# Interactions of some palladium(II) complexes of N-alkyl-substituted diethylenetriamine with anionic micelles. A kinetic study

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## Abstract

The kinetics of the substitution reactions between anions ($S_2O_3^{2-}$, $SCN^-$, $Br^-$, $I^-$) and the palladium(II) complexes $[Pd(N\text{-}N\text{-}N)X]^{m+}$, where N-N-N = $H_2N[CH_2]_2NH[CH_2]_2NH_2$ (with $X^- = NO_2^-$), $Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$ (with $X^- = Cl^-$) and $Et_2N[CH_2]_2NH[CH_2]_2NEt_2$ (with $X = H_2O$ and $X^- = Cl^-$), have been studied at 25 °C and ionic strength 0.03 mol dm$^{-3}$ in water and in the presence of the anionic micelle-forming surfactant sodium dodecyl sulfate (SDS). All the reactions exhibit a first-order dependence on both the substrate and the anion concentration. The substitution rates in water depend on the steric hindrance of the palladium(II) complexes and the nucleophilicity of the entering anions. The presence of SDS retards the reactions because of the binding of the palladium(II) complexes to the anionic micellar aggregates. The binding constants of these complexes, estimated from the kinetic data, have been found to depend on both the charge of the complexes and the hydrophobicity of the ligand N-N-N coordinated to the metal.

## Introduction

The number of mechanistic studies on substitution reactions at square-planar metal complexes has notably increased in the last fifteen years probably due to the discovery of antitumor properties of some platinum(II) substrates [1] and to the further clinical use [2] of cisplatin and its derivatives in cancer treatment.

Two basic mechanisms are accepted for the substitution processes in these complexes: an associative mechanism [3] and a less common, but equally well argued, dissociative one [4]. The associative mechanism implies, in the most general case, two parallel paths involving the direct attack at the metal of the nucleophile (Y) and the solvent, respectively. In the latter case the intermediate solvato species formed is further converted quickly by the nucleophile into the substitution product. Two terms are therefore present in the rate law, the observed pseudo-first-order rate constant assuming the form ([Y] ≫ [complex]).

$$k_{obs} = k_1 + k_2[Y] \quad (1)$$

The relative contribution of the two terms to the overall reaction rate depends on the effectiveness of the solvent and of the entering group as nucleophiles and on the steric hindrance of the ligands coordinated to the metal [5, 6]. Our previous kinetic investigation [7] concerning the water replacement in the complex $[Pd(Et_4dien)(H_2O)]^{2+}$, where $Et_4dien = Et_2N[CH_2]_2NH[CH_2]_2NEt_2$, by several substituted thioureas in water and in aqueous micellar solutions has shown that the reaction rates in water depend on both the steric and the inductive effects (acting in the opposite direction) of the alkyl groups present in the entering thiourea molecule. Moreover it has been observed that binding of the nucleophiles to cationic (CTAN) and anionic (SDS) micelles occurs to an extent depending on the hydrophobic character and number of alkyl substituents of the parent thiourea, the association with cationic micellar aggregates being in all cases larger than that with anionic ones.

Continuing our investigations of the micellar effects on the kinetics and the mechanism of inorganic reactions, we have now studied some substitution reactions at square-planar palladium(II) complexes involving anionic entering ligands and metal complexes of dien derivatives (see reactions (2) and (3) in the following) in aqueous solution in the absence and in the presence of the micelle-forming surfactant sodium dodecyl sulfate (SDS). The main purpose of this work was to ascertain

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the role of the steric hindrance and the hydrophobicity of the dien derivatives coordinated to palladium(II) in determining both the reactivity of these systems in the media considered and the interactions of the complexes under study with the SDS micellar aggregates. As far as we know, apart from our recent previous investigation [7], no other kinetic study [8] of micellar effects upon this type of reactions exists in spite of the extensive kinetic data available in water and other solvents. Chemical equilibria, reactivities as well as reaction mechanisms are well known to be modified, sometimes to a notable extent, by the presence of organized assemblies [7–9].

