# Mechanism of Complex Formation Between Benzene-1,2-diol and Aquapalladium(II). Equilibria and Kinetics in Acidic Aqueous Perchlorate Media

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

Palladium(II) aqua-ions, in acidic aqueous perchlorate solution, react rapidly with benzene-1,2-diol (catechol) to form a 1 : 1 green complex. From equilibrium spectrophotometric data the reaction quotient $K_{eq.}\{Pd^{2+} + H_2cat \rightleftharpoons [Pd(cat)] + 2H^+\}$ is found to be (6 ● 2) × $10^{-3}$ mol dm$^{-3}$ at 25 °C and $I = 0.20$ mol dm$^{-3}$. The rate of the forward reaction, first order in the concentration of each reagent and with a combined $[H^+]^{-1}$ and $[H^+]^{-2}$ dependence, is interpreted in terms of reactions involving $[Pd(OH)]^+$ and $Pd[OH]_2$ with the diol to give a 1 : 1 chelate complex. The reverse reaction has been investigated independently by treating the complex with excess of $HClO_4$ and the two-stage mechanism is discussed with reference to a general scheme which takes into account the possible intermediate species.

BENZENEDIOLS are widely investigated substrates which in turn can act as potentially bidentate ligands [1] towards several metal ions, or as reversible two-electron reductants [2] with formation of the corresponding quinones.[3]

Several papers have been published on the mechanism of complex formation of $Fe^{III}$,[4] $Tl^{III}$,[5] $V^{V}$,[6] $Ni^{II}$,[7] $Co^{II}$,[7] $Mo^{VI}$,[8,9] and $W^{VI}$ [9] with benzene-1,2-diol as well as on the redox reaction with oxidizing metal species such as $Fe^{III}$,[10] $Tl^{III}$,[11] $Mn^{III}$,[12] and $Co^{III}$,[13] and inert complexes such as $[Fe^{III}L_3]^{3+}$ [14] (L = 1,10-phenanthroline-type ligands), and others.[15]

Very little work has been reported on the kinetics and mechanism of the reactions of aquapalladium(II) either as a co-ordination centre or as an oxidizing species.[16-18] In the present paper we report the results of an investigation on the interaction between aquapalladium(II) and benzene-1,2-diol to give a 1 : 1 chelate complex.

## EXPERIMENTAL

*Materials.*—Perchloric acid, sodium perchlorate, and benzene-1,2-diol were analytical grade chemicals (Merck). Stock solutions of aquapalladium(II) were prepared from palladium(II) sulphate (Alfa) and 0.1 mol dm$^{-3}$ perchloric acid. The solid dissolved almost completely with the aid of an ultrasonic bath and the small undissolved quantity was removed by filtration. In some cases the sulphate ion was removed from these solutions by adding a slight excess of barium perchlorate and filtering. The sulphate-free solutions showed the same behaviour in the kinetic experiments as those containing sulphate. The aquapalladium(II) concentrations of stock solutions were determined from absorbance measurements at 380 nm ($\varepsilon$ = 80 dm$^3$ mol$^{-1}$ cm$^{-1}$). This method gave results in agreement with those obtained by using the method of Poë and Vaughan.[19] The palladium solutions were stored in the dark and freshly prepared every few days.[20] Doubly distilled water was used in the preparation of all stock solutions and these were shown to be free of chloride.

*Measurements.*—Kinetic measurements were carried out at 25.0 ± 0.1 °C using a Durrum–Gibson stopped-flow apparatus † equipped with a 2-cm quartz cell. Solutions of palladium(II) sulphate and benzene-1,2-diol of the required concentration, acidity, and ionic strength were prepared from stock solutions, and absorbances were measured at 660 nm.

In the formation experiments solutions of aquapalladium(II) and benzene-1,2-diol (in at least 10-fold excess) were mixed in the stopped-flow apparatus and values of rate constants were obtained from gradients (over at least two half-times) of plots of $\ln(A_\infty - A_t)$ *vs.* time, where $A_t$ is the absorbance at time $t$ and $A_\infty$ is the final absorbance.

