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# Kinetics for Anation of Aqua Palladate(II) Complexes

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We have previously shown that the stepwise anations and acid hydrolyses in the palladium(II)[1,2,3] and platinum(II)[4,5] chloro and bromo systems can be described by the following reaction mechanism (Fig. 1):

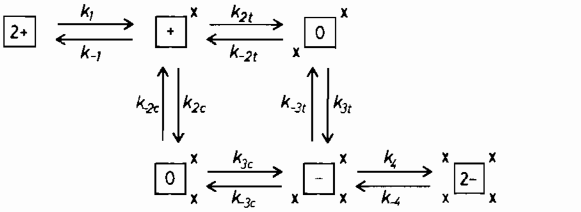

Fig. 1. Reaction mechanism according to Ref. 3 and 4. Horizontal arrows denote fast reactions, vertical arrows slow reactions.

A recent article by Bekker and Robb[6] reports results for the chloride anation of *cis*- and *trans*-$PdCl_2$, which seriously disagree with our findings, because they are based on hypotheses which are contrary to our previous work.[3]

Pearson and Hynes[7] have also obtained some discordant results for these two reactions. The conclusions of these authors are inconsistent with the extended experimental information now available, so alternative interpretations of their experiments are needed.

In order to avoid confusion, a discussion of the reaction mechanism and the experimental techniques for these systems therefore seems desirable. Reliable equilibrium data and absorption spectra for the individual complexes are of great importance for a successful interpretation of kinetic studies in these systems. Ref. 1 gives stability constants and absorption spectra for the palladium chloro and bromo complexes and a review of relevant previous stability studies. Our values for the stability constants in these systems have been verified recently.[8,9] Pearson and Hynes[7] reacted equilibrated palladium(II) perchlorate solutions containing various concentrations of chloride ($10^{-4}$ *M* to $10^{-1}$ *M*) with excess chloride. Bekker's and Robb's[6] experimental design was similar. For low concentrations of chloride in the original palladium solution. Pearson and Hynes observed only one slow reaction, called A. For intermediate concentrations, they found one fast reaction, called C, which was followed by the slow reaction A. At chloride concentrations of 0.1 *M*, no reaction was observed. They interpreted reaction A as the anation of *trans*-$PdCl_2$ and reaction C as the anation of *cis*-$PdCl_2$, according to the following model (Fig. 2):

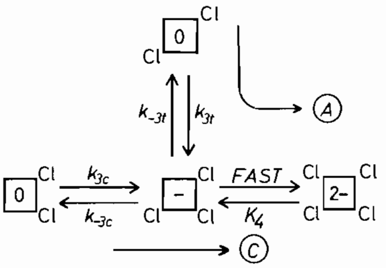

Fig. 2. Reaction model according to Pearson and Hynes.[7]

A fast equilibrium between $PdCl_3^-$ and $PdCl_4^{2-}$ was assumed. It is true that this reaction is fast compared to the anation of the *trans*-isomer, but it is definitely *not* fast compared to the anation of the *cis*-isomer (*vide infra*).

## The Slow Reaction, A

Using the assumption of a rapid equilibrium between $PdCl_3^-$ and $PdCl_4^{2-}$, Pearson and Hynes[7] derived the following expression for the observed rate constant:

$$k_{obs} = \frac{k_{3t}[Cl^-] + k_{3t}K_4^{-1} + k_{-3t}K_4^{-1}[Cl^-]^{-1}}{1 + K_4^{-1}[Cl^-]^{-1}} \qquad (1)$$

which was simplified to

$$k_{obs} = \frac{k_{3t}[Cl^-] + k_{3t}K_4^{-1}}{1 + K_4^{-1}[Cl^-]^{-1}} \qquad (2)$$

since $k_{-3t}K_4^{-1}[Cl^-]^{-1} \ll k_{3t}K_4^{-1}$, *i.e.* the reverse reaction was neglected. By plotting $k_{obs}(1 + K_4^{-1}[Cl^-]^{-1})$ *vs.* $[Cl^-]$ they obtained straight lines for different values of $K_4$ giving $k_{3t}$ as the slope and small intercepts. However, eqn. (2) may be rewritten:

$$k_{obs} = k_{3t}[Cl^-] \times \frac{[Cl^-] + K_4^{-1}}{[Cl^-] + K_4^{-1}} \qquad (3)$$

Therefore, the expression for the observed rate constant should be expected to obey

$$k_{obs} = k_{3t}[Cl^-] \qquad (4)$$

if the reverse reaction is suppressed and the reaction model given in Fig. 2 is correct.