## Experimental

In the present work, performed at 25.0 °C and ionic strength 0.03 mol $dm^{-3}$, we have measured the rates of the substitution reactions (2), where the coordinated ligand N-N-N is dien with $X^- = NO_2^-$ and $Y^{n-} = I^-$, or Me$_5$dien ($Me_2N[CH_2]_2NMe[CH_2]_2NMe_2$) with $X^- = Cl^-$ and $Y^{n-} = Br^-$, or Et$_4$dien with $X^- = Cl^-$ and $Y^{n-} = Br^-$ and $S_2O_3^{2-}$ as well as with $X = H_2O$ and $Y^{n-} = S_2O_3^{2-}$ and $SCN^-$ (reaction (3)).

$$[Pd(N\text{-}N\text{-}N)X]^+ + Y^{n-} \longrightarrow [Pd(N\text{-}N\text{-}N)Y]^{(2-n)+} + X^- \tag{2}$$

$$[Pd(N\text{-}N\text{-}N)(H_2O)]^{2+} + Y^{n-} \longrightarrow [Pd(N\text{-}N\text{-}N)Y]^{(2-n)+} + H_2O \tag{3}$$

All the complexes $[Pd(N\text{-}N\text{-}N)Cl]NO_3$ were prepared by the standard procedure [6, 7, 10]. The complex $[Pd(Et_4dien)(H_2O)](NO_3)_2$ was obtained by treating with $AgNO_3$ the respective chloro complex as previously [7] described, whereas the complex $[Pd(dien)(NO_2)]NO_3$ was prepared by treating the corresponding aquo complex, synthesized as for the previous complex, with an equivalent amount of $NaNO_2$ and crystallized by addition of methanol to its highly concentrated solution. All the N-alkyl-substituted diethylenetriamines were from K & K. The (Fluka) anionic surfactant sodium dodecyl sulfate (SDS) was purified by recrystallization from ethanol. $HNO_3$ and all the (sodium) salts used were of reagent grade and were employed as received. Standard solutions of the surfactant in water were obtained by weight. All the solutions were used immediately after preparation. The presence of hydroxo species in solution was avoided by maintaining the pH of all the media considered between 3.8 and 4.0 by addition of $HNO_3$.

In all cases the ionic strength ($\mu$) was 0.03 mol $dm^{-3}$ (supporting electrolyte $NaNO_3$). In the presence of surfactant the ionic strength of the intermicellar aqueous phase was calculated [7, 11] by means of the following expression: $\mu = \alpha C + c.m.c + [NO_3^-]_{add}$, where $\alpha$ (= 0.2 [7, 12]) is the ionization degree of the micelle, $C$ (= [SDS] − $c.m.c$) is the micellized surfactant concentration, and $[NO_3^-]_{add}$ represents the concentration of $HNO_3$ and $NaNO_3$ added. The value of $2.4 \times 10^{-3}$ mol $dm^{-3}$ was used [7, 13] for the critical micelle concentration ($c.m.c$) of the surfactant under the experimental conditions of this work.

Kinetic measurements were made at the wavelength of maximum absorption of the complexes with a Durrum-Gibson model D-110 stopped-flow or alternatively a stopped-flow SFA-11 HI-TECH accessory connected to a Lamda 5 Perkin-Elmer spectrophotometer interfaced to an Apple II computer. In all cases pseudo-first-order conditions were used with an excess of nucleophile, the concentration of the palladium complex being in the range $5 \times 10^{-4}$–$1 \times 10^{-5}$ mol $dm^{-3}$. The values of the observed pseudo-first-order rate constants, $k_{obs}$, estimated as previously described [7], were accurate to better than ±5%. For all the solutions examined straight lines were obtained by plotting $k_{obs}$ against the nucleophile concentration, yielding both the $k_1$ (intercept) and $k_2$ (slope) values in accordance with eqn. (1) or only one of these rate constants. For $[Pd(dien)(NO_2)]^+$ reacting with $I^-$ in the presence of SDS the $k_1$ values were obtained with large uncertainties.

