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Spontaneous Solvolysis Reactions of Some Pd(II)–dien Complexes in Aqueous Solution: Equilibrium and Kinetic Data

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The spontaneous solvolysis reactions and corresponding equilibria of a series of complexes of the type Pd(R_5dien)$X^{(2-n)+}$ (R_5dien = methyl- and ethyl-substituted diethylenetriamine; X^{n-} = Cl^-, Br^-, I^-, py) were studied with kinetic and spectrophotometric techniques. The aquation and reverse anation rate constants strongly depend on the nature of R_5dien and X^{n-} and vary by 6 orders of magnitude for the complexes selected. The solvolysis equilibrium constant, however, is almost independent of R_5dien and X^{n-} and has an average value of 3.6×10^{-4} M at 25 °C. This value implies that significant quantities of the complexes are present as the aquated products especially at low complex concentrations. The mechanistic implication of these results is discussed in reference to the general behavior of square-planar complexes.

Introduction

A recent note[1] called attention to the fact that the reaction of Pt(dien)OH_2^{2+} (dien = diethylenetriamine) with chloride ion (eq 1) does not go to completion at low chloride ion concentrations.

$$\mathrm{Pt(dien)OH_2^{2+} + Cl^-} \underset{k_{aq}}{\overset{k_{an}}{\rightleftharpoons}} \mathrm{Pt(dien)Cl^+ + H_2O} \quad K_1 \qquad (1)$$

This is due to a contribution from the reverse solvolysis (aquation) reaction, such that $k_{obsd} = k_{aq} + k_{an}[Cl^-]$ and $K_1 = k_{an}/k_{aq}$. The available kinetic[2] and equilibrium[3] data underline the validity of the above statement, and the corresponding values of K_1 are 3×10^3 and 2.7×10^3 M^{-1}, respectively.[1] In the presence of an excess of chloride ion, the value of $k_{an}[Cl^-]$ is such that it overrules the contribution of k_{aq} and the reaction goes to completion.[4,5] It follows, however, that complexes such as Pt(dien)Cl^+ will undergo spontaneous solvolysis in the absence of added chloride ion. This is of fundamental importance in the substitution behavior of such complexes, for which it is known that the solvolysis reaction path plays an important role. In addition, it has been claimed[6-10] that spontaneous solvolysis reactions form an integral part of the isomerization reactions of sterically hindered Pt(II) complexes in contrast to arguments in favor of a dissociative reaction mode.[11-15] Therefore, any information regarding the spontaneous solvolysis reactions of Pt(II) complexes in particular, or of closely related square-planar complexes in general, is of fundamental interest in the understanding of the chemical behavior of such complexes in solution.

Very similar preliminary observations have been reported for the corresponding complexes of Pd(II). It was found[16,17] that the UV–visible absorption spectra of a series of isolated complexes of the type [Pd(R_5dien)Cl]X (R = H, Me, Et; X = Cl, ClO_4) differed considerably from those observed in the presence of an excess of Cl^- due to the occurrence of a spontaneous solvolysis process in the former case. Our general interest in such solvolysis reactions has encouraged a detailed investigation of the kinetic and equilibrium data for such reactions.

Experimental Section

The following complexes were prepared in earlier studies[17-20] performed in this laboratory: [Pd(dien)Cl]Cl; [Pd(1,1,7,7-Me_4dien)Cl]ClO_4; [Pd(1,1,4,7,7-Me_5dien)Cl]ClO_4; [Pd(1,4,7-Et_3dien)Cl]ClO_4; [Pd(1,1,7-Et_3dien)Cl]ClO_4; [Pd(1,1,7,7-Et_4dien)-Cl]ClO_4; [Pd(1,1,7,7-Et_4dien)Br]ClO_4; [Pd(4-Me-1,1,7,7-Et_4dien)-Cl]ClO_4. In addition, [Pd(4-Me-1,1,7,7-Et_4dien)Br]PF_6 and [Pd-(4-Me-1,1,7,7-Et_4dien)I]ClO_4 were prepared according to the method described before.[16] All complexes were recrystallized a number of times with $NaClO_4$ or NH_4PF_6 as precipitating reagent. Microanalyses were in excellent agreement with the theoretically expected values.[21]

The required aquo complexes were prepared "in situ" by treating the corresponding chloro complexes with equivalent quantities of $AgClO_4$ as described in detail before.[17] These were characterized from their UV–visible spectra, which were found to be in good agreement with those reported in the literature.[17,19,22,23] The Pd(4-Me-1,1,7,7-Et_4dien)py^{2+} complex species was also prepared in situ by treating the corresponding aquo complex with pyridine. Chemicals of analytical reagent grade and doubly distilled water were used throughout this study.

