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Catalyzed Substitution on Cationic Palladium(II) Complexes. II. Mercury(II) and Cadmium(II) Catalyzed Displacement of Coordinated Halides

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A kinetic study of Hg^{II} *and* Cd^{II} *catalyzed solvolysis of complexes of the type* $[Pd(AAA)X]^+$ *(AAA = 1,1,7,7-tetraethyldiethylenetriamine* (Et_4dien) *and 4-methyl-1,1,7,7-tetraethyldiethylenetriamine* $(MeEt_4dien)$*; X = Cl, Br, I) has been carried out in methanol at 25° C. The first-order dependence of the reaction rate on* $[M^{++}]$ *is explained in terms of a solvent attack on a labile binuclear adduct of the type* $-\overset{|}{\underset{|}{Pd}}-X\cdots M^{II}$ *in equilibrium with the substrate.*

A correlationship is found between the catalytic efficiency and the affinity of metal ions for halide ions.

Introduction

It is a fairly old observation that certain metal ions (Hg^{II}, Ag^{I}, Tl^{III} *etc.*) strongly accelerate the substitution of coordinated halides and pseudohalides by water molecules and the bulk of the kinetic information comes from studies of aquation on octahedral complexes of Co^{III}, Cr^{III} and Rh^{III}.[1,3] Mercury(II) catalyzed aquation of cobalt(III) complexes has been extensively studied in order to shed light on the nature of the activated complex in the acid hydrolysis reactions as well as to verify to what extent the transition state of a Hg^{++} catalyzed aquation can be related to that of an inner sphere electron-transfer reaction. Very little is known on metal catalyzed removal of coordinated groups from square planar complexes of low spin d^8 metal ions. This paper reports the kinetics of mercury(II) and cadmium(II) catalyzed solvolysis of substrates of the type $[Pd(AAA)X]^+$ (AAA = 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) and 4-methyl-1,1,7,7-tetraethyldiethylenetriamine ($MeEt_4dien$); X = Cl, Br, and I) in methanol at 25° C. The displacement of nitro and azido groups from the same complexes was proved to be acid catalyzed[4].

Experimental

Preparation of the Complexes

$[Pd(Et_4dien)X]NO_3$ (X = Cl, Br, I) were prepared by reacting $[Pd(Et_4dien)Cl]Cl$[5] with two equivalents of $AgNO_3$ in methanol under magnetic stirring for 24 hr at room temperature. After removal of AgCl the resulting solution was reacted with one equivalent of LiX and concentrated to a small volume on a steam bath. Upon cooling the mixture in an ice–salt bath, the final product was separated out, the solid collected in a filter, washed with a minimum amount of ice–methanol and recrystallized from methanol.

Anal. Calcd. % for $PdC_{12}H_{29}N_4O_3Cl$: C, 34.35; H, 6.97; N, 13.35; Cl, 8.49. Found: C, 34.22; H, 6.85; N, 13.31; Cl, 8.29. Calcd. % for $PdC_{12}H_{29}N_4O_3Br$: C, 31.6; H, 6.30; N, 12.07; Br, 17.22. Found: C, 32.82; H, 6.56; N, 12.89; Br, 18.49. Calcd. % for $PdC_{12}H_{29}N_4O_3I$: C, 28.20; H, 5.72; N, 10.96; I, 24.83. Found: C, 28.40; H, 5.78; N, 11.06; I, 24.93.

$[Pd(MeEt_4dien)Cl]PF_6$ was prepared by literature methods[5]. The corresponding bromo and iodo derivatives were prepared by reacting $[Pd(MeEt_4dien)Cl]PF_6$ with one equivalent of $AgNO_3$ in methanol for two days under magnetic stirring. AgCl was filtered out and the remaining solution was divided into two equal portions which were reacted with one equivalent of LiBr or LiI respectively. After concentration the crystalline products were obtained by using the same treatment as above.

Anal. Calcd. % for $PdC_{13}H_{31}N_3BrPF_6$: C, 27.80; H, 5.56; N, 7.48; Br, 14.22. Found: C, 27.95; H, 5.70; N, 7.66; Br, 14.40. Calcd. % for $PdC_{13}H_{31}N_3IPF_6$: C, 25.65; H, 5.13; N, 6.90; I, 20.84. Found: C, 25.72; H, 5.20; N, 7.40; I, 21.02.

