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The Kinetics of the Linkage Isomerization of $Pd(Et_4dien)SCN^+$ as a Function of Pressure, Temperature, Solvent and Thiocyanate Concentration

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The linkage isomerization of $Pd(Et_4dien)SCN^+$ was investigated as a function of temperature, pressure and $[SCN^-]$, in aqueous solution and in DMF. These results are compared with more limited kinetic data on the same reaction of $Pd(MeEt_4dien)SCN^+$ and the substitution reaction with Br^-. Contrary to previous studies, a significant first-order dependence of the rate of isomerization on $[SCN^-]$ was found. An I_a mechanism is postulated for all the above-mentioned reactions.

Introduction

The extent by which the reactivity of a ligand—in particular the mechanism of its release—is influenced by steric crowding by the remaining ligand/s on a metal center continues to arouse interest and some controversy [1–4]. Numerous examples can be cited where the addition of more bulky substituents onto the 'inert' ligands of square planar complexes dramatically retards the rate of reaction [1, 3, 5, 6]. The pertinent question is whether retardation is merely due to the substituents partially blocking the entering group from bonding to the metal in a typically associative fashion, or whether some degree of dissociation of the leaving group is necessary in order to reach the transition state.

The linkage isomerization of the thiocyanato ligand in $Pd(Et_4dien)SCN^+$ [**] is very relevant to this discussion, because the reaction is believed to be solely motivated by the considerable steric restrictions imposed by the terminal ethyl groups on the Pd–SCN linkage. The latter is nonlinear, compared with the linear Pd–NCS form which otherwise makes up the thermodynamically less stable isomer [7, 8].

The established solvolysis pathway and the additional thiocyanate dependent contribution can be represented by the equations:

$$Pd(Et_4dien)SCN^+ + \text{solvent} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pd(Et_4dien)(\text{solvent})^{2+} + SCN^- \quad (1)$$

$$Pd(Et_4dient)(\text{solvent})^{2+} + SCN^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Pd(Et_4dien)NCS^+ + (\text{solvent}) \quad (2)$$

$$Pd(Et_4dien)SCN^+ + SCN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Pd(Et_4dien)NCS^+ + SCN^- \quad (3)$$

As the formal kinetics of the reaction have been well established, both in aqueous solution [8] and N,N-dimethylformamide [9], this reaction appears to be well suited to a high pressure investigation. In addition, earlier studies [10, 11] of the volumes of activation of a number of substitution reactions of $Pd(Et_4dien)X^{n+}$ complexes provide a sound basis for comparison and the eventual elucidation of the mechanisms involved.

Experimental

Materials

$[Pd(Et_4dien)SCN]SCN$, $[Pd(Et_4dien)SCN]PF_6$ and $[Pd(MeEt_4dien)SCN]PF_6$ were prepared according to the procedures described by Basolo *et al.* [8]. These complexes were stored under vacuum at −30 °C. The corresponding isothiocyanato complexes were prepared by standard techniques [5].

$Pd(Et_4dien)OH_2^{2+}$ and $Pd(MeEt_4dien)OH_2^{2+}$ were synthesized by stirring solutions of the respective $[Pd(Et_4dien)Br]Br$ complex [5] with solid Ag_2O in the dark. After several hours the mixture was filtered and titrated to a pH of *ca.* 5.1 with 0.1 *M* $HClO_4$.

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**Et_4dien ≡ 1,1,7,7-tetraethyldiethylenetriamine and $MeEt_4dien$ = 4-methyl-1,1,7,7-tetraethyldiethylenetriamine. Also referred to as: N'-[2-(diethylamino)ethyl]-N,N-diethylethane-1,2,-diamine ≡ teden, in ref. 10.

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The purity of the above-mentioned complexes, which were isolated in the solid state, was confirmed by microanalysis * and by a comparison of their IR spectra** with those reported in the literature [8, 12]. The UV/visible spectra of all species were recorded on a Zeiss DMR 10 spectrophotometer and were compared with the available literature data [5, 13, 15]. The following adsorption maxima correspond to those complexes whose spectra have not been previously published: $[Pd(MeEt_4dien)SCN]PF_6$, 391 nm ($\epsilon = 430$), *ca.* 317 nm(sh) ($\epsilon = 1240$); $[Pd(MeEt_4dien)NCS]PF_6$, 328 nm ($\epsilon = 1360$); $Pd(MeEt_4dien)OH_2^{2+}$ at pH = 2.1, 330 nm ($\epsilon = 1220$), 229 nm ($\epsilon = 11100$); $Pd(MeEt_4dien)OH^+$ at pH = 11.0, 308 nm ($\epsilon = 770$), 217 nm ($\epsilon = 1770\ M^{-1}\ cm^{-1}$).

The water used in making up the solutions was deionized, then distilled twice prior to use. N,N-Dimethylformamide was purified by standard methods [16]. All other chemicals were of analytical grade.