UV–visible absorption spectra were recorded on Zeiss DMR 10 and Perkin-Elmer 555 spectrophotometers. Kinetic measurements were performed in the thermostated (±0.1 °C) cell compartment of the former spectrophotometer or, in the case of fast reactions, on an Aminco stopped-flow instrument. The reported rate constants were calculated from pseudo-first-order plots that were linear for at least 2–3 half-lives of the reaction. A Radiometer PHM 64 instrument of which the reference electrode was filled with 3 M NaCl was used for pH measurements. Care should be taken that the pH electrode is inserted for only short periods of time into solutions containing aquo complexes of Pd(II) since some of these are very labile and may interact with chloride ions from the reference electrode. Alternatively, such measurements can be performed in a way that they do not interfere with the reaction or equilibrium under study, i.e., after completion of the kinetic or spectrophotometric analysis or on a sample of the test solution that is discarded after the measurement.

Results and Discussion

For each member of the series of complexes studied in this investigation it was observed that the UV–visible absorption spectrum of an aqueous solution of the isolated complex differed markedly from that obtained in the presence of an excess

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Table I. Kinetic and Equilibrium Data for the System[a]

$$\mathrm{Pd(R_5dien)X^{(2-n)+} + H_2O \underset{k_{an}}{\overset{k_{aq}}{\rightleftharpoons}} Pd(R_5dien)OH_2{}^{2+} + X^{n-}}$$

R_5dien	X^{n-}	k_{aq}, s^{-1}	k_{an}, M^{-1} s^{-1}	10^4K_{kin},[b] M	10^4K_{eq},[c] M
dien	Cl^-	37.8 ± 0.4[d]			10 ± 5
1,1,7,7-Me_4dien	Cl^-	0.90 ± 0.01[e]	$(1.91 \pm 0.05) \times 10^3$ [h]	4.7 ± 0.1	3.9 ± 0.5
1,1,4,7,7-Me_5dien	Cl^-	0.244 ± 0.004[e]	$(6.3 \pm 0.2) \times 10^2$ [h]	3.9 ± 0.1	2.9 ± 0.7
1,4,7-Et_3dien	Cl^-	10.8 ± 0.0[d]	$(2.68 \pm 0.08) \times 10^4$ [i]	4.0 ± 0.1	3 ± 2
1,1,4-Et_3dien	Cl^-	0.74 ± 0.02[d]	$(1.56 \pm 0.01) \times 10^3$ [j]	4.8 ± 0.2	3.7 ± 0.6
1,1,7,7-Et_4dien	Cl^-	$(2.1 \pm 0.1) \times 10^{-3}$ [d]	4.19 ± 0.06[i]	5.0 ± 0.3	8 ± 3
	Br^-	$(1.74 \pm 0.07) \times 10^{-3}$ [f]	3.23 ± 0.07	5.4 ± 0.3	5 ± 1
4-Me-1,1,7,7-Et_4dien	Cl^-	$(6.5 \pm 0.1) \times 10^{-4}$	1.89 ± 0.02	3.4 ± 0.1	3.5 ± 0.3
	Br^-	$(4.99 \pm 0.01) \times 10^{-4}$	1.51 ± 0.02	3.3 ± 0.1	2.9 ± 0.4
	I^-	$(2.44 \pm 0.01) \times 10^{-4}$ [d]	2.25 ± 0.09	1.08 ± 0.05	1.3 ± 0.3
	py	$(7.3 \pm 0.3) \times 10^{-6}$ [g]	$(4.3 \pm 0.1) \times 10^{-2}$	1.7 ± 0.1	1.2 ± 0.5