## Results and discussion

In aqueous solutions the complexes $[Pd(N\text{-}N\text{-}N)X]^+$ are more or less hydrolyzed [14], depending on the nature of N-N-N, X and the ionic strength. Under our experimental conditions appreciable amounts of aquo species are present only in the case of $[Pd(Et_4dien)Cl]^+$ as shown by the conductivity of aged solutions of this complex and by the spectral changes associated with the addition of $Cl^-$. Nevertheless the kinetic values relative to the replacement of $Cl^-$ in $[Pd(Et_4dien)Cl]^+$ by $Y^{n-}$ could be obtained by choosing a selective wavelength for this process or/and taking advantage of the difference in the time scale of the processes.

Table 1 shows that in the absence of surfactant both the rate constants $k_1$ and $k_2$ could be obtained only for the unhindered substrate $[Pd(dien)(NO_2)]^+$ reacting with $I^-$. Here, although water is much less nucleophilic than iodide, there is a well defined solvolytic contribution to the substitution process. For the bulkier complexes $[Pd(Me_5dien)Cl]^+$ and $[Pd(Et_4dien)Cl]^+$, only one of the two terms of the rate law (1) is appreciable. Thus, while with $Br^-$ the rate of reaction is controlled by solvolysis ($k_1$), the kinetic contribution of the direct nucleophilic path ($k_2$) becomes dominant with the strong nucleophile $S_2O_3^{2-}$, which is able to force the steric

TABLE 1. First-order ($k_1$ ($s^{-1}$)) and second-order ($k_2$ ($dm^3\ mol^{-1}\ s^{-1}$)) rate constants for reactions (2) and (3) in the absence and in the presence of the anionic surfactant SDS ($t = 25$ °C; $\mu = 0.03$ mol $dm^{-3}$)

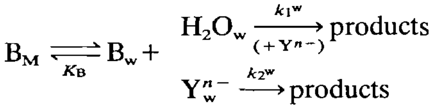
| $10^3 \times$ [SDS] (mol $dm^{-3}$) | ($Et_4$dien)($H_2O$)[a] | | ($Et_4$dien)Cl[a] | | ($Me_5$dien)Cl[a] | (dien)($NO_2$)[a] | |
|---|---|---|---|---|---|---|---|
| | $S_2O_3^{2-}$[b] | $SCN^-$[b] | $S_2O_3^{2-}$[b] | $Br^-$[b] | $Br^-$[b] | $I^-$[b] | |
| | $10^{-1} \times k_2$ | $10 \times k_2$ | $10 \times k_2$ | $10^4 \times k_1$ | $10 \times k_1$ | $10^2 \times k_1$ | $k_2$ |
| 0 | 72.6 | 51.5 | 54.7 | 23.0 | 2.80 | 6.5 | 14.6 |
| 3.0 | 11.3 | 3.30 | | | 1.98 | | |
| 3.5 | | 2.62 | 24.6 | 6.9 | 1.75 | | |
| 4.0 | 5.46 | 2.31 | | 5.2 | 1.58 | | |
| 5.0 | 2.56 | | 4.17 | 3.1 | | | |
| 6.0 | | | 2.44 | 1.85 | 0.92 | c | 12.7 |
| 7.0 | | | 2.00 | 1.62 | 0.70 | | |
| 7.5 | | 0.52 | | | | c | 10.9 |
| 10.0 | 0.52 | 0.32 | 1.20 | | | c | 9.7 |
| 13.0 | | | | | | c | 8.8 |
| 15.0 | 0.25 | | | | | | |
| 16.0 | | | | | | c | 8.2 |
| 20.0 | 0.21 | | | | | c | 6.6 |
| 25.0 | | | | | | c | 5.8 |

[a] Ligands coordinated to palladium(II). [b] Entering group. [c] Values very inaccurate.

barrier. In the case of the nucleophile $Br^-$ the smaller value of $k_1$ obtained with the coordinated ligand $Et_4$dien is in line with the larger extent of steric strain imposed by this ligand with respect to $Me_5$dien. The different nature of the leaving group does not allow a comparison with the $k_1$ value relative to the unhindered dien complex. In the reactions of the aquo species $[Pd(Et_4dien)(H_2O)]^{2+}$, because of the absence of the solvolytic pathway, each entering anion can show its nucleophilic effectiveness toward the reaction centre.