Kinetic Measurements

The reactions were followed *in situ* spectrophotometrically. Those in aqueous media were conducted in a single beam instrument incorporating a high pressure vessel in which a quartz cell was fitted with a movable teflon stopper [17]. The reactions in DMF were carried out in a sealed quartz–teflon cell assembly surrounded by water inside a pressure vessel [17], and the change in absorbance with time was monitored on a Cary 15 spectrophotometer. In both cases the isomerization was followed at 325 nm. The complex concentration was maintained at 5×10^{-4} *M* throughout and the ionic strength was adjusted with $NaClO_4$ in aqueous solutions and $KClO_4$ in DMF.

The anation reactions of $Pd(Et_4dien)OH_2^{2+}$ and $Pd(MeEt_4dien)OH_2^{2+}$ were initiated in a 1 cm rectangular quartz cell thermostated at (10.0 ± 0.1 °C) by rapidly mixing two solutions *in situ*: one containing the complex and the other the required amount of SCN^-. The pH of the solutions was adjusted to *ca.* 5 prior to mixing to ensure that the initial complex remained in the aquo form.

All the observed rate constants, k_{obs}, presented here are the result of at least two independent experiments.

Determination of pK_a Values

The acid dissociation constants of $Pd(Et_4dien)OH_2^{2+}$ and $Pd(MeEt_4dien)OH_2^{2+}$ were determined by spectrophotometric titration in the absence of 'inert' electrolyte at 20 °C. The respective pK_a values were calculated to be 7.50 ± 0.08 and 6.71 ± 0.18. The former is in exact agreement with the value of 7.5 reported by Goddard and Basolo [14] using the potentiometric method.

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**Using KBr pellets in a Beckman IR 4240 instrument.

Results

The temperature and pressure dependence of the rates of isomerization of $Pd(Et_4dien)SCN^+$ and $Pd(MeEt_4dien)SCN^+$ are presented in Tables I and II.

The data presented in Fig. 1 are somewhat surprising, in that k_{obs} for the isomerization of $Pd(Et_4dien)SCN^+$ shows a marked sensitivity to the thiocy-

TABLE I. Temperature Dependence of the Rate Constant of Isomerization of $Pd(REt_4dien)SCN^+$.

Temperature °C	$10^4\ k_{obs}$, s^{-1}	
	$Pd(Et_4dien)SCN^+$ [a]	$Pd(MeEt_4dien)SCN^+$ [b]
20	1.91 ± 0.16	1.84 ± 0.06
25	3.23 ± 0.08	2.94 ± 0.08
30	5.35 ± 0.15	4.84 ± 0.15
35	8.88 ± 0.12	7.23 ± 0.28
40	13.6 ± 0.3	11.7 ± 0.3

[a] $\mu = 0.1\ M$. [b] $\mu = 0.5\ M$.

TABLE II. Pressure Dependence of the Rate Constant of Isomerization of $Pd(REt_4dien)SCN^+$ at 30 °C in Aqueous Solution.

Pressure, bar	$10^4\ k_{obs}$, s^{-1}	
	$Pd(Et_4dien)SCN^+$ [a]	$Pd(MeEt_4dien)SCN^+$ [b]
1	5.35 ± 0.15	4.84 ± 0.15
250	6.12 ± 0.12	5.32 ± 0.26
500	6.78 ± 0.10	6.14 ± 0.17
750	7.34 ± 0.09	6.73 ± 0.17
1000	8.48 ± 0.09	7.29 ± 0.01
1250	8.92 ± 0.09	8.63 ± 0.22
1500	10.03 ± 0.08	9.28 ± 0.28

[a] $\mu = 0.1\ M$. [b] $\mu = 0.5\ M$.

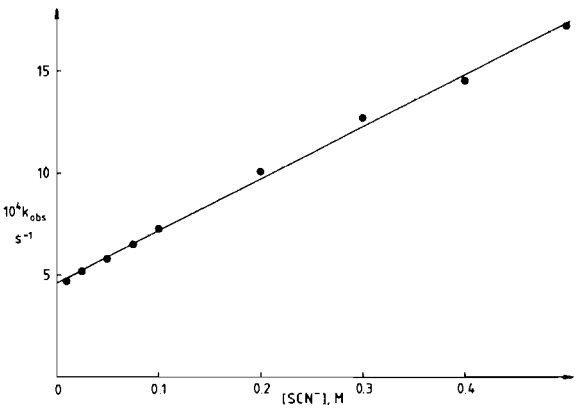

Fig. 1. Plot of k_{obs} *versus* $[SCN^-]$ at 30 °C and $\mu = 0.5\ M$ for the Isomerization of $[Pd(Et_4dien)SCN]SCN$.

TABLE III. Pressure Dependence of the Rate of Isomerization of $Pd(Et_4dien)SCN^+$ as a Function of Thiocyanate Concentration at 30 °C and $\mu = 0.5$ *M*.

