

Kinetics of Interaction of [Pd(dien)Br⁺] with Inosine

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The kinetics of interaction of [Pd(dien)Br⁺] with inosine have been investigated by stopped-flow spectrophotometry. The rate decreases by the addition of Br⁻ ions; at higher concentration of Br⁻ the reaction becomes reversible. The mechanism of the reaction involves a direct S_N2 reaction and a solvolytic path. Their kinetic parameters are discussed and compared to previous results on similar systems.

Introduction

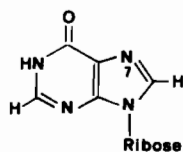
The mechanisms of substitution of palladium(II) complexes have received considerably less attention than their platinum(II) analogs. The most detailed studies concern different Pd(II)–triamine complexes, Pd(AAA)X; the mechanism of displacement of X by other ligands has been investigated by several authors [1–7]. It is now well known that a solvolytic mechanism contributes to the reaction rate and, in cases of certain sterically hindered complexes it is the only reaction path observed.

The present paper reports the results of a kinetic study on the substitution of [Pd(dien)Br⁺] by inosine, aimed to further elucidate the contribution and kinetic characteristics of this solvolytic process.

Experimental

Materials

The [Pd(dien)Br]Br complex used has been prepared by a slightly modified version of Mann's method, using PdCl₂ (Engelhart Industries) as starting material [2, 8]. Inosine which is a nucleoside derivative was a Raylo Co. product:



The aqueous solution of the aquo complex [Pd(dien)H₂O]²⁺ was obtained from the bromo complex by precipitating the bromide ions, using two

equivalents of AgNO₃. To avoid the difficulties caused by the colloidal nature of AgBr, the ionic strength of the solution was brought to 1M by means of LiClO₄; the solution was centrifugated at 7000 rpm, then filtered.

The product of the reaction could not be isolated and characterized. However, by analogy to Pt(II)–inosine complexes [9, 10], it is probable that the coordination takes place at the N₇ position of inosine.

Kinetics

The reactions were studied by stopped-flow spectrophotometry using a Durrum–Gibson system (Durrum Instrument Co.) coupled to a Jarrel–Ash 0.25m monochromator. The U.V. source used consists of a deuterium lamp and a stabilized D.C. power supply of our own construction. The drive syringes and the observation cell of the stopped-flow system were maintained at 25 ± 0.1 °C.

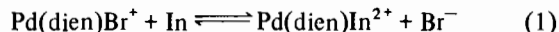
The reactions were carried out in bi-distilled water and the ionic strength of the solutions was maintained at 1M by means of LiClO₄. The concentration of the Pd(II) complexes was in the range of 2 × 10⁻⁴M to 1 × 10⁻³M. The concentration of inosine was varied between 1 × 10⁻³M and 5 × 10⁻²M and that of KBr added between 0 and 1M.

The reaction between [Pd(dien)Br⁺] and inosine produces an increase in absorbance at λ = 345 nm. The reaction of [Pd(dien)H₂O]²⁺ with Br⁻ causes an increase in absorbance at λ = 310 nm and that with inosine leads to a decrease in absorbance at λ = 300 nm. The pseudo first-order rate constants were obtained from the photographs of the oscillograms using the relationship: k_{obs}t = ln[(A₀ - A_∞)/(A - A_∞)] where A₀, A and A_∞ represent the absorbances at 0, t and infinite time respectively. In cases where the pseudo first-order conditions were not respected, the rate constants were obtained from the initial portion of the integrated rate law.

Results

The preliminary kinetic experiments, which were carried out at constant Pd(dien)Br⁺ concentrations

indicated that both inosine (In) and Br^- had an influence on the rate of reaction. Moreover, it appeared quite early that in presence of higher concentrations of Br^- the reaction became reversible:



Even in these cases the change in absorbance continued to follow an exponential law. The integrated rate-law for a reversible system consisting of two pseudo-first-order reactions is given by equation (2):

$$\ln[X_e/(X_e - X)] = (k_f + k_r)t \quad (2)$$

where X and X_e represent the concentration of the product at time t and at equilibrium; k_f and k_r are the observed rate constants for the forward and the reverse reaction respectively.