In the presence of the anionic surfactant SDS the relative contribution of the two terms of eqn. (1) to the overall substitution rate is the same one as seen above (in the absence of surfactant) for all the reactions examined. In fact we can observe from Table 1 that the substitution occurs through two pathways in the case of the palladium complex of the unsubstituted dien (even if the $k_1$ values are inaccurate), whereas for the remaining complexes only one path, associated either with the rate constant $k_1$ or with $k_2$, contributes significantly to the formation of the final product. Moreover it can be seen that, for each path involved in a given substitution process, the rate constant (either $k_1$ or $k_2$) undergoes a continuous decrease as the surfactant concentration increases, indicating the existence of interactions between the anionic micelles and the reacting species. It is also apparent that the addition of the same amount of surfactant to water causes a reduction in rate, which depends on the charge and the type of palladium(II) complex used.

The observed dependences of the rate constants upon the SDS concentration are consistent with Scheme 1, which considers only the partitioning of the cationic palladium complex (indicated by B) between water (w) and the anionic micellar pseudo-phase (M) with binding constant $K_B$ ($= [B]_M/[B]_w C$).



$$B_M \underset{K_B}{\rightleftharpoons} B_w + \begin{cases} H_2O_w \xrightarrow[(+Y^{n-})]{k_1^w} \text{products} \\ Y_w^{n-} \xrightarrow{k_2^w} \text{products} \end{cases}$$

Scheme 1.

According to this scheme the substitution reaction occurs in the intermicellar aqueous phase and the (apparent) rate constants ($k_1$ and $k_2$) of the two possible paths leading to the reaction products are given by eqns. (4) and (5), respectively, where the rate constants for the corresponding reaction in water are here represented by $k_1^w$ and $k_2^w$.

$$k_1 = k_1^w/(1 + K_B C) \qquad (4)$$

$$k_2 = k_2^w/(1 + K_B C) \qquad (5)$$

We wish to point out that the use [7, 11, 12, 15] of the ionic-exchange model for the distribution of two micellar counter-ions between the anionic micellar and aqueous pseudo-phases shows [7] that, under the experimental conditions of the present work, the binding constant $K_B$ remains substantially unchanged over the [SDS] range investigated.

Examining now the kinetic data (Table 1) obtained from the substitution reaction (3) involving the divalent cationic complex $[Pd(Et_4dien)(H_2O)]^{2+}$, we can see from Fig. 1 that straight lines are obtained for both the entering ligands used ($Y^{n-} = S_2O_3^{2-}$ and $SCN^-$) when $1/k_2$ is plotted against $C$ in accordance with eqn. (5), enabling us to estimate the binding constants $K_B$