In the decomposition experiments, mixtures of palladium(II) sulphate and benzene-1,2-diol solutions (at $[H^+] = 0.004$ mol dm$^{-3}$) were prepared quickly and then mixed in the stopped-flow apparatus with solutions of perchloric acid. In these experiments the reaction occurred in two stages (a fast step followed by a slower one). The second stage was slow enough to allow a good estimate to be made of the absorbance ($A_{tr}$) at the end of the first stage. The rate constants for the fast step were determined from plots of $\ln(A_t - A_{tr})$ *vs.* time. Rate constants for the slow step were determined from plots of $\ln(A_t - A_\infty)$ *vs.* time.

The concentrations reported throughout this work refer to the reaction mixtures after mixing the reagent solutions in the stopped-flow apparatus. In the palladium(II) sulphate solutions of low acidity the stoicheiometric hydrogen-ion concentration was found to agree with that calculated from pH measurements (using a Metrohm E 388 potentiometer). Spectra of mixtures of palladium(II) sulphate and benzene-1,2-diol were recorded (using Perkin-Elmer EPS 3T or Pye Unicam SP 8000 spectrophotometers) as quickly as possible after mixing the solutions.

## RESULTS AND DISCUSSION

*Equilibrium and Stoicheiometry.*—When solutions of low acidity containing aquapalladium(II) are mixed with an excess of benzene-1,2-diol (catechol) a green colour rapidly appears (half-times of a few seconds) and the mixture then slowly darkens (half-times of the order of 20 min) with the formation of a black precipitate. The spectrum of the mixture before it darkens shows a broad band in the region 300—400 nm, and another with a

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† Control experiments were carried out with iron(III) perchlorate (2 × $10^{-4}$ mol dm$^{-3}$) and salicylic acid (2 × $10^{-3}$ mol dm$^{-3}$), both in 0.02 mol dm$^{-3}$ perchloric acid; on mixing these solutions in the apparatus the absorbance of the mixture remained unchanged over a period of 10 min, and no diffusion of the iron(III) solution into the cell was detected.

maximum near 660 nm. The green colour is discharged by the addition of an excess of perchloric acid. These observations can be interpreted as resulting from the rapid reversible formation of a palladium(II)–catechol complex.

TABLE 1

Values of $10^2\ k_{obs.}/s^{-1}$ and of absorbance at equilibrium ($A_\infty$) for the formation reaction of [Pd(cat)] at different acidities and catechol concentrations *

| $10^3[H_2cat]$/mol dm$^{-3}$ | [H$^+$]/mol dm$^{-3}$ 0.0030 | 0.0050 | 0.0100 | 0.0200 | 0.0400 |
|---|---|---|---|---|---|
| 4.00 | 6.1<br>(0.398) | | | | |
| 7.00 | 8.8<br>(0.431) | 3.2<br>(0.444) | | | |
| 10.0 | 12<br>(0.468) | 5.0<br>(0.495) | 1.7<br>(0.167) | 1.1<br>(0.051) | 0.9<br>(0.015) |
| 20.0 | 26<br>(0.509) | 8.8<br>(0.553) | 2.8<br>(0.268) | 1.5<br>(0.091) | 1.1<br>(0.029) |
| 30.0 | 35<br>(0.553) | 11.5<br>(0.568) | 3.5<br>(0.337) | 2.0<br>(0.137) | 1.2<br>(0.041) |
| 40.0 | 52<br>(0.585) | 17<br>(0.602) | 4.5<br>(0.377) | 2.2<br>(0.194) | 1.7<br>(0.055) |

* Ionic strength $I = 0.2$ mol dm$^{-3}$ Na[ClO$_4$], 25.0 °C, $[Pd]_t = 4.0 \times 10^{-4}$ mol dm$^{-3}$.

