Mechanisms of Complex Formation in the Reactions of 1,2-Dihydroxybenzene and 1,2-Dihydroxy-4-methylbenzene with Palladium(II) Chloride and with Aquapalladium(II). Equilibria and Kinetics in Acid Media

By **John S. Coe,*** Chemistry Department, King's College, Strand, London WC2R 2LS
Edoardo Mentasti, Istituto di Chimica Analitica, Università di Torino, Via P. Giuria 5, 10125 Torino, Italy

Palladium(II) chloride and aquapalladium(II) ions react rapidly with benzene-1,2 diols (1,2-dihydroxybenzene and 1,2-dihydroxy-4-methylbenzene) to form a green 1:1 complex. The reactions are reversed by addition of an excess of acid. Values of equilibrium constants for the overall reactions have been determined both from measurements on the equilibrium mixtures and from kinetic parameters. The green product is considered to be a chelate complex of Pd^0 and an *o*-quinone and the mechanisms are discussed in terms of a general scheme that takes into account possible intermediate species.

IN an earlier paper [1] we reported equilibrium and kinetic studies on the reaction of aquapalladium(II), $Pd(aq)^{2+}$, with 1,2-dihydroxybenzene (H_2cat) in aqueous acid solution. The mechanism of this reaction appeared to be rather complicated and the nature of the product remained uncertain. The present investigation was undertaken to provide further support for the mechanism proposed and to obtain further evidence for the nature of the product.

EXPERIMENTAL

Analytical grade 1,2-dihydroxy-4-methylbenzene (H_2-Mecat) (Merck) and palladium(II) chloride were used. Other materials, instruments, methods, and reaction conditions were as reported earlier.[1]

RESULTS

The three reactions studied were (1) $Pd(aq)^{2+}$ with H_2-Mecat, (2) $PdCl_2$ with H_2Mecat, and (3) $PdCl_2$ with H_2cat. In each case the general pattern is similar to that reported earlier for the reaction of $Pd(aq)^{2+}$ with H_2cat.[1] When solutions of the reagents are mixed a green colour rapidly appears (half-times of a few seconds) and the mixtures then slowly darken (half-times of 10—20 min) with formation of a black precipitate. The green colour (corresponding to an absorption band with a maximum near 660 nm) is discharged by the addition of an excess of acid. As before,[1] these observations have been interpreted as resulting from the rapid reversible formation of a palladium–diol complex which, in solutions of low acidity, decomposes slowly to give Pd metal and an *o*-quinone. In this Section the treatment of the results (Tables 1—3) is summarised with reference to the three main aspects of the study, *i.e.* the equilibrium established before the onset of the darkening process, the kinetics of formation of the complex (at low acidities), and the kinetics of the reverse process (at higher acidities) in which the reagents are regenerated. In describing the various plots, the ordinate is named first and the intercept is the value of the ordinate at zero on the abscissa.

(1) *The Reaction of* $Pd(aq)^{2+}$ *with* H_2Mecat.—In this case the detailed study of the kinetics of the complex formation was hampered by the occurrence of an induction period, as shown by the sigmoid shape of the traces of absorbance *versus* time (t), from the stopped-flow measurements, and plots of $\ln(A_\infty - A_t)$ *versus* t were not linear. However, it appears qualitatively that the rates of reaction are independent of acid concentration in the range $[H^+] = 0.003$—0.03 mol dm^{-3}. From these kinetic runs it was possible to obtain reliable values of A_∞ (Table 1), corresponding to the situation before the onset of the darkening process. The plot of $[Pd]_t/A_\infty$ *versus* $[H^+]^2/[H_2Mecat]$ is linear with gradient $G_1 = (3.2 \pm 0.1) \times 10^{-2}$ and intercept $I_1 = (8 \pm 1) \times 10^{-4}$ mol dm^{-3}.