It can be easily shown that the interpretation of stopped-flow data yields the observed rate constant, k_{obs} , related to k_f and k_r by the equation:

$$k_{\text{obs}} = k_f + k_r \quad (3)$$

The influence of the concentration of inosine on k_{obs} is illustrated by Figure 1. It is quite obvious that neither a simple $\text{S}_{\text{N}}2$ mechanism nor a linear equation, $k_{\text{obs}} = k_0 + k_y [\text{Y}]$, which is the most commonly observed for Pt(II) and Pd(II) substitutions, can account for the data.

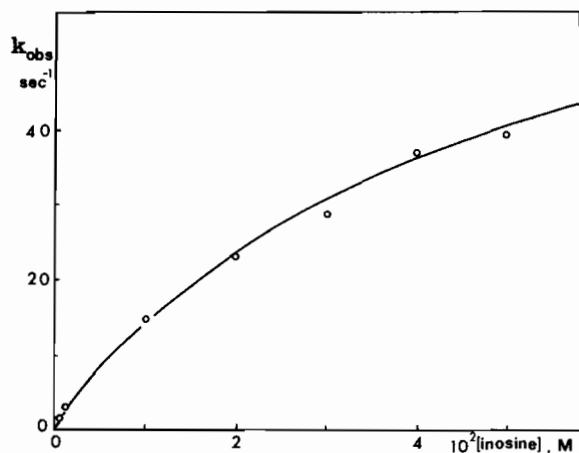


Fig. 1. Influence of the concentration of inosine on k_{obs} . ($T = 25^\circ\text{C}$; $[\text{KBr}] = 1 \times 10^{-2}\text{M}$; $\mu = 1$).

The influence of Br^- ions depends very strongly on whether high or low inosine concentrations are used; in all cases, the graph of k_{obs} vs. $[\text{Br}^-]$ decreases first, passes through a minimum and finally increases at higher Br^- concentrations. Whereas the changes in k_{obs} are quite important at low inosine concentration (e.g. Figure 2), as the concentration of inosine increases, the influence of Br^- becomes less important. The rate constants are presented in Table 1.

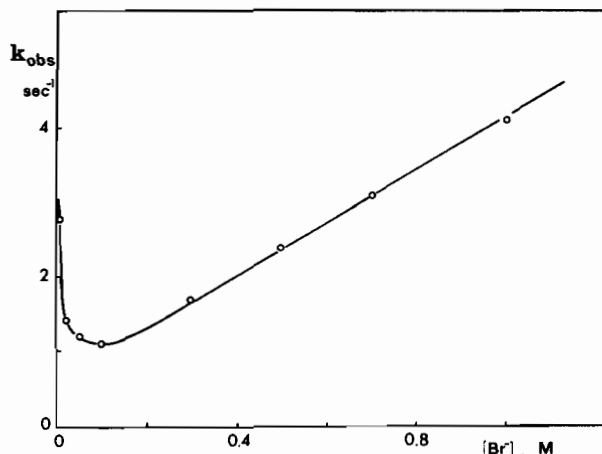


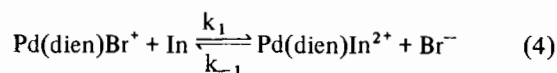
Fig. 2. Influence of the concentration of KBr on k_{obs} . ($T = 25^\circ\text{C}$; $[\text{Inosine}] = 1 \times 10^{-3}\text{M}$; $\mu = 1$).

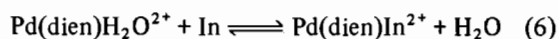
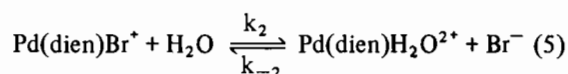
TABLE I. Observed Rate Constants at Various Br^- and Inosine Concentrations.