[a] Data measured at 25 °C and ionic strength 0.1 M, unless otherwise indicated. [b] $K_{kin} = k_{aq}/k_{an}$. [c] K_{eq} determined spectrophotometrically; see Discussion. [d] Data taken from ref 20. [e] Data taken from ref 25. [f] Data taken from ref 18; ionic strength 0.05 M. [g] Extrapolated from kinetic data at higher temperatures; viz. $k_{aq} = (1.07, 3.12, 5.24, \text{and } 8.39) \times 10^{-5}$ s^{-1} at 29.3, 39.1, 44.6, and 50.0 °C, respectively; $\Delta H^{\ddagger} = 18.7 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = -19.2 \pm 1.5$ cal K^{-1} mol^{-1}. [h] Data taken from ref 17. [i] Extrapolated from kinetic data at higher pH according to the method described elsewhere;[26] viz. $k_{an} = (1.34 \pm 0.04) \times 10^4$ s^{-1} at pH = pK_a = 7.3. [j] Data taken from ref 27.

of the anating nucleophile. This is in agreement with earlier observations referred to in the Introduction[16,17] and can only be ascribed to a spontaneous solvolysis (aquation) process of the complex in the absence of free nucleophile, i.e. the reverse of reaction 1. This implies that such spectra should be recorded in the presence of an excess of the anating nucleophile. This was indeed done in some cases[16,17] but not in all,[24] resulting in some spectral discrepancies.

The recently reported data[17] for a series of dien, Me_3dien, Et_3dien, Me_4dien, and Me_5dien complexes took account of this phenomenon, and spectra recorded in the present study agreed within 2% of the molar extinction coefficients reported before. Similar agreement was found for some of the Et_4dien and $MeEt_4$dien complexes.[16] In addition, the following spectra were recorded for complexes of the type Pd(4-Me-1,1,7,7-Et_4dien)$X^{(2-n)+}$ [X^{n-}, λ_{max}/nm (ϵ/M^{-1} cm^{-1})]: Br^-, 365 (700 ± 10); I^-, 408 (730 ± 20); py, 315 (1215 ± 20).

One way to determine the equilibrium constant for the spontaneous solvolysis process is from kinetic data. The rate constants for the solvolysis reaction (k_{aq}) can be obtained from the contribution of this reaction path during substitution reactions, i.e. the nucleophile-independent pathway. In the present study the solvolysis rate constant was determined from the intercept of a plot of the observed first-order rate constant vs. [OH^-], where OH^- is the substituting nucleophile. For many of the investigated complexes the observed rate constant is independent of [OH^-], i.e. only the solvolysis path is observed. The corresponding values of k_{aq} are summarized in Table I. It follows that k_{aq} varies between 40 and (7×10^{-6}) s^{-1} at 25 °C depending on the steric crowding on the dien ligand and the nature of the leaving group X^{n-}. Our earlier studies demonstrated that this remarkable change in k_{aq} correlates nicely with an increase in $\Delta H^{\ddagger}$ and almost constant $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values.[20,25] This is in line with an associative mechanism in which the entrance of a solvent (water) molecule is hindered by steric effects.[25]

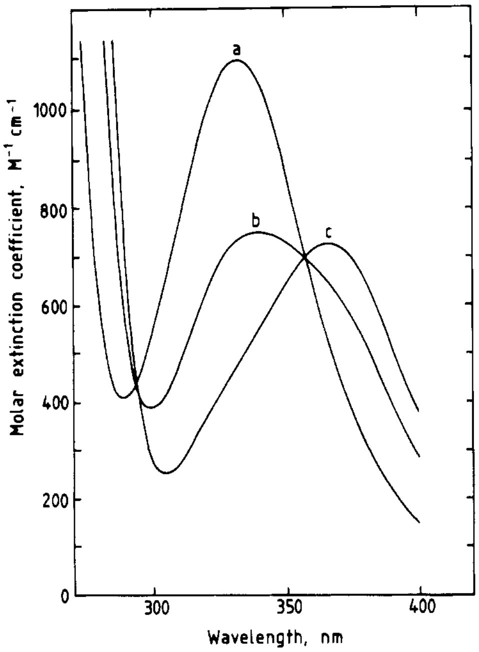

Figure 1. Typical example of the spontaneous solvolysis of Pd($MeEt_4$dien)Br^+ at 25 °C (ionic strength 0.1 M; [Pd(II)] = 1.4×10^{-3} M): (a) Pd($MeEt_4$dien)$OH_2{}^{2+}$; (b) equilibrated Pd($MeEt_4$dien)Br^+; (c) Pd($MeEt_4$dien)Br^+ measured in an excess of Br^-.