All the compounds were characterized by their u.v. and i.r. spectra. The molar conductivity in methanol at 18° C is in the range 90–100 Ω^{-1} cm^2 mol^{-1} and is fully consistent with that of 1:1 electrolytes.[6] All the attempts to isolate the final products of the reactions $[Pd(chelate)X]^+ + M^{++} + MeOH \rightarrow [Pd(chelate)MeOH]^{++} + MX^+$ as pure compounds were unsuccessful. The u.v. spectrum of $[Pd(Et_4dien)(MeOH)]^{++}$ presents an absorption maximum at 329 nm (ε 1170) in a good agreement with that found for the corresponding aquo complex[7]. The solvent methanol was purified by distillation after heating under reflux over magnesium metal. $HClO_4$, $LiClO_4$, $Cd(NO_3)_2$, LiBr were all of reagent grade purity.

Mercuric Ion Solutions

HgO was dissolved in perchloric acid solutions and reprecipitated by adding sodium carbonate. This procedure was repeated twice and the standard solution of $Hg(ClO_4)_2$ was prepared in methanol by reacting HgO with concentrated $HClO_4$ in the ratio 1:3. The Hg^{II} content was analyzed by precipitating $[Cu(en)_2]$ HgI_4[8]. The solution were Hg^I-free as determined by addition of Cl^-.

Kinetics

The u.v. spectra of the starting material and that of the final compounds were recorded using an OPTICA CF 4R double beam recording spectrophotometer. The rate of slower reactions was followed spectrophotometrically with a Beckmann D. U. instrument equipped with a Saitron 301 photometer and a Servogor S potentiometric recorder. All the experiments were carried out at 25° C maintaining the ionic strength constant at 1.0 or 0.1M using $LiClO_4$.

The reagent solution was placed in the spectrophotometer cell and the appropriate amount of the pre-thermostated complex solution was added by means of a calibrated hypodermic syringe to start the reaction. The wavelength was locked at a fixed value and the recorder bed was allowed to move at a known rate. The reactions which were too fast for this method to be used were followed with a Durrum–Gibson stopped-flow spectrophotometer using the technique described in the previous paper[4]. All reactions were carried out in the presence of a sufficient excess of reagent to ensure first-order kinetics and the pseudo-first-order rate constants were determined graphically from the plot of $\log(A_\infty - A_t)$ against time (A_t and A_∞ are the absorbances of the reaction mixture at time "t" and after 10 half-lives, respectively).

Results and Discussion

The rates of the reactions:

$$[Pd(AAA)X]^+ + M^{++} + MeOH \rightarrow [Pd(AAA)MeOH]^{++} + MX^+ \quad (1)$$

were studied in the presence of a constant excess of perchloric acid. The Hg^{2+} varied within the concentration range 0.003–0.05M whereas that of Cd^{++} was within 0.05–0.3M. The values of the pseudo-first-order rate constants (k_{obsd}, s^{-1}) are collected in Table I. Plots of k_{obsd} *vs.* $[M^{++}]$ are straight lines Figure 1) throughout the metal concentration range examined. In the reactions with Hg^{++} the rate law is:

$$-d[Complex]/dt = k_{(Hg^{++})}[Hg^{++}][Complex] \quad (2)$$

A contribution of a reagent independent term (k_1) is observed only when Cd^{++} is used as reagent because of its minor effectiveness as catalyst with respect to Hg^{++}. In no case was any dependence on the acidity noted and, as might be expected for a reaction between two positive ions, the reactions showed some dependence on the ionic strength of the medium. The results of the investigation carried out on the com-

TABLE I. The Mercury(II) and Cadmium(II) Catalyzed Solvolysis of $[Pd(AAA)X]^+$ at 25° C in Methanol. Dependence of Pseudo-first-order Rate Constants, k_{obsd}, on the Metal Ions Concentration and Ionic Strength ($LiClO_4$).