The green colour is similar to that produced on mixing catechol with iron(III) solutions [4] which suggests that the absorption at 660 nm may be due mainly to the co-ordinated catechol. The absorption in the region 300—400 nm is typical of palladium(II) complexes with ligands having oxygen-donor atoms. The darkening is explained by the occurrence of intramolecular electron transfer to give palladium metal and *o*-benzoquinone. The latter is unstable in aqueous solution and undergoes coupling reactions (with itself and with unreacted catechol) to give dark coloured products.[21] Although the darkening process is slow enough not to interfere with the kinetic study of the reverse of complex formation (see below), it occurs too rapidly to allow the Pd : catechol ratio in the complex to be determined by Job's method. However, the kinetic study of the complex-formation reaction gives $A_\infty$ values for a series of acid and catechol concentrations (Table 1) and these results are consistent with the stoicheiometry (H$_2$cat = catechol) in equation (1). If ε = molar absorption coefficient of [Pd(cat)] at

$$Pd^{2+} + H_2cat \xrightleftharpoons{K_{eq.}} [Pd(cat)] + 2\,H^+ \qquad (1)$$

660 nm and $[Pd]_t$ = stoicheiometric concentration of palladium, then for a path length of 2 cm equations (2) and (3) are obtained, which combine to give equation (4). Under our experimental conditions the concentrations of

$$A_\infty = 2\varepsilon[Pd(cat)] = 2\varepsilon K_{eq.}[H^+]^{-2}[H_2cat][Pd^{2+}] \qquad (2)$$

$$\begin{aligned}[Pd]_t &= [Pd^{2+}] + [Pd(cat)]\\ &= [Pd^{2+}]\{1 + K_{eq.}[H^+]^{-2}[H_2cat]\}\end{aligned} \qquad (3)$$

$$\frac{[Pd]_t}{A_\infty} = \frac{1}{2\varepsilon} + \frac{[H^+]^2}{2\varepsilon K_{eq.}[H_2cat]} \qquad (4)$$

catechol and acid (except at the lowest concentrations) are very much greater than $[Pd]_t$. Figure 1 shows that the plot of $[Pd]_t/A_\infty$ against $[H^+]^2/[H_2cat]$ is linear as required by equation (4), and from this plot the values of $K_{eq.}$ and ε are obtained as given in Table 2.

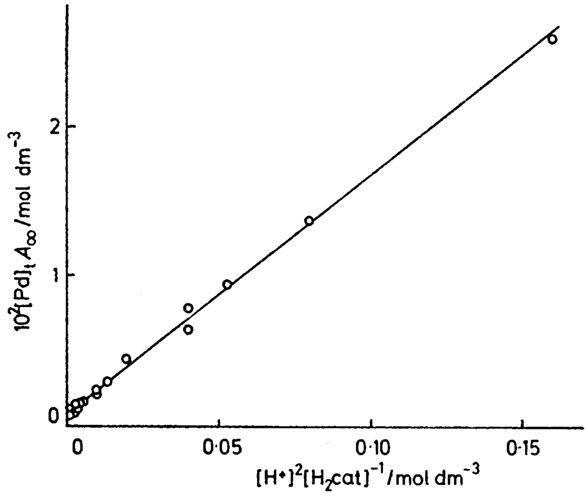


FIGURE 1 Plot of equilibrium data for [Pd(cat)] formation, $10^2[Pd]_t/A_\infty$ *vs.* $[H^+]^2/[H_2cat]$. See equation (4)

TABLE 2

Values of derived constants (25.0 °C, $I = 0.2$ mol dm$^{-3}$ Na[ClO$_4$]); the various constants have the meanings shown in Scheme 1 except that $K_{eq.}$ is defined by equation (1) and ε is the molar absorption coefficient of species (IV) at 660 nm. The first two columns show the equations used to deduce the given values and the Figure that represents the results

| Equation | Figure | Constant | Value |
|---|---|---|---|
| (4) | 1 | $K_{eq.}$ | $(6 \pm 2) \times 10^{-3}$ mol dm$^{-3}$ |
| (6) | | $k_{-1}/K_4$ | $(8 \pm 2) \times 10^{-3}$ s$^{-1}$ |
| (6) | 2 | $k_1K_{1a}K_{2a}$ | $(8.5 \pm 0.5) \times 10^{-5}$ mol dm$^{-3}$ s$^{-1}$ |
| (6) | 2 | $k_2K_{1a}$ | $(3.0 \pm 0.5) \times 10^{-3}$ s$^{-1}$ |
| (7) | 3 | $k_{-3}/K_5$ | $26 \pm 2$ dm$^3$ mol$^{-1}$ s$^{-1}$ |
| (8) | 4 | $K_3K_5$ | $(1.3 \pm 0.2) \times 10^{-2}$ mol dm$^{-3}$ |
| (8) | 4 | ε | $700 \pm 200$ dm$^3$ mol$^{-1}$ cm$^{-1}$ |
| (4) | 1 | ε | $700 \pm 200$ dm$^3$ mol$^{-1}$ cm$^{-1}$ |