TABLE 1

Absorbance values (A_∞ at 660 nm, 2-cm cell) at equilibrium in the reactions of $Pd(aq)^{2+}$ with H_2Mecat at 25 °C, $I = 0.2$ mol dm^{-3}

$10^3[H_2Mecat]$/ mol dm^{-3}	$[H^+]$/mol dm^{-3}				
	0.003	0.005	0.01	0.02	0.03
5	0.187	0.114	0.237		
10	0.222	0.180	0.347	0.187	0.114
20	0.244	0.208	0.420	0.284	0.187
30	0.260	0.222	0.456	0.328	0.244
40	0.301	0.222	0.495	0.367	0.284
$10^4[Pd]_t$/ mol dm^{-3}	2.00		4.00		

Kinetic measurements on the reaction in which the reagents are regenerated show that two stages are involved, a fast reaction followed by a slow one. The separation between the two stages was not so clear as in the case of the reaction of Pd^{2+} with H_2cat.[1] Furthermore, the total absorbance changes in the second (slow) stage were very small. Although no precise values of rate constants could be obtained for these reverse reactions, it appears qualitatively that each stage involves an acid dependence, the rates increasing with the first power of $[H^+]$ in each stage.

(2) *The Reaction of* $PdCl_2$ *with* H_2Mecat.—(*a*) *Equilibria.* Plots of $[Pd]_t/A_\infty$ *versus* $[H^+]^2$ (each at a given $[H_2Mecat]$) are linear with common intercept I_2 *ca.* 7×10^{-4} mol dm^{-3} and gradients G_2 (dm^3 mol^{-1}). The plot of G_2 *versus* $[H_2Mecat]^{-1}$ is linear with gradient $G_3 = (0.63 \pm 0.03)$ and intercept $I_3 = (7 \pm 2)$ dm^3 mol^{-1}.

(*b*) *Kinetics of formation.* Plots of $k_{obs.}$ *versus* $[H_2Mecat]$ (each at a given $[H^+]$, see Tables 2 and 3) are parallel straight lines with gradient $G_4 = (7 \pm 1)$ dm^3 mol^{-1} s^{-1} and intercepts I_4. The plot of $(I_4)^{-1}$ *versus* $[H^+]^{-2}$ is linear with gradient $G_5 = (1.9 \pm 0.1) \times 10^{-4}$ mol^2 dm^{-6} s and intercept $I_5 = (2.5 \pm 0.5)$ s.

(*c*) *Kinetics of decomposition* (*regeneration of reagents*). A one-stage reaction was observed with $k_{obs.}$ a linear function of $[H^+]^2$.

TABLE 2

Values of $10^2\ k_{obs.}/s^{-1}$ and of absorbance at equilibrium (in parentheses) for the formation reactions at 25 °C, $I = 0.2$ mol dm^{-3} *

	$[H^+]$			
	0.003	0.005	0.007	0.010
$10^3[H_2Mecat]/$mol dm^{-3}				
4	7.1 (0.203)	13.4 (0.086)	19.8 (0.092)	
7	9.1 (0.267)	14.2 (0.161)	21.8 (0.143)	
10	11.4 (0.276)	17.0 (0.222)	23.2 (0.200)	30.4 (0.092)
20	17.7 (0.310)	23.0 (0.333)	30.0 (0.333)	38.8 (0.170)
30		32.0 (0.398)	37.8 (0.372)	44.0 (0.244)
40		37.0 (0.398)	42.3 (0.432)	51.5 (0.296)
$10^3[H_2cat]/$mol dm^{-3}				
7	11.7 (0.119)			
10	13.9 (0.161)			
20	25.0 (0.252)	18.6 (0.131)	21.1 (0.149)	
30	40.9 (0.319)	27.3 (0.194)	24.9 (0.244)	28.5 (0.119)
40	47.4 (0.366)	32.6 (0.236)	27.9 (0.337)	29.9 (0.167)
$10^4[PdCl_2]_t/$mol dm^{-3}	4.00		8.00	

* Absorbance values (A_∞) at 660 nm, 2-cm cell, are in parentheses.

(3) *The Reaction of* $PdCl_2$ *with* H_2cat.—(*a*) *Equilibria.* The plot of $[Pd]_t/A_\infty$ *versus* $[H^+]^2/[H_2cat]$ is linear with gradient $G_6 = 1.8 \pm 0.1$ and intercept $I_6 = (7 \pm 2) \times 10^{-4}$ mol dm^{-3}.

(*b*) *Kinetics of formation.* Plots of $k_{obs.}$ *versus* $[H_2cat]$ (each at a given $[H^+]$, see Tables 2 and 3) are linear with gradients decreasing (to about unity) as $[H^+]$ increases to 0.01 mol dm^{-3} and intercepts I_7 proportional to $[H^+]^2$. The plot of I_7 *versus* $[H^+]^2$ has a gradient $G_7 = (2.6 \pm 0.2) \times 10^3$ dm^6 mol^{-2} s^{-1}.