	$\mu = 1M$	
Complex	$10^3[Hg^{++}]M$	k_{obsd} (s^{-1})
$[Pd(Et_4dien)Cl]^+$	3.12	4.9×10^{-2}
	6.25	11.0×10^{-2}
	12.5	14.9×10^{-2}
	25.0	31.2×10^{-2}
$[Pd(Et_4dien)Br]^+$	3.12	3.0×10^{-1}
	6.25	6.7×10^{-1}
	9.37	10.0×10^{-1}
	12.5	15.6×10^{-1}
$[Pd(Et_4dien)I]^+$	6.25	49
	9.37	95
	12.5	107
	25.0	232
$[Pd(MeEt_4dien)Cl]^+$	3.12	8.4×10^{-3}
	6.25	14.6×10^{-3}
	9.37	25.4×10^{-3}
	12.5	27.1×10^{-3}
	25.0	55.2×10^{-3}
$[Pd(MeEt_4dien)Br]^+$	3.12	3.7×10^{-2}
	6.25	10.3×10^{-2}
	9.37	18.1×10^{-2}
	12.5	22.8×10^{-2}
	25.0	47.7×10^{-2}
$[Pd(MeEt_4dien)I]^+$	6.25	9.3
	9.37	21.6
	12.5	28.6
	25.0	52.4

	$10^2[Cd^{++}]M$	k_{obsd} (s^{-1})
$[Pd(MeEt_4dien)Cl]^+$	5.0	1.9×10^{-5}
	10.0	3.1×10^{-5}
	20.0	5.7×10^{-5}
	30.0	8.2×10^{-5}
$[Pd(MeEt_4dien)Br]^+$	5.0	1.9×10^{-5}
	10.0	3.0×10^{-5}
	20.0	5.7×10^{-5}
	30.0	7.3×10^{-5}
$[Pd(Et_4dien)Cl]^+$	5.0	4.6×10^{-5}
	10.0	6.7×10^{-5}
	20.0	14.3×10^{-5}
	30.0	22.7×10^{-5}
$[Pd(Et_4dien)Br]^+$	5.0	5.5×10^{-5}
	10.0	8.9×10^{-5}
	20.0	18.5×10^{-5}
	30.0	25.6×10^{-5}

TABLE I. (Cont.)

$\mu = 0.1M$

	$10^3[Hg^{++}]M$	k_{obsd} (s^{-1})
$[Pd(Et_4dien)Cl]^+$	3.12	3.3×10^{-2}
	6.25	7.2×10^{-2}
	9.37	8.7×10^{-2}
	12.5	11.2×10^{-2}
	25.0	19.5×10^{-2}
	50.0	43.5×10^{-2}
$[Pd(Et_4dien)Br]^+$	3.12	2.4×10^{-1}
	6.25	3.8×10^{-1}
	9.37	6.3×10^{-1}
	12.5	7.8×10^{-1}
	25.0	14.9×10^{-1}
$[Pd(Et_4dien)I]^+$	3.0	26
	6.0	52
	10.0	80
	15.0	118
	20.0	158

plexes $[Pd(Et_4dien)X]^+$ at ionic strength 0.1 and $1.0M$ are collected in Table I. In Table II are reported the values of the pseudo-first-order rate constants for chlorid displacement by Br^- from the complexes $[Pd(Et_4dien)Cl]^+$ and $[Pd(MeEt_4dien)Cl]^+$. The substitution rate is independent of the nucleophile concentration and the rate law is $k_{obsd} = k_1$.

TABLE II. Pseudo-first-order Rate Constants for the Chloride Displacement by Br^- from $[Pd(AAA)Cl]^+$ in Methanol at 25° C, $\mu = 1M$.

Complex	10^2 [Br^-], M	10^5 k_{obsd}
$[Pd(MeEt_4dien)Cl]^+$	1.0	1.20
	40.0	1.30
	70.0	1.30
$[Pd(Et_4dien)Cl]^+$	10.0	2.70
	40.0	2.80
	70.0	2.80

In the mechanistic study of the nucleophilic substitution of N_3 and NO_2 coordinated to palladium(II) in unhindered and hindered complexes of the type $[Pd(AAA)X]^+$ [4], a first-order rate dependence on the proton concentration has been rationalized in terms of a mechanism involving a rapid pre-equilibrium between the substrate and one monoprotonated form in solution. The proton attack on coordinated N_3 and NO_2 weakens the palladium–nitrogen bond and favours the facile displacement of the basic groups by