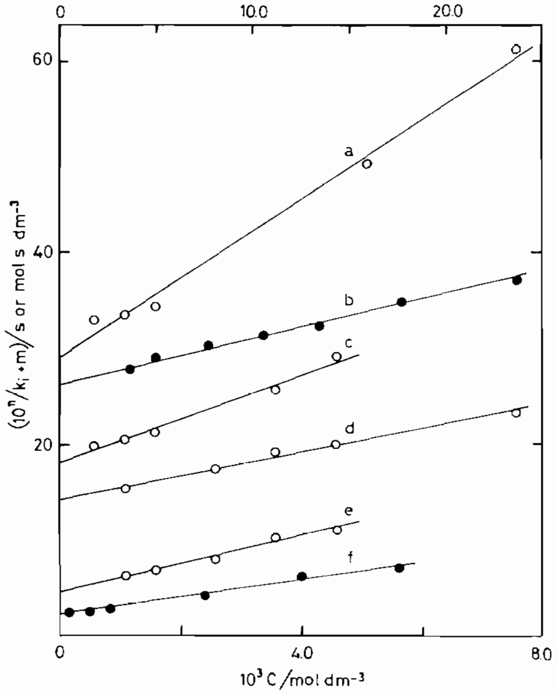


Fig. 1. Plot of $1/k_2$ or $1/k_1$ against $C$ (●, upper abscissa scale; ○, lower abscissa scale) in the presence of SDS for: (a) $[Pd(Et_4dien)(H_2O)]^{2+} + SCN^-$ reaction ($k_i = k_2$; $n = 0$; $m = 30$); (b) $[Pd(dien)(NO_2)]^+ + I^-$ reaction ($k_i = k_2$; $n = 2$; $m = 20$); (c) $[Pd(Me_5dien)Cl]^+ + Br^-$ reaction ($k_i = k_1$; $n = 0$; $m = 15$); (d) $[Pd(Et_4dien)Cl]^+ + S_2O_3^{2-}$ reaction ($k_i = k_2$; $n = 0$; $m = 15$); (e) $[Pd(Et_4dien)Cl]^+ + Br^-$ reaction ($k_i = k_1$; $n = -3$; $m = 5$); (f) $[Pd(Et_4dien)(H_2O)]^{2+} + S_2O_3^{2-}$ reaction ($k_i = k_2$; $n = 1$; $m = 2.5$).

from the slope ($= K_B/k_2^w$) and the $k_2^w$ values found for the reactions in the absence of surfactant. It should be noted that the least-squares treatment of the kinetic data yields substantially zero intercepts in agreement with the fact that in the present cases eqn. (5) reduces simply to $k_2 = k_2^w/K_BC$, $K_B$ being very large and $1 \ll K_BC$. These findings add support to the validity of the assumption made previously [7] about the expected value of the binding constant of the same ionic complex in the presence of the surfactant SDS.

The estimated $K_B$ values (Table 2) for the two reactions investigated are equal to each other and, therefore, independent of the charge and the nucleophilic character of the entering ligand, confirming the reaction scheme proposed. Moreover the $K_B$ value obtained now for the doubly charged palladium complex under examination is larger than that found before [13, 16] for the hydrophilic cationic species $Ni^{2+}$ and $[Co(NH_3)_5Cl]^{2+}$ for which binding to the anionic SDS micelles is ascribed to electrostatic interactions. Therefore the present $K_B$ value would be indicative of the existence of additional hydrophobic interactions due to the presence of the ligand $Et_4dien$ coordinated to palladium(II).

For the substitution reactions (2) involving univalent cationic palladium complexes, the plots of $1/k_1$ or of $1/k_2$ against $C$ (Fig. 1) are also linear as expected from eqns. (4) or (5), respectively, yielding the values of the binding constants $K_B$ ($=$slope$\times k_1^w$ or slope$\times k_2^w$) reported in Table 2. Due to the inaccuracy of the rate constants $k_1$ for the reaction of $[Pd(dien)(NO_2)]^+$ with $I^-$, no value of $K_B$ has been obtained utilizing this path.

For the complexes $[Pd(Me_5dien)Cl]^+$ and $[Pd(dien)(NO_2)]^+$ the above plots give appreciable intercepts because of the fact that the unity is not negligibly small compared with $K_B$. These intercepts are equal to $3.3 \pm 0.5$ s ($= 1/k_1^w$) and $(6.4 \pm 0.3)10^{-2}$ mol s dm$^{-3}$ ($= 1/k_2^w$), respectively, yielding values for $k_1^w$ and $k_2^w$ in fair agreement with those found by independent measurements in water (Table 1). These results corroborate further the reaction scheme proposed for the substitution processes in the anionic micellar media.