TABLE 3

Values of $k_{obs.}/s^{-1}$ and of absorbance at the end of fast step ($A_{tr}$) for the decomposition reactions of [Pd(cat)] *

| [H$^+$]/mol dm$^{-3}$ | $k_{obs.}$ Fast step | Slow step | $A_{tr}$ |
|---|---|---|---|
| 0.010 | | 0.008 | 0.187 |
| 0.020 | | 0.02 | 0.125 |
| 0.040 | | 0.02 | 0.076 |
| 0.050 | 1.10 | 0.03 | 0.060 |
| 0.100 | 2.35 | | 0.032 |
| 0.150 | 3.85 | | 0.020 |
| 0.200 | 5.25 | | 0.018 |

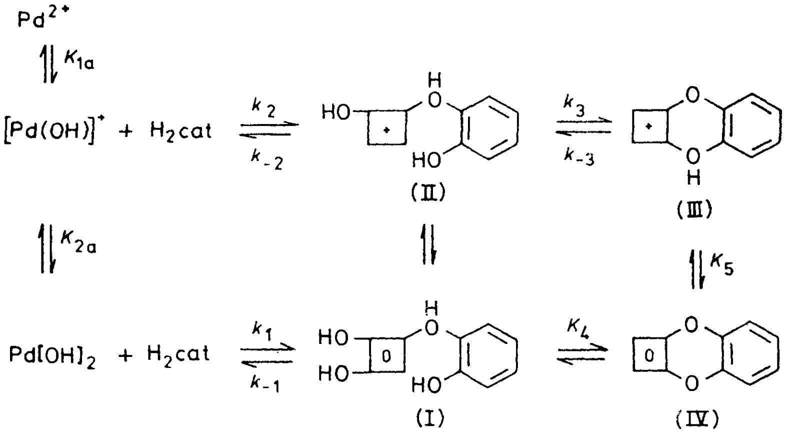
* $[Pd]_t = 2.0 \times 10^{-4}$ mol dm$^{-3}$, $[H_2cat]_t = 1.0 \times 10^{-2}$ mol dm$^{-3}$, $I = 0.20$ mol dm$^{-3}$ Na[ClO$_4$], 25.0 °C. (For the experimental details of the decomposition experiments, see the Experimental section.)

*Kinetics of Reversible Complex Formation.*—The rate constants obtained in the study of the formation of the complex are given in Table 1 and those obtained for the reverse reaction are in Table 3 together with values of the absorbance ($A_{tr}$) measured between the two distinguishable stages of the reverse reaction. The main features of these results are as follows. (i) For the formation reactions plots of $k_{obs.}$ *vs.* $[H_2cat]$ are linear with an intercept independent of $[H^+]$ and with a gradient ($G$) that fits an expression of the form (5) ($a$ and $b$ are constants). The plot of $G[H^+]$ against $[H^+]^{-1}$ is shown in Figure 2. (ii) For the decomposition of [Pd(cat)]

$$G = a[H^+]^{-2} + b[H^+]^{-1}$$

$$\text{or} \qquad G[H^+] = a[H^+]^{-1} + b \qquad (5)$$

into $Pd^{2+}$ and catechol the rate constants for each step are acid dependent. In the first (rapid) step $k_{obs.}$ is proportional to $[H^+]$ (see Figure 3) whilst in the second (slow) step the dependence is more complicated. Values of $k_{obs.}$ for this slow step are less reliable than other rate constants reported here because the slow step is accompanied by rather small total absorbance changes.



