+] + K_1[Fe^{2+}][O_2]} \quad (3)$$

$$\frac{1}{v_0} = \frac{[H^+]}{[Fe^{2+}]} \cdot \frac{1}{4K_1[O_2][Pd]_0(k_1 + k_2K_2[SO_4^{2-}])} + \frac{1}{4(k_1 + k_2K_2[SO_4^{2-}])[Pd]_0} \quad (4)$$

From the gradient and intercept of the plot of $1/v_0$ against [H^+] and the appropriate values of the iron(II), sulphate, and total palladium concentrations we obtain the values $K_1[O_2] = 0.88$ and $(k_1 + 0.1\ k_2K_2) = 5.2 \times 10^{-4}$ s^{-1}. Similarly, from the plot of $1/v_0$ against 1/[Fe^{2+}] we obtain $K_1[O_2] = 0.81$ (in good agreement) and $(k_1 + 0.2\ k_2K_2) = 9.8 \times 10^{-4}$ s^{-1}. From these results the quantity k_2K_2/k_1 is found to be $\simeq 75$. With the above values we can calculate the gradient of the plot of v_0 against $[Pd]_0$ (7.1×10^{-4}) and compare it with the experimental values (6.9×10^{-4}). Also, the ratio gradient : intercept for the plot of v_0 against [SO_4^{2-}] gives $k_2K_2/k_1 \simeq 60$ which, considering the uncertainties in evaluating the intercept, must be considered in good agreement with the value obtained above from the other plots. It is also possible to estimate the value of k_1 as *ca.* 10^{-4} s^{-1}. Considering the results for experiments in which iron(III) was added initially, we find that the plots of $1/v_0$ against 1/[Fe^{2+}] conform well to equation (2) in that gradients and intercepts increase with $[Fe^{III}]_0$ but the ratios remain constant (Table 3). The main anomaly is in the plots of $1/v_0$ against [H^+]. In these the gradients appear to be independent of $[Fe^{III}]_0$ but the intercepts increase significantly with increasing $[Fe^{III}]_0$. There is another anomaly in that the rates do not increase linearly with sulphate-ion concentration when iron(III) is present initially. Both these effects could result from dependence of k_3 on acid and sulphate concentrations. This might be expected, for example, if the species denoted by 'Fe^{III}' in the mechanism is actually [$Fe(SO_4)(OH)$], leading to a factor of the form [SO_4^{2-}]/[H^+] to be included in the k_3 term.

Our conclusion is that the proposed mechanism accounts very satisfactorily for almost all our results. One surprising feature of the mechanism is the absence of any competition by Fe^{2+} for the palladium(I) intermediate. If such a step were introduced it would lead to a rate equation with a more complicated dependence on the iron(II) concentration than we have observed. (The exact nature of the [Fe^{2+}] dependence is one of the main points of controversy in discussions of the uncatalysed oxidation of iron(II) by molecular oxygen.[8]) By formulating the intermediate as Pd^IO_2 we suggest that when the complex [(X) or (Y)] breaks down the O_2 molecule remains in close enough proximity to the palladium entity to ensure that the path k_4 is favoured. It seems, however, that chloride ion is able to compete for the intermediate since reduction of Pd^{II} to Pd^0 by Fe^{II} occurs rapidly in the presence of chloride.

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