(*c*) *Kinetics of decomposition.* As above.

DISCUSSION

Reaction of $Pd(aq)^{2+}$ *with* H_2Mecat.—The equilibrium data can be treated exactly as in the case of H_2cat,[1] except that we now consider the product to be species (VII) (Scheme, R = Me) rather than that corresponding to (IV) (*i.e.* a complex of Pd^{II} with the catechol anion) in the scheme previously given.[1] We thus have equation (i) and from the values of G_1 and I_1 [see part (1) of the Results section] we deduce the values of ε and $K_{eq.}$ as given in Table 4.

$$\frac{[Pd]_t}{A_\infty} = \frac{[H^+]^2}{2\varepsilon K_{eq.}[H_2Mecat]} + \frac{1}{2\varepsilon} \qquad \text{(i)}$$

The kinetics of the formation reactions appear to be different from those of H_2cat[1] but the decomposition reactions follow a similar pattern.

Reactions of $PdCl_2$ *with* H_2Mecat *and* H_2cat.—Compared with the system studied previously[1] the reactants now include the species $PdCl^+$ and $PdCl_2$ and, in principle, both of these on reaction with the diols can give intermediates and products that are capable of aquation, chloride substitution, and protonation reactions. A complete scheme that takes into account all these possibilities would be intractable so we have been forced to make some assumptions which are mainly justified by the fact that, as shown below, they lead to a reasonably consistent interpretation of the results. First, we consider only one sequence of reactions as shown in the Scheme. The reactant palladium species are considered to be in rapid equilibrium among themselves, as are the product *o*-quinone complexes, and this will tend to keep the chloride ion concentration within a fairly narrow range if the formation constants (K_{1c}, K_{1c}', *etc.*) do not differ very markedly. (For the series $PdCl^+$, $PdCl_2$, $PdCl_3^-$, $PdCl_4^{2-}$ the formation constants decrease by a factor of about 10 at each step.[2]) The main implication in selecting the reaction sequence shown is that the kinetic behaviour is then considered to be dominated by the reactivity of Pd^{2+}. This corresponds to the behaviour recently reported[3] for the reactions of thallium(III) ions with catechol in the presence of chloride. Similarities between Pd^{II} and Tl^{III} in their reactions with diols have previously been noted.[1] We have also assumed that the absorption coefficients (at 660 nm) of the quinone complexes are approximately equal, *i.e.* that absorption at this wavelength is mainly determined by the quinone ligand.

TABLE 3

Values of $k_{obs.}/s^{-1}$ for the decomposition reactions at 25 °C, $I = 0.2$ mol dm^{-3}, [diol] = 0.01 mol dm^{-3}, $[PdCl_2] = 5.0 \times 10^{-4}$ mol dm^{-3}

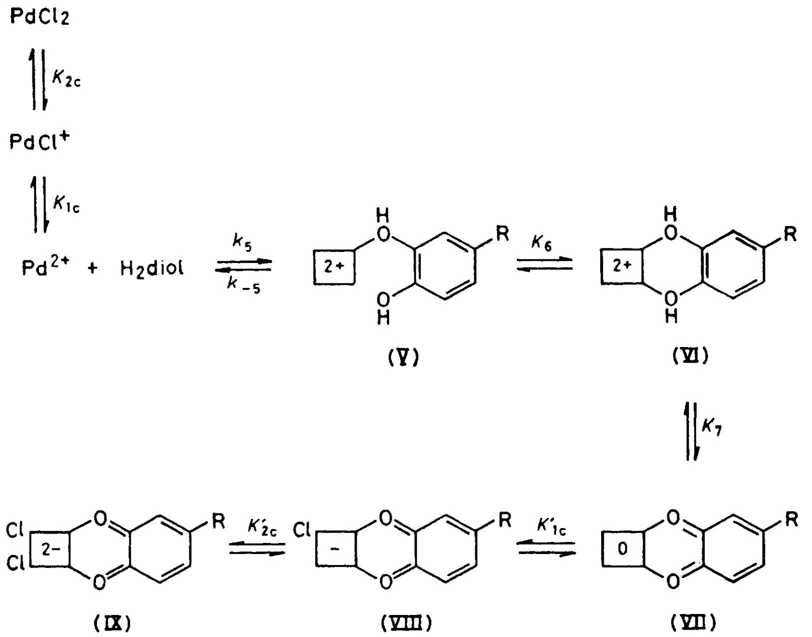
(*a*) H_2Mecat					
$10^2[H^+]/$mol dm^{-3}	4.0	7.0	10	15	20
$k_{obs.}/s^{-1}$	1.1	2.6	5.0	9.2	16
(*b*) H_2cat					
$10^2[H^+]/$mol dm^{-3}	4.1	7.1	10.1	15.1	20.1
$k_{obs.}/s^{-1}$	1.1	2.6	4.9	9.6	16.6

With these assumptions, and taking species (V) to be in negligible concentration, the following equations (ii) and (iii) are deduced where $f[Cl^-] = K_{1c}[Cl^-] + K_{1c}K_{2c}[Cl^-]^2$, $g[Cl^-] = K_{1c}'[Cl^-] + K_{1c}'K_{2c}'[Cl^-]^2$, and $K_{eq.} = K_5K_6K_7$; H_2diol = H_2cat or H_2Mecat.

$$\frac{[Pd]_t}{A_\infty} = \frac{(1 + f[Cl^-])}{2\varepsilon K_{eq.}(1 + g[Cl^-])} \cdot \frac{[H^+]^2}{[H_2diol]} + \frac{[H^+]^2}{2\varepsilon K_7(1 + g[Cl^-])} + \frac{1}{2\varepsilon} \qquad \text{(ii)}$$

$$k_{obs.} = \frac{k_5[H_2diol]}{(1 + f[Cl^-])} + \frac{k_{-5}[H^+]^2}{K_6K_7(1 + g[Cl^-] + [H^+]^2/K_7)} \qquad \text{(iii)}$$

Equations (ii) and (iii) are of the correct form to account for the equilibria and kinetic measurements reported for the reaction of $PdCl_2$ with H_2Mecat [see Results section (2*a*) and (2*b*)].



SCHEME The method of representing the palladium centres is that used by L. I. Elding, *Acta Chem Scand.*, 1970, **24**, 1341, the symbol in the centre of a square shows the charge on the complex, and corners with no ligands attached are assumed to be occupied by water molecules. R = H or Me; H^+ and Cl^- have been omitted. $K_{1c} = [PdCl^+]/[Pd^{2+}][Cl^-]$, $K_{2c} = [PdCl_2]/[PdCl^+][Cl^-]$, $K_{1c'} = [(VIII)]/[(VII)][Cl^-]$, $K_{2c'} = [(IX)]/[(VIII)][Cl^-]$, $K_6 = [(VI)]/[(V)]$, $K_7 = [(VII)][H^+]^2/[(VI)]$. This Scheme may be regarded as an extension of Scheme 1 of reference 1

TABLE 4

Values of quantities derived from the plots described in the Results section

Reaction	ϵ/dm³ mol⁻¹ cm⁻¹	$10^2K_{eq.}$/mol dm⁻³	$10^4K_7(1 + g[Cl^-])$ [a]/ mol² dm⁻⁶		$\frac{10^{-2}(1 + f[Cl^-])}{K_{eq.}(1 + g[Cl^-])}$ [a] / dm³ mol⁻¹	
			(*i*)	(*ii*)	(*i*)	(*ii*)
$Pd(aq)^{2+} + H_2Mecat$	650 ± 100	2.5 ± 0.5				
$PdCl_2 + H_2Mecat$	700		1.3 ± 0.7	0.8 ± 0.2	9 ± 3	7.5 ± 1.5
$PdCl_2 + H_2cat$	700 ± 150				22 ± 10	26 ± 3
$Pd(aq)^{2+} + H_2cat$ [b]	700 ± 100	0.8				

[a] Column (*i*) are values from equilibrium data; column (*ii*) are values from kinetic data. [b] Values from ref. 1.

From these we identify the following relationships shown below. Thus, the quantity $K_7(1 + g[Cl^-])$ is evaluated as $1/(2\varepsilon I_3)$ from the equilibrium data and as G_5/I_5 from the kinetic data. Similarly, the quantity $(1 + f[Cl^-])/$

$$I_2 = 1/2\varepsilon \qquad G_3 = \frac{(1 + f[Cl^-])}{2\varepsilon K_{eq.}(1 + g[Cl^-])}$$

$$I_3 = \frac{1}{2\varepsilon K_7(1 + g[Cl^-])} \qquad G_4 = \frac{k_5}{(1 + f[Cl^-])}$$

$$I_5 = K_6/k_{-5} \qquad G_5 = \frac{K_6K_7(1 + g[Cl^-])}{k_{-5}}$$

$K_{eq.}(1 + g[Cl^-])$ is equal to $2\varepsilon G_3$ (from the equilibrium data) and $1/(G_4G_5)$ (from the kinetic data). The numerical values of these quantities are collected in Table 4.

For the reactions of $PdCl_2$ with H_2cat more appropriate forms of equations (ii) and (iii) can be obtained by assuming that, as H_2cat is a stronger acid than H_2Mecat (and this is probably also true of the complexed diols), species (VI) (R = H) is not present in significant concentration. The second term on the right-hand side of equation (ii) then disappears and the term $[H^+]^2/K_7$ is eliminated from equation (iii). With these modifications [see Results section (3)] the equations for I_6 and G_6 below are obtained. The modified form of equation (iii)

$$I_6 = 1/2\varepsilon \quad G_6 = \frac{(1 + f[Cl^-])}{2\varepsilon K_{eq.}(1 + g[Cl^-])}$$

does not account satisfactorily for the behaviour of the gradients of the plots of $k_{obs.}$ *versus* $[H_2cat]$ (which are found to be acid-dependent) but it does predict the correct form for the intercepts I_7. However, if the limiting gradient (as $[H^+]$ becomes large) is taken as unity [see Results section (3*b*)] then we have also $G_7 = (1 + f[Cl^-])/K_{eq.}(1 + g[Cl^-])$. The numerical values of these quantities are also given in Table 4, and it is seen that the results collected in Table 4 taken together illustrate the general consistency of the present treatment with quite good agreement between the results obtained from the independent equilibrium and kinetic data.

The data in Table 3 [Results sections (2*c*) and (3*c*)] are consistent with a mechanism for the decomposition reactions (regeneration of reagents) that involves a rate-determining step such as the one labelled k_{-5} in the Scheme, thus adding to the general consistency of the present results. However, at the higher acidities used in these decomposition reactions there may be radical changes in the balance of species present in equilibrium and we cannot therefore identify the particular one involved. The fact that corresponding values of $k_{obs.}$ for H_2cat and H_2Mecat are also identical suggests that the rate-determining step involves the oxygen *meta* to the methyl group in H_2Mecat.

Two further deductions may be made from the values in Table 4. First, two independent calculations give a value of about 20 for the quantity $(1 + f[Cl^-])/(1 + g[Cl^-])$. If this is dominated by the value of the numerator we can estimate the chloride concentration as about 4×10^{-4} mol dm^{-3}, which seems a reasonable value. Second, two independent calculations give the value of the ratio $K_{eq.}$ (for H_2Mecat)/$K_{eq.}$(for H_2cat) as approximately 3. This result throws some light on the question of the nature of the reaction product. In our earlier investigation [1] we suggested tentatively that, from the nature of its spectrum, the product might be a complex of palladium(0) with the quinone rather than a complex of Pd^{II} with the diol anion. If the latter were the product we might expect $K_{eq.}$ for H_2Mecat to be smaller than $K_{eq.}$ for H_2cat, since H_2cat is the stronger acid. That the converse is true is consistent with the fact that H_2Mecat is a stronger reducing agent than H_2cat ($E^\ominus$ values at 25 °C for the quinone/diol systems are 0.74 and 0.79 V respectively). Species (VII) is an intermediate in the overall process $Pd^{II} + H_2\text{diol} \rightleftharpoons Pd^0 + \text{quinone} + 2H^+$ so we might expect the equilibrium labelled K_7 to be displaced more towards (VII) in the case of H_2Mecat than for H_2cat. This conclusion with regard to the product shows that the present reactions are similar to those of Pd^{II} with benzene-1,4-diol [4] and Fe^{III} with catechol.[5]

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