$T = 25^\circ\text{C}$, $[\text{Pd}(\text{dien})\text{Br}^+] = 1.0 \times 10^{-3}\text{M}$, $\mu = 1$.

[KBr] M	[Inosine] M	k_{obs} , sec^{-1}
—	5×10^{-3}	18.5
—	1×10^{-2}	22
—	2×10^{-2}	26
—	3×10^{-2}	33
—	4×10^{-2}	37
—	5×10^{-2}	44
10^{-2}	1×10^{-3}	2.0
10^{-2}	2×10^{-3}	3.1
10^{-2}	5×10^{-3}	8.0
10^{-2}	1×10^{-2}	15
10^{-2}	2×10^{-2}	23.5
10^{-2}	3×10^{-2}	28.5
10^{-2}	4×10^{-2}	37
10^{-2}	5×10^{-2}	38.5
5×10^{-3}	1×10^{-3}	2.8
2×10^{-2}	1×10^{-3}	1.4
5×10^{-2}	1×10^{-3}	1.2
1×10^{-1}	1×10^{-3}	1.1
3×10^{-1}	1×10^{-3}	1.7
5×10^{-1}	1×10^{-3}	2.4
7×10^{-1}	1×10^{-3}	3.1
1	1×10^{-3}	4.1
1×10^{-1}	5×10^{-3}	3.9
1×10^{-1}	1×10^{-2}	6.8
1×10^{-1}	2×10^{-2}	12
1×10^{-1}	4×10^{-2}	27
1×10^{-1}	5×10^{-2}	30

The observed data can be rationalized by the following mechanism:





The main characteristics of this mechanism are: *i*) all the steps are reversible, *ii*) equation (4) represents the direct reaction path assumed to be an S_N2 substitution and *iii*) equations (5) and (6) imply the formation of an aquo intermediate which reacts with inosine to form the final product.

The steady-state approximation for the aquo intermediate $[Pd(dien)H_2O]^{2+}$ leads to the following relationship:

$$k_{obs}^* = k_1 [In] + k_{-1} [Br^-] + \frac{k_2 k_3 [In] + k_{-2} k_{-3} [Br^-]}{k_{-2} [Br^-] + k_3 [In]} \quad (7)$$

The different parameters of equation (7) have been obtained by iteration methods; first, k_1 and k_{-1} were evaluated at high concentrations of inosine and of Br^- , then the other parameters were obtained and the squares of the relative error, $(k_{calc} - k_{obs})^2 / k_{obs}^2$ were minimized. The rate parameters are summarized in Table II, together with the apparent equilibrium constant obtained from the relationship: $K = k_1/k_{-1} = k_2 k_3 / k_{-2} k_{-3}$. The agreement between k_{obs} and the calculated values using equation (7) is generally within 10% over a 50 fold increase in inosine concentration and a 1000 fold increase in Br^- concentration.

TABLE II. Rate Parameters at 25 °C and 1M Ionic Strength.

k_1	=	$500 \pm 50 M^{-1} sec^{-1}$
k_{-1}	=	$3.4 \pm 0.3 M^{-1} sec^{-1}$
k_{-2}/k_3	=	1.15 ± 0.2
k_2	=	$18 \pm 3 sec^{-1}$
k_{-3}	=	$0.1 \pm 0.02 sec^{-1}$
K	=	150 ± 30

In order to verify the assumptions made, the reactions of the aquo complex $[Pd(dien)H_2O]^{2+}$ with inosine (k_3) and Br^- (k_{-2}) have been investigated. In all cases, second order reactions were obtained. The values of the rate constants at 25 °C and at 1M ionic strength are $k_{-2} = (2.7 \pm 0.4) \times 10^4 M^{-1} sec^{-1}$ and $k_3 = (1.4 \pm 0.4) \times 10^4 M^{-1} sec^{-1}$. The high value of these rate constants as compared to $k_2 = 18 sec^{-1}$

indicates clearly that the steady-state hypothesis is reasonable. The ratio $k_{-2}/k_3 = 1.9$ calculated from these data is however slightly different from that given in Table II ($k_{-2}/k_3 = 1.15$). This discrepancy is probably due to the relatively large errors which affect k_{-2} and k_3 , due to the small signal involved in these reactions.