Careful study of reaction A, however, reveals the existence of non-zero intercepts when the experimental rate constant is plotted *vs.* chloride concentration (Ref. 3, Fig. 2). Intercepts have also been observed for the corresponding reactions in the Pt(II)-chloro[4] and Pt(II)-bromo[5] systems. Thus, all experiments indicate a *two-term rate law* with a rate constant:

$$k_{obs} = k_{3t}[X^-] + \text{const.} \tag{5}$$

The constant term in this equation is not caused by the reverse reaction described by $k_{-3t}$, since this has been suppressed in the concentration ranges used. The additional term appears in the rate expression since the anation of the species in the upper row of Fig. 1 can occur by the two *parallel* reaction paths, marked $k_{2c}$ and $k_{3t}$. When excess chloride is added to solutions containing a mixture of different complexes, the equilibria denoted by horizontal arrows are established rapidly (because of the *trans*-effect). Subsequently, the *equilibrium mixture* of *trans*-$PdX_2$, $PdX^+$ and $Pd^{2+}$ reacts *via* the two parallel slow paths, denoted by $k_{2c}$ and $k_{3t}$, to the *equilibrium mixture* of *cis*-$PdX_2$, $PdX_3^-$ and $PdX_4^{2-}$. If the concentration of halide added is sufficiently large to suppress the reverse reactions, the rate can be expressed as:

$$\text{Rate} = k_{3t}[X^-]\,[\textit{trans}\text{-}PdX_2] + k_{2c}[X^-]\,[PdX^+] \tag{6}$$

The equilibration between $PdX^+$ and *trans*-$PdX_2$ is rapid, so

$$[PdX^+] = [\textit{trans}\text{-}PdX_2]\,K_{2t}^{-1}\,[X^-]^{-1} \tag{7}$$

where $K_{2t}$ is the stability constant $k_{2t}/k_{-2t}$. Therefore, we obtain a pseudo-first order reaction with a rate constant

$$k_{obs} = k_{3t}[X^-] + k_{2c}/K_{2t} \tag{8}$$

in agreement with eqn. (5) (*cf.* Ref. 3). The analogous mechanism for the corresponding platinum complexes has been described in full detail previously.[4,5]

Bekker and Robb[6] obtained straight lines with small intercepts for plots of $k_{obs}$ for the slow reaction *vs.* $[Cl^-]$, exactly as anticipated from eqn. (8). The slope was correctly identified as $k_{3t}$. The values obtained, (29.3 ± 1.5) $M^{-1}$ $s^{-1}$ at 25 °C and (33.6 ± 1.7) $M^{-1}$ $s^{-1}$ at 24.9 °C, agree satisfactorily, in view of the experimental errors, with our value of (21.7 ± 0.2) $M^{-1}$ $s^{-1}$ at 25.0 °C.[3] However, Bekker and Robb identified the intercept of the line with the rate constant for the reverse reaction, $k_{-3t}$. But the reverse reaction is completely negligible in the chloride concentration range used according to equilibrium data.[1] The intercept should therefore be identified with the quantity $k_{2c}/K_{2t}$ in eqn. (8), *not* with $k_{-3t}$. Their experimental value of 0.7 $s^{-1}$ for the intercept agrees excellently with our value of 0.82 ± 0.07 $s^{-1}$ (Ref. 3, Table V), whereas $k_{-3t}$ is only (2.7 ± 0.9) × $10^{-2}$ $s^{-1}$.[3] This means that the stability constant $K_{3t} = 1/2.1 \times 10^2\ M^{-1} = 48\ M^{-1}$ calculated by Bekker and Robb in their Table 3 has no physical meaning. Our experiments indicate $K_{3t} = 800\ M^{-1}$ (Ref. 3, Table VI).