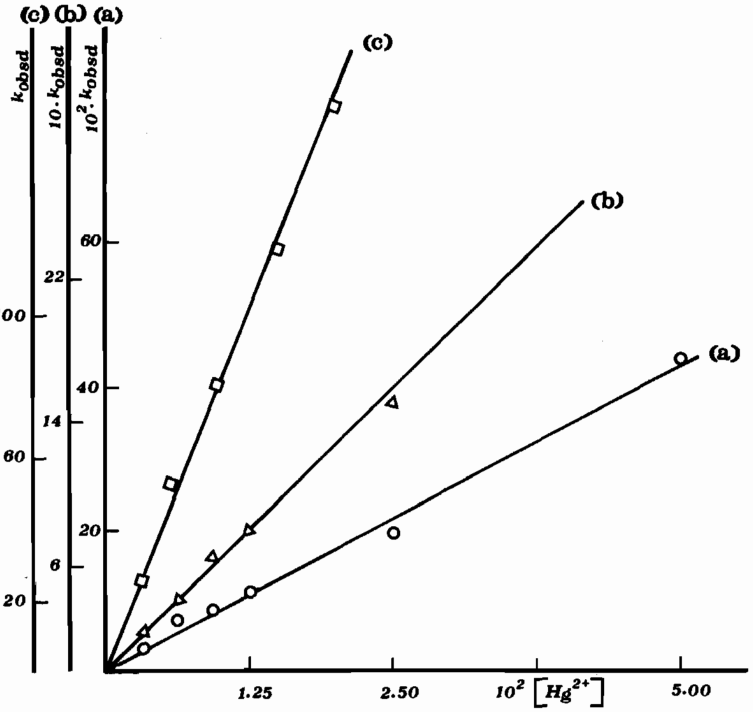
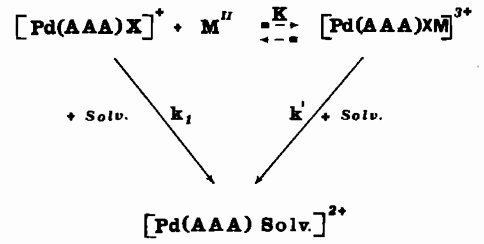


Figure 1. Dependence of pseudo-first-order rate constants, k_{obsd} (s^{-1}), on the concentration of mercury(II) in the reaction $[Pd(Et_4dien)X]^+ + Hg^{++} + MeOH \rightarrow [Pd(Et_4dien)MeOH]^{++} + HgX^+$ in methanol at 25° C; $\mu = 0.1M$. a) X = Cl; B) X = Br; c) X = I.

the solvent or a nucleophile. Likewise, the catalytic efficiency of Cd^{++} and Hg^{++} in removing Cl, Br and I from the coordination sphere of palladium(II) in the same complexes can be ascribed to the affinity of the metal ions for the coordinated halide. The reaction mechanism involves the formation of a binuclear adduct of the type $-\overset{|}{\underset{|}{Pd}}-X-M$, in equilibrium with the substrate.



k_1 and k' are the rate constants for the attack of MeOH on the substrate and the adduct, respectively, and K is the stability constant for formation of the binuclear adduct.

Kinetic and thermodynamic evidence has been produced for the formation of bimolecular adducts between electrophilic metal ions and halide complexes of Co^{III} [9,10] and Cr^{III} [11,13]. Recently Shaw[14] has shown that the attack of mercuric halides on neutral complexes of platinum and palladium of the type MX_2L_2 (X = halide group; L = tertiary phosphine or arsine) gives adducts of the type $MX_2L_2HgX_2$ having a double halide bridge between the metal atoms. For a kinetic scheme in which there is prior equilibrium between M^{++} and the complex with a nucleophilic attack by the solvent on both the substrate and the binuclear adduct, the observed pseudo-first-order rate constant is related to the mechanistically derived rate constants by the relationship

$$k_{obsd} = \frac{k_1 + k'\,K[M^{++}]}{1 + K[M^{++}]} \tag{3}$$

When Cd^{++} is used as catalyst and the reaction rate is slow enough to allow a comparison to be made, it can be seen that the spectrum of the substrate is virtually identical to that of the reaction mixture. This fact indicates that the equilibrium in the reaction scheme is well over to the left. Since $K[M^{++}] \ll 1$, equation (3) assumes the simpler form

$$k_{obsd} = k_1 + k_{(M^{++})}\quad [M^{++}] \tag{4}$$

in which $k_{(M^{++})}$ is a composite term given by the product $k' \cdot K$.

The mechanism then predicts that a plot of the observed pseudo-first-order rate constants (k_{obsd}) against $[M^{++}]$ should yield a straight line, the intercept and slope of which will give k_1 and $k_{(M^{++})}$ respectively. The values of these kinetic parameters were determined by such graphs as that reported in Figure 1 and are collected in Table III. As said above, the solvolytic path related to the independent rate term k_1 assumes relevance only in the reactions with the less effective catalyst Cd^{++}, while it becomes undetectable in the reactions with Hg^{++} in which the second order term $k_{(Hg^{++})}$ dominates the process. The values of k_1 obtained graphically for the complexes $[Pd(Et_4dien)Cl]^+$ and $[Pd(MeEt_4dien)Cl]^+$ are 2.4×10^{-5} s^{-1} and 1.0×10^{-5} s^{-1} respectively and agree well with the values 2.7×10^{-5} s^{-1} and 1.2×10^{-5} s^{-1} independently obtained in the nucleophilic substitutions with Br^- (Table II).