Pressure, bar	$10^3 k_{obs}$, s^{-1}			$10^4 k_1$ s^{-1}	$10^3 k_3$ $M^{-1} s^{-1}$
	[SCN⁻] 0.2 *M*	[SCN⁻] 0.35 *M*	[SCN⁻] 0.5 *M*		
1	1.00 ± 0.14	1.31 ± 0.12	1.72 ± 0.05	5.0 ± 0.7	2.40 ± 0.20
250	1.08 ± 0.02	1.58 ± 0.09	1.95 ± 0.03	5.2 ± 0.9	2.90 ± 0.25
500	1.20 ± 0.01	1.70 ± 0.19	2.11 ± 0.06	6.1 ± 0.6	3.03 ± 0.17
750	1.32 ± 0.04	1.94 ± 0.21	2.33 ± 0.03	6.9 ± 0.2	3.37 ± 0.44
1000	1.40 ± 0.02	2.34 ± 0.23	2.52 ± 0.03	7.8 ± 0.4	3.73 ± 0.46

anate concentration. Earlier work [8] conducted at a considerably lower [SCN⁻] failed to detect this relationship. A linear least-squares treatment of the values in Fig. 1 resulted in an intercept (k_1) of $(4.59 \pm 0.13) \times 10^{-4}$ s^{-1} and a slope (k_3) of $(2.55 \pm 0.05) \times 10^{-3}$ $M^{-1} s^{-1}$ at 30 °C. The rates of isomerization of $Pd(Et_4dien)SCN^+$ were also determined as a function of pressure at three thiocyanate ion concentrations and these data are presented in Table III, together with the k_1 and k_3 values obtained at each pressure by the above-mentioned least-squares method. The resulting activation volumes are -11.4 ± 1.0 and -10.3 ± 1.1 cm^3 mol^{-1}, respectively. Although the former extrapolated value is subject to larger errors it is, nonetheless, in good agreement with the directly obtained value given in Table IV.

In order to be able to make a more direct comparison of these data with existing information dealing with the hydrolysis reactions (k_1 path) in a series of similar complexes [10, 15], the substitution reactions of both thiocyanato species were investigated in the presence of bromide ion. These results are shown in Table IV.

TABLE IV. Temperature and Pressure Effect of the Bromide Substitution in $Pd(REt_4dien)SCN^+$ at $\mu = 0.5$ *M* and $[Br^-] = 0.3$ *M*.

Temperature, °C	Pressure, bar	k_{obs}, s^{-1}	
		$Pd(Et_4dien)SCN^+$	$Pd(MeEt_4dien)SCN^+$
20	1	2.38 ± 0.15	1.02 ± 0.03
25		4.14 ± 0.18	2.00 ± 0.06
30		6.84 ± 0.23	3.06 ± 0.06
35		9.67 ± 0.38	5.44 ± 0.26
40		17.3 ± 1.1	7.92 ± 0.30
30	200	7.72 ± 0.23	
	250		3.31 ± 0.02
	400	8.53 ± 0.15	
	500		3.56 ± 0.10
	600	9.23 ± 0.30	
	750		3.78 ± 0.08
	800	10.1 ± 0.3	
	1000	10.8 ± 0.2	4.68 ± 0.10
	1250		5.18 ± 0.14
	1500		5.56 ± 0.36

Plots of ln*k* *versus* pressure proved to be linear in all cases—as were those for the hydrolysis of all the other $Pd(Et_4dien)X^{n+}$ complex ions [10]—so that the $\Delta V^{\neq}$ values could be obtained from linear least-squares analyses of these data. The activation parameters are summarized in Table V.

The second step (k_2) in the overall hydrolysis pathway involves the rapid anation of the aquo intermediate to form the isothiocyanato isomer [14]. Pseudo-first-order rate constants for the anation of $Pd(Et_4dien)OH_2^{2+}$ and $Pd(MeEt_4dien)OH_2^{2+}$ are listed in Table VI as a function of [SCN⁻]. The mean second-order rate constants calculated from these values are 9.4 ± 0.7 and 5.0 ± 1.1 $M^{-1} s^{-1}$ respectively. Goddard and Basolo [14] reported a value of 75.1 $M^{-1} s^{-1}$ at 25 °C and $\mu = 0.02$ for the former complex. Furthermore, they identified 85% of the initial product as $Pd(Et_4dien)NCS^+$ with the remainder as $Pd(Et_4dien)SCN^+$, while we found a similar ratio of 80 : 20 at 10 °C. The second-order rate constants are therefore the sum of two anation rate constants. The final equilibrium ratio, which favors the N-bonded isomer almost completely, is established at a much slower rate.

Following the lead of Johnson, Lim and Burmeister [9], the temperature, pressure, and thiocyanate concentration dependence of the rates of isomerization were also investigated in DMF for the $Pd(Et_4dien)SCN^+$ substrate. The rate data are given in Table VII. The rate constant at 30 °C and resulting activation parameters are: $k = 2.02 \times 10^{-4}$ s^{-1}, $\Delta H^{\neq} = 76.6 