The anation rate constant (k_{an}) can be measured independently by using the corresponding aquo complex as starting material. The observed pseudo-first-order rate constants depend linearly on the anating nucleophile concentration in all cases. For the unsubstituted dien complex the reaction is too fast to be measured by stopped-flow technique, whereas an indirect method[26] was employed to estimate k_{an} for the 1,4,7-Et_3dien complex. k_{an} varies between 2.7×10^4 and 4×10^{-2} M^{-1} s^{-1} at 25 °C (see Table I) and parallels the values of k_{aq}. The resulting equilibrium constant, K_{kin} ($=k_{aq}/k_{an}$), varies very little with the nature of R_5dien or X^{n-}, indicating that these groups influence k_{aq} and k_{an} to the same extent. It is important to note that the K_{kin} values are subjected to remarkably small error limits due to the high accuracy with which the kinetic data could be measured.

An alternative method to determine the equilibrium constant for a spontaneous solvolysis process is to analyze the UV-visible spectra of equilibrated solutions. The Pd(R_5dien)$X^{(2-n)+}$ and Pd(R_5dien)$OH_2{}^{2+}$ species usually exhibit significantly different absorption spectra[16,17] enabling such a procedure. A typical example is given in Figure 1. When the [Pd($MeEt_4$dien)Br]PF_6 complex is dissolved in water, spontaneous solvolysis occurs and the equilibrium position is reached (see

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rate data in Table I). Addition of an excess of bromide to the equilibrated solution produces the spectrum of the bromo complex. From these and the spectral properties of the aquo species, K_{eq} can be determined in the usual way. The results are also included in Table I. It is however important to note that the accuracy with which K_{eq} can be determined depends strongly on the spectral characteristics of the species involved. Furthermore, adequate time must be allowed for such solutions to reach equilibrium as seen from the rate constants in Table I. In the case of the pyridine complex equilibration is indeed very slow, and possible protonation of free pyridine ($pK_a = 5.25$) must also be taken into account. The values of K_{eq} (in Table I) were determined for complex concentrations between 2×10^{-4} and 2×10^{-3} M and are the average of between three and seven determinations depending on the accuracy of the spectral method. Furthermore, these values are independent of the complex concentration employed and show no trend when the free nucleophile concentration is changed by addition of small quantities of the nucleophile.

Although the values of K_{eq} are subjected to considerably larger error limits than those of K_{kin}, a good correlation between these data does exist. An important result is the observation that both K_{kin} and K_{eq} are fairly constant for the series of complexes for which k_{aq} and k_{an} vary by at least 6 orders of magnitude. In addition, the magnitude of the equilibrium constants is such that for instance approximately 80% of the Pd(MeEt$_4$dien)Br$^+$ species will exist in solution as the aquo complex when the total complex concentration is 8×10^{-5} M. It follows that although the values of K_{kin} and K_{eq} are relatively small (ca. 3×10^{-4} M), they are such that considerable solvolysis occurs especially at low complex concentrations. Furthermore, these values are very close to that found for the solvolysis of Pt(dien)Cl$^+$ in aqueous medium, viz. 3.3×10^{-4} M[1] (see Introduction). Even more surprising is the fact that equilibrium constants estimated for the spontaneous solvolysis of *cis*-Pt(PEt$_3$)$_2$(R)Br in methanol also vary from $(0.7\text{-}2) \times 10^{-4}$ M for R = C_6H_5, *p*-MeC$_6$H$_4$, *o*-MeC$_6$H$_4$, *o*-EtC$_6$H$_4$, and 2,4,6-Me$_3$C$_6$H$_2$.[6] Very similar results were reported for a series of complexes of the type *cis*-Pt(PEt$_3$)$_2$(C$_6$H$_5$)X (X = Cl, Br, I).[8] It follows that such completely different complexes do exhibit solvolysis equilibrium constants very similar to that found in this investigation.

Although it is obvious that one cannot generalize this tendency, the good agreement does stress the fundamental importance of spontaneous solvolysis reactions in processes involving such complexes, especially in the case of the antitumor or catalytic activity of Pt(II) and Pd(II) complexes in general.