Figure 2 shows that a plot of the log of the rate constants for the mercury-catalyzed solvolysis, $k_{(Hg^{++})}$,

TABLE III. A Summary of the Kinetic Data for Uncatalyzed and Catalyzed Solvolysis of $[Pd(AAA)X]^+$ at 25° C in Methanol. The Effectiveness of Mercury(II) and Cadmium(II) Ions in the Catalysis and the Stability Constants (K) for the Complexing of such Species with Free Halides.

Reagent = Hg^{++}				Reagent = Cd^{++}				
Ligand	X	$k_{(Hg^{++})}$ M^{-1} s^{-1}	$\log K_{(HgX^+)}$	Ligand	X	$10^4\,k_{(Cd^{++})}$ M^{-1} s^{-1}	$10^5\,k_1$ s^{-1}	$\log K_{(CdX^+)}$
$MeEt_4dien$	Cl	2.3	6.74[a]	$MeEt_4dien$	Cl	2.45	1.0	1.54[b]
	Br	18.6	9.05[a]		Br	2.30	1.0	1.65[c]
	I	2112	12.87[a]					
Et_4dien	Cl	12.8	6.74	Et_4dien	Cl	7.0	2.4	1.54
	Br	80	9.05		Br	8.5	2.4	1.65
	I	9120	12.87					
Et_4dien[d]	Cl	8.3	6.74					
	Br	59.3	9.05					
	I	7700	12.87					

[a] In $NaClO_4$ 0.5M at 25° C, ref. 19. [b] In $NaClO_4$ 3M at 25° C, ref 19. [c] In $NaClO_4$ 2M at 25° C, ref. 19. [d] Data at ionic strength O. 1M.

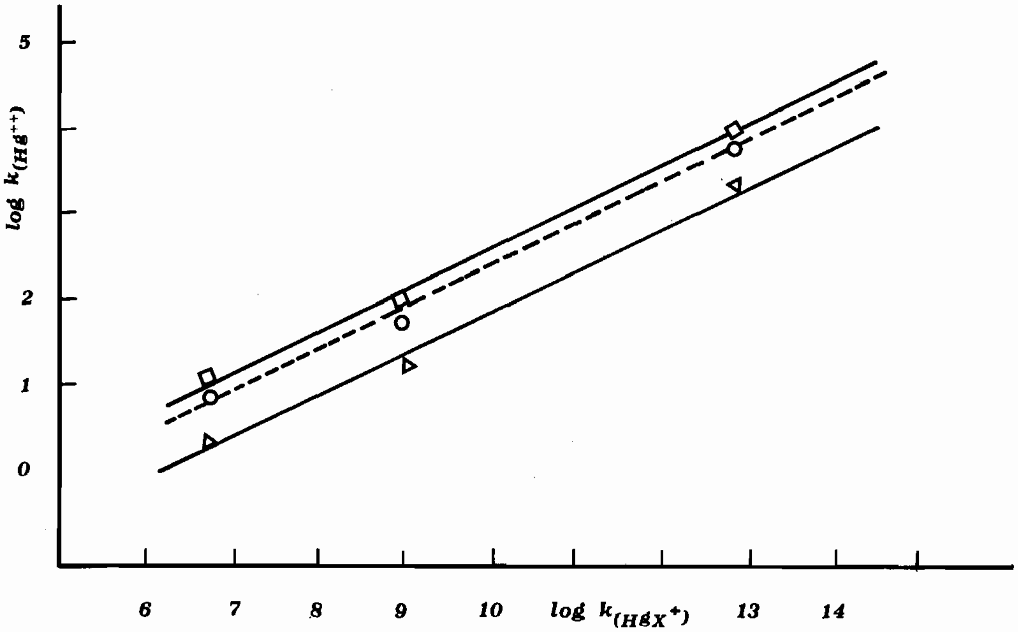


Figure 2. The logarithm of the rate of Hg^{II}-catalyzed solvolysis as a function of the logarithm of the stability constants (K) for the complexing of Hg^{++} with free halides; △ (AAA) = MeEt$_4$dien, $\mu = 1M$; □ (AAA) = Et$_4$dien, $\mu = 1M$; ○ (AAA) = Et$_4$dien, $\mu = 0.1M$.