SCHEME 1 $K_{1a} = [Pd(OH)^+][H^+]/[Pd^{2+}]$; $K_{2a} = [Pd(OH)_2][H^+]/[Pd(OH)^+]$; $K_3 = k_3/k_{-3} = [(III)]/[(II)]$; $K_4 = [(IV)]/[(I)]$; $K_5 = [(IV)][H^+]/[(III)]$

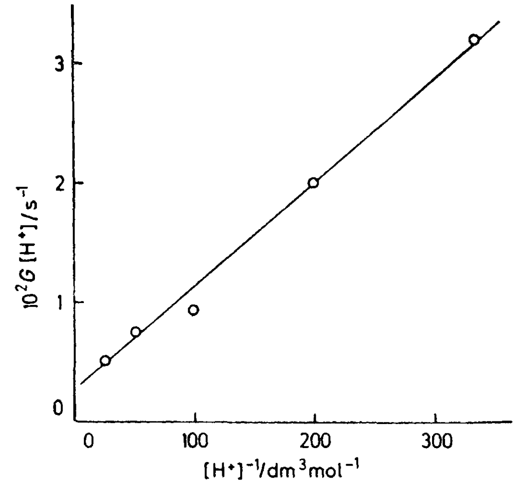


FIGURE 2 Plot of $G[H^+]$ *vs.* $[H^+]^{-1}$ for the formation of [Pd(cat)] ($G$ = gradient of plots of $k_{obs.}$ *vs.* $[H_2cat]$, see text)

Most of the results obtained can be accounted for in terms of Scheme 1 (above) in which the method of representing the palladium(II) centres is that used by Elding [22] (the symbol in the centre of a square shows the charge of the complex species, and corners shown with no ligands attached are assumed to be occupied by water molecules). Protons liberated in some of the steps shown have been omitted for clarity. The acid protons represented in the various complexes are arbitrarily shown as attached to the oxygen atoms of catechol [species (II), for example, might equally well be represented with one of the catechol protons attached to the OH oxygen on the palladium(II) centre, thus making it into a water molecule]. Scheme 1 follows the pattern observed in other reactions of this kind (*e.g.* the reactions of catechol with $Fe^{III}$ [4] and with $Tl^{III}$ [11]) in which the kinetic form of the acid dependence arises from the acid properties of the metal aqua-ion. In outline, the suggestion is that the formation reactions occur by two routes with $k_1$ and $k_2$ as rate-determining steps followed by formation of the product (IV) in fast reactions. In the reverse process, which is measured at higher acidities than those used in the formation reactions, the main

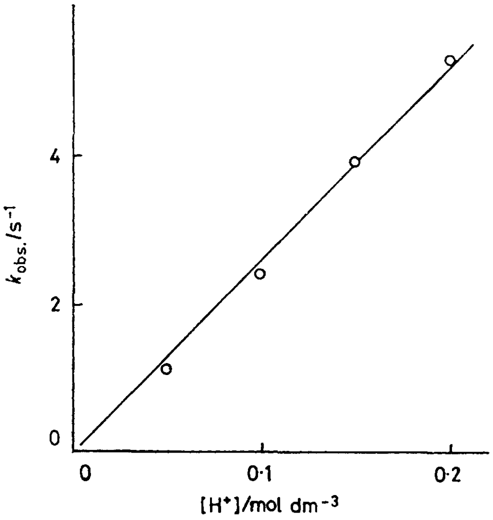


FIGURE 3 Variation with acidity of the observed rate constant $k_{obs.}$ for the fast decomposition step [see equation (7)]

route for the return of (IV) to $Pd^{2+}$ and catechol is *via* (III) and (II).

With a few simplifying assumptions the expressions for the observed rate constants deduced from Scheme 1 fit the data quite well. The main assumption is that the $pK_a$ values for catechol are considerably reduced by co-ordination to the palladium(II) aqua-ion, with the consequence that the only complex species in significant concentration is (IV). Species (I) and (II) are likely to undergo rapid ring-closure reactions and will therefore be present in low concentration in the course of the formation process, with (II) at a lower concentration than (I). Except at the lowest acid concentration, the unreacted palladium will be mainly in the form of the simple $Pd^{2+}$ ion. These assumptions are in fact implicit in the deduction of equation (4). In the reverse process the first step involves the rate-determining opening of the chelate ring ($k_{-3}$), and the species present in significant concentration at the end of this stage are (II) and (IV). The second (slow) step is probably $k_{-2}$ (see Scheme 1). However, as stated above, the observed rate constants for this step, especially those at the higher acid concentrations, are calculated on the basis of rather small absorbance changes and they are given only to indicate an order of magnitude.