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Registry No. Pd(dien)Cl$^+$, 17549-31-4; Pd(1,1,7,7-Me$_4$dien)Cl$^+$, 89397-61-5; Pd(1,1,4,7,7-Me$_5$dien)Cl$^+$, 21007-58-9; Pd(1,4,7-Et$_3$dien)Cl$^+$, 88056-33-1; Pd(1,1,4-Et$_3$dien)Cl$^+$, 88228-48-2; Pd-(1,1,7,7-Et$_4$dien)Cl$^+$, 17787-28-9; Pd(1,1,7,7-Et$_4$dien)Br$^+$, 17685-73-3; Pd(4-Me-1,1,7,7-Et$_4$dien)Cl$^+$, 46848-25-3; Pd(4-Me-1,1,7,7-Et$_4$dien)Br$^+$, 58619-24-2; Pd(4-Me-1,1,7,7-Et$_4$dien)I$^+$, 58619-25-3; Pd(4-Me-1,1,7,7-Et$_4$dien)py^{2+}, 91606-31-4.

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Syntheses and Properties of Rotaxane Complexes. 2.[1] Rotaxanes Consisting of α- or β-Cyclodextrin Threaded by (μ-α,ω-Diaminoalkane)bis[chlorobis(ethylenediamine)cobalt(III)] Complexes

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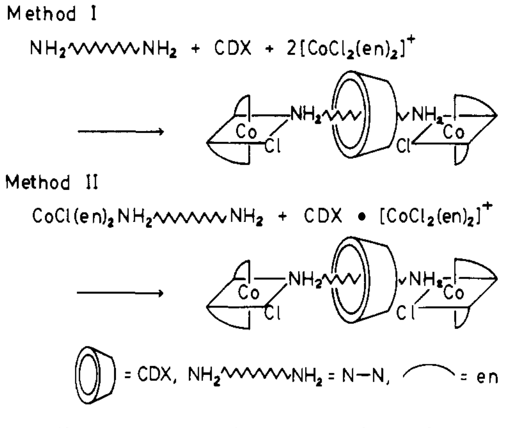
The reactions between *cis*-[CoCl$_2$(en)$_2$]Cl and 1,10-, 1,12-, and 1,14-diaminoalkanes (N-N) in the presence of α- or β-cyclodextrin (α- or β-CDX) gave the rotaxanes [2]-[[(en)$_2$ClCo(N-N)CoCl(en)$_2$]X$_4$]-[CDX]. These rotaxanes were characterized by the decomposition of CDX in the compounds, elemental analyses, SP-Sephadex C-25 column chromatography, molecular rotations, and electronic absorption, circular dichroism, and ^{13}C NMR spectroscopy. The best yields were obtained for N-N = 1,12-diaminododecane (19% for the rotaxane containing α-CDX and 7% for that containing β-CDX).

Introduction

A rotaxane is a compound consisting of a ring threaded by chain-bearing end groups that are so bulky that the chain cannot be extruded from the ring. In a previous paper,[1] the syntheses of rotaxanes in relatively high yields were reported, where the ring was α- or β-cyclodextrin (α- or β-CDX) and the chain was the dimeric cobalt(III) complexes, (μ-α,ω-diaminoalkane)bis[chlorobis(ethylenediamine)cobalt(III)] ([(en)$_2$ClCo(N-N)CoCl(en)$_2$]$^{4+}$).[1,2] This was the first example of the rotaxanes containing chiral rings and also the first example of the rotaxanes containing metal complexes.

Syntheses of rotaxanes will provide a better understanding of nonbonded interactions and inclusion phenomena. This paper describes more extensive preparations of a number of [2]-[[(en)$_2$ClCo(N-N)CoCl(en)$_2$]X$_4$]-[α- or β-CDX] rotax-

Scheme I[5]



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(1) Part 1: Ogino, H. *J. Am. Chem. Soc.* **1981**, *103*, 1303.

(2) Abbreviations: en, ethylenediamine; ocn, 1,8-diaminooctane; den, 1,10-diaminodecane; don, 1,12-diaminododecane; tden, 1,14-diaminotetradecane; pxyn, *p*-xylenediamine; N-N, α,ω-diaminoalkane; Me$_2$SO, dimethyl sulfoxide; tart, tetranegative ion of tartrate.

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