The analysis of the $K_B$ values of Table 2 shows that for the complex $[Pd(Et_4dien)Cl]^+$ the kinetic data for the two different anions examined provide an average $K_B$ value equal to $4.9 \times 10^3$ dm$^3$ mol$^{-1}$. Moreover the binding constants of all the univalent cationic complexes are significantly smaller than that found for the doubly charged complex $[Pd(Et_4dien)(H_2O)]^{2+}$ in agreement with electrostatics and depend notably on the type of palladium substrate used, increasing in the following order: $[Pd(dien)(NO_2)]^+ < [Pd(Me_5dien)Cl]^+ < [Pd(Et_4dien)Cl]^+$. The $K_B$ values relative to $[Pd(dien)(NO_2)]^+$ are 1:9:71. An opposite trend would

TABLE 2. Kinetic parameters and binding constants obtained in the presence of SDS ($t = 25$ °C; $\mu = 0.03$ mol dm$^{-3}$)

| Complex | Entering ligand | Slope | $K_B$ (dm$^3$ mol$^{-1}$)$^a$ |
|---|---|---|---|
| $[Pd(Et_4dien)(H_2O)]^{2+}$ | $S_2O_3^{2-}$ | $30 \pm 2^b$ | $(2.2 \pm 0.2)10^4$ |
| | $SCN^-$ | $(4.1 \pm 0.2)10^{3b}$ | $(2.1 \pm 0.2)10^4$ |
| $[Pd(Et_4dien)Cl]^+$ | $S_2O_3^{2-}$ | $(1.21 \pm 0.06)10^{3b}$ | $(6.6 \pm 0.5)10^3$ |
| | $Br^-$ | $(1.4 \pm 0.1)10^{6c}$ | $(3.2 \pm 0.3)10^3$ |
| $[Pd(Me_5dien)Cl]^+$ | $Br^-$ | $(2.3 \pm 0.2)10^{3c}$ | $(6.4 \pm 0.6)10^2$ |
| $[Pd(dien)(NO_2)]^+$ | $I^-$ | $4.7 \pm 0.2^b$ | $(6.4 \pm 4)$ |

$^a K_B =$ slope$\times k_2^w$ or slope$\times k_1^w$. $^b$Slope (s) obtained from the $1/k_2$ against $C$ plot. $^c$Slope (dm$^3$ s mol$^{-1}$) obtained from the $1/k_1$ against $C$ plot.

be expected if the solubilization of these complexes in the micellar pseudo-phase were hindered by the steric hindrance of the coordinated dien derivatives. Indeed the observed $K_B$ order appears to be correlated to the increasing hydrophobicity of the ligand N-N-N through addition of alkyl substituents to the parent dien molecule. The different leaving groups ($NO_2^-$ and $Cl^-$) coordinated to the metal are hydrophilic species and should not substantially affect the hydrophobic interactions between micelles and the solubilized complex. Thus we can conclude that the solubilization of the univalent cationic palladium complexes examined as well as that of the divalent cationic one in the negatively charged micelles occurs by both electrostatic and hydrophobic interactions, being then favored by a higher positive charge of the ionic complex and a larger hydrophobicity of the ligand coordinated to palladium(II). The significant role of the hydrophobicity of coordinated ligands in determining the association of other ionic metal complexes with nonionic micelles has been evidenced previously [17, 18].

The observed contribution of the two types of interactions to the solubilization process of the palladium(II) complexes under study would suggest a binding site of the solubilized substrates in an intermediate micellar region between the hydrophobic core and the hydrophilic surface, that is in the so-called palizade layer. If we consider the binding constants of the three univalent ionic complexes examined, this conclusion would be also supported [7, 18–20] by the estimated value for the incremental transfer free energy per mole of the substrates from water to the SDS micelles ($\Delta\mu°_c = -1.3 \pm 0.1$ kJ $mol^{-1}$).

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