against the log of the stability constants for the complexing of Hg^{++} with the free halides gives straight lines of the same slope for the two series of complexes. On the basis of the proposed mechanism it can be argued that the sequence of reactivity found, I > Br > Cl, is determined by the stability of the binuclear adduct whereas the solvolysis rate constant k′ of the adduct does not vary significantly with the nature of the coordinated halide. It is noteworthy that the values of the rate constants k_1 for the spontaneous solvolysis (Table III) indicate that the lability of Cl and Br groups is the same in any complex, as already found by Basolo[5] who studied the same reactions in water. Furthermore a recent kinetic study of nucleophilic substitutions on unhindered complexes [Pd(dien)X]$^+$ has pointed out that the lability of Cl, Br and I does not vary significantly in methanol[15]. A comparison of the catalytic rates and stability constants of mercury(II) and cadmium(II) ions, which is of particular interest since Hg^{++} and Cd^{++} are isoelectronic and have the same charge, shows that the affinity of the cationic species for the halide is the main factor controlling the relative effectiveness of the catalyst, although the size of the cation might affect the catalytic activity. On the basis of the rate law found and the linear relation between the catalytic rate constants and the stability constants for the complexing of Hg^{++} with free halides, it is not possible to rule out an alternative mechanism involving as rate determining step an electrophilic attack by Hg^{++} on the free end of the halide coordinated to the metal. If such a mechanism were operative it should be characterized by a halide-bridged transition state M···X···Pt(chelate). Provided that the rate law term $k_{(M^{++})}$ [M^{++}][Complex] is associated with a mechanism involving halide ion bridging in the transition state, this transition state resembles that for electron-transfer reactions[16]. Bifano and Link[17] in a detailed kinetic study of the Hg^{II}-catalyzed aquation of some chloro–amine complexes of Co^{III}, found that no free energy correlation exists between transition states generated in these aquations and in the Fe^{II} reduction of the same complexes, whereas the energies of the transition states for spontaneous and catalyzed aquations are related. In other words there is no duality of mechanism in the breaking of the Co–Cl and Co–Cl–Hg bonds although the two leaving groups are sensitive in a different way to the nature of ancillary ligands.

It is well known that in nucleophilic substitution reactions of palladium(II) complexes containing N-ethyl substituted amines as ligands the kinetic features are similar to those of octahedral complexes[5,7], since the steric hindrance of the substituted alkyl groups hinders the bimolecular attack by nucleophiles and the solvolysis rate controls completely the substitution. Some exceptions to this pattern of behaviour have been discussed in detail in the previous paper[4]. In the reactions of [Pd(Et$_4$dien)Cl]$^+$ and [Pd(MeEt$_4$ dien)Cl]$^+$ with Br$^-$ (Table II) we find no contribution of a k_2 term and the solvolytic path is the principal pathway for the substitution. Very little is known on the detailed role of the solvent molecule in the solvolytic path and the nature of the activation process. Recently Gray[18] has suggested that an associative mechanism is operative for the solvolysis of these axially blocked substrates in protic solvents whereas a dissociative process occurs in dipolar aprotic solvents. If we now turn to a comparison of the data for mercury(II) and cadmium(II) catalyzed solvolysis with those for the spontaneous solvolysis we find that either in the uncatalyzed or in the catalyzed substitution the complexes having Et_4dien as ligand are about three times more reactive than those with $MeEt_4$dien. For a rigorous discussion of the data, we should compare k_1 with the first-order rate constant for solvolysis where the leaving group is HgX^+ (k′ in the reaction scheme). However, if we assume that the magnitude of the affinity of metal ions for halide bound to palladium(II) does not change much as the nature of the ancillary ligand is varied, the discussion can be made. The correlation found above suggests that the response of the two leaving groups X^- and MX^+ to the addition of a methyl group in the N-hydrogen bond of the chelate ring is parallel, indicating that the mechanism does not vary on changing the nature and the sizes of the leaving group. Although it is difficult to define the extent to which bond making is relevant in the activation process, it appears that the role of the solvent in the transition state of catalyzed solvolysis is the same as in the transition state of spontaneous solvolysis.

Acknowledgements

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