## The Fast Reaction, C

Pearson's and Hynes's[7] assumption (*cf.* Fig. 2) that the equilibration between $PdCl_3^-$ and $PdCl_4^{2-}$ is rapid compared to the anation of the *cis*-isomer is certainly not valid. For instance, for a concentration of chloride of 0.1 *M*, the experimental rate constant for anation of *cis*-$PdCl_2$ is[3] $k_{-3c} + k_3[Cl^-] = 14\ s^{-1} + 5400 \times 0.1\ s^{-1} = 550\ s^{-1}$ compared to $k_{-4} + k_{4c}[Cl^-] = 8.9\ s^{-1} + 180 \times 0.1\ s^{-1} = 27\ s^{-1}$ for the anation of $PdCl_3^-$.[2]

A correct interpretation of reaction C will therefore be:

$$\textit{cis}\text{-}PdCl_2 \ \underset{}{\overset{\textit{fast}}{\rightleftarrows}}\ PdCl_3^- \ \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}}\ PdCl_4^{2-}$$

If the concentration of chloride is large enough to displace the fast equilibrium to the right completely, the observed reaction will therefore be the anation of $PdCl_3^-$ with a rate constant of $k_{-4} + k_4[Cl^-]$. The value of 210 $M^{-1}$ $s^{-1}$ for the slope found by Pearson and Hynes and improperly identified with $k_{3c}$, agrees satisfactorily with our determination of $k_4$ = 180 ± 3 $M^{-1}$ $s^{-1}$.[2] On the other hand, their calculation of a rate constant for the reverse reaction ($k_{-3c} = 0.06\ s^{-1}$) from the slope and an equilibrium constant $K_{3c}$, will of course be without physical significance because of the wrong assignments ($k_{-3c}$ is 14 ± 3 $s^{-1}$, Ref. 3). This fact might also explain why Pearson and Hynes did not succeed to describe the *trans*- and *cis*-effects using the simple equation by Martin *et al.*[10] In fact, such a description is possible for the complete set of our rate constants for both the chloro and bromo complexes of palladium.[3]

Pearson's and Hynes's observation that the anation of $PdCl_3^-$ is too fast for the stopped-flow technique is not consistent with our results. When palladium solutions with an initial concentration of chloride of 0.1 *M* are reacted with excess chloride, the observed rate constant will be about 100 $s^{-1}$ for $[Cl^-]$ = 0.5 *M* (*cf.* Ref. 2, Fig. 6). It should be mentioned that Syrkin *et al.*[11] obtained $k_4$ = 125 ± 10 $M^{-1}$ $s^{-1}$ and $k_{-4}$ = 5.6 ± 0.5 $s^{-1}$ from a T-jump study in rather good agreement with our results.[2]

Bekker and Robb[6] also tried to study the anation of *cis*-$PdCl_2$. The concentration of chloride in their kinetic runs at 25 °C varied within the rather narrow interval of 65 m*M* to 110 m*M*. For 65 m*M* chloride, the rate constant for anation of the *cis*-isomer will be $k_{-3c} + k_{3c}[Cl^-] = 14\ s^{-1} + 0.065 \times 5400\ s^{-1} = 365\ s^{-1}$ (*cf.* Ref. 3, Table VII). Therefore, it will be impossible to follow this reaction by the stopped-flow method for the experimental conditions used by these authors. The reaction observed in their experiments is – as in the case of Pearson and Hynes – mainly the anation of $PdCl_3^-$. Consequently, the rate and equilibrium constants calculated by Bekker and Robb in their Table 2 will have no physical significance.

Possibly, their intercepts (called $k_{3c}$) might correspond to $k_{-4}$, but the slopes are much too large compared to our values of $k_4$, even if differences in ionic strength are considered. The reason is probably that the fast preceding anation of *cis*-$PdCl_2$ will disturb the kinetics during the first half-life observed.

Unfortunately, Bekker's and Robb's interpretation of their experiments will invalidate the major part of their discussion, including the comparisons of specific rate constants and the calculations of activation parameters (except $\Delta H^{\neq}_{3t}$ and $\Delta S^{\neq}_{3t}$).

For an unambiguous investigation of the anation of *cis*-$PdX_2$ it will be necessary to follow the reaction at a wavelength where the molar absorptivities of $PdX_3^-$ and $PdX_4^{2-}$ are equal so that the slow subsequent anation of $PdCl_3^-$ causes no change of absorbance, and to use so large a concentration of free ligand that the reverse reaction described by $k_{-3c}$ is suppressed:

$$cis\text{-}PdX_2 \xrightarrow{k_{3c}} PdX_3^- \overset{slow}{\rightleftarrows} PdX_4^{2-}$$

This procedure has been described elsewhere for the palladium[3] and platinum[4,5] complexes.

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