Discussion

The substitution reactions of $Pt(II)-$ and $Pd(II)-$ triamine complexes follow a general rate law of the type $k_{obs} = k_o + k_y [Y]$. The widely accepted mechanism implies accordingly two parallel reactions: an S_N2 path (k_y) and a ligand independent path, involving the solvent as the nucleophilic agent (k_o) [11].

In the present case, basically the same mechanism is operating. The main difference between this system and those giving linear k_{obs} vs. $[Y]$ plots resides in the values of the rate constants involved.

In the cases where the general mechanism applies, presumably the entering ligand reacts much faster with the aquo complex than does Br^- . It can be easily seen from equation 7 that, if only the forward reaction is considered, in the case where $k_3 [In] \gg k_{-2} [Br^-]$ the denominator disappears yielding $k_f = k_1 [In] + k_2$.

In the present case, due to the relatively low reactivity of inosine, its affinity toward the aquo complex is about the same as that of Br^- ($k_{-2}/k_3 = 1.15$); this leads to the more complex rate law. Of course, further complications arise from the fact that the reaction is reversible.

The contribution of the two reaction paths is a function of the concentration of inosine and of Br^- . At low inosine concentration and in the absence of added Br^- , the main reaction path implies the solvent as the nucleophilic agent; the contribution of the S_N2 mechanism at $10^{-3} M$ of inosine and $10^{-3} M$ of Br^- is about 6%. As the concentrations of inosine and Br^- increase, the steady-state concentration of $[Pd(dien)H_2O]^{2+}$ decreases. This leads to an increasing contribution of the S_N2 path to the overall rate (~25% at $10^{-2} M Br^-$, ~75% at $10^{-1} M Br^-$ and ~97% at $1 M Br^-$ at low inosine concentrations).

The results are similar to those obtained for the analogous $Pt(II)$ complex; however, in the latter case no reversibility could be observed [10]. It should be noted that the rate constants for the $Pd(II)$ complex are, under comparable conditions, about 10^5 greater than those of its $Pt(II)$ analog. Similar differences were noted in the reactions of analogous $Pt(II)$ and $Pd(II)$ complexes with pyridine [1].

The rate of formation of the aquo complex ($k_2 = 18 sec^{-1}$) is 1.2×10^4 times greater than the literature value obtained for $[Pd(Et_4dien)Br]^+$ ($1.5 \times$

*In this particular case, k_{obs} contains the sum of the rate constants of the forward and of the reverse reactions (see eq. 3.) The concentration of Br^- comprises KBr added and one equivalent of Br^- per $[Pd(dien)Br] Br$.

10^{-3} sec^{-1}) [3].* This dramatic change in reactivity is consistent with earlier results showing that the decrease in steric hindrance enhances greatly the rate of this process [2].

It has to be noted that about the same change in reactivity is observed for the reaction of Br^- with $[\text{Pd}(\text{dien})\text{H}_2\text{O}]^{2+}$ and $[\text{Pd}(\text{Et}_4\text{dien})\text{H}_2\text{O}]^{2+}$ where the rate constants are respectively $2.7 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ and $1.2 \text{ M}^{-1} \text{ sec}^{-1}$ [3].*

In summary, the general mechanism of the substitution, of square complexes of Pt(II) and Pd(II) applies also to the interaction of inosine with $[\text{Pd}(\text{dien})\text{Br}]^+$. However, due to the relatively low reactivity of inosine, the solvolytic reaction path contributes more than usual and its detailed kinetic analysis is possible. The kinetic data obtained fit well in the general framework of substitution reactions of Pt(II) and Pd(II)-triamine complexes.

*In the case of $[\text{Pd}(\text{Et}_4\text{dien})\text{Br}]^+$ for several ligands, such as I^- , N_3^- , SCN^- , NO_2^- , only the solvolytic mechanism is operating.

Acknowledgements

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