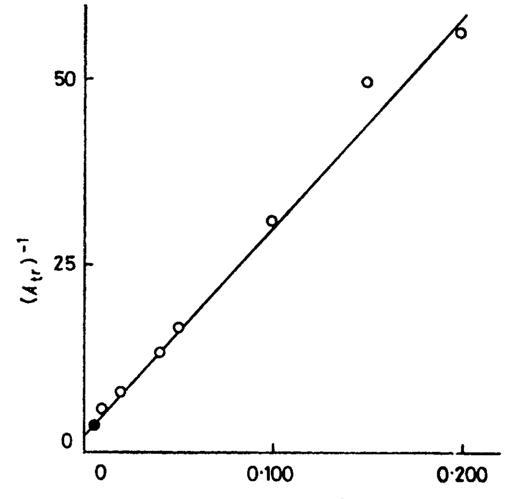


FIGURE 4 Plot of data to illustrate equation (8). The point (●) represents the absorbance of the undecomposed complex solution (see Experimental section) taking into account the dilution. $[Pd]_t = 2 \times 10^{-4}$ mol $dm^{-3}$

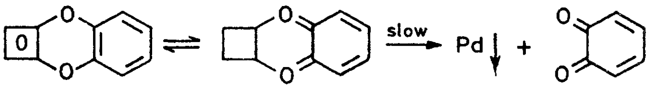
The equations below [formation reaction (6); reverse reaction, fast step (7); between steps (8)] are deduced from Scheme 1 with the assumptions outlined above. These equations were tested by making the appropriate graphical plots as shown in Figures 2, 3, and 4 [these correspond to equations (6), (7), and (8) respectively]. From these results the values of many of the constants have been derived (Table 2) and these show good internal consistency. The two values of ε agree well. Furthermore, the constant $K_{eq.}$ is equal to $K_{1a}K_{2a}k_1K_4/k_{-1}$ and, inserting the values of these quantities from the results in Table 2, this gives $K_{eq.} = (10 \pm 3) \times 10^{-3}$ mol $dm^{-3}$, in reasonable agreement with the value obtained from the equilibrium measurements.

$$k_{obs.} = \left(\frac{k_1K_{1a}K_{2a}}{[H^+]^2} + \frac{k_2K_{1a}}{[H^+]}\right)[H_2cat] + \frac{k_{-1}}{k_4} \quad (6)$$

$$k_{obs.} = k_{-3}[H^+]/K_5 \quad (7)$$

$$\frac{[Pd]_t}{A_{tr}} = \frac{1}{2\varepsilon} + \frac{1}{2\varepsilon}\left(\frac{[H^+]}{K_3K_5}\right) \quad (8)$$

Finally, we speculate briefly about the nature of species (IV). As represented in Scheme 1, the implication is that it is a complex of $Pd^{II}$ and the doubly charged catechol anion. Ultimately species (IV) decomposes into $Pd^0$ and *o*-benzoquinone, a process involving electron transfer. It seems unlikely that such an electron-transfer process would be very slow so it may be more appropriate to formulate (IV) as a complex of $Pd^0$ and the quinone, and to suppose that the decomposition of this complex is the slow process observed when darkening occurs in the reaction mixtures (see above), *i.e.* as shown in Scheme 2. This type of reaction has been observed in the reaction of palladium(II) compounds with benzene-1,4-diol[23] where a $Pd^0$–quinone complex can be isolated before it decomposes slowly into Pd metal and *p*-benzoquinone. It may also be significant that on mixing palladium(II) sulphate with a benzene-1,2-diol of high reduction potential (such as Tiron, 4,5-dihydroxybenzene-1,3-disulphonic acid) a stable yellow (rather than an unstable green) complex is formed; *i.e.* if the stable 1,2-diol complexes of $Pd^{II}$ are yellow, then the green colour observed in the present experiments (and in the reaction of $Fe^{III}$ with catechol)[4] may be due to a species in which electron transfer has already occurred prior to decomposition into oxidized and reduced products.



SCHEME 2

This work was carried out with the aid of a N.A.T.O. grant.

[0/285 *Received*, 18*th February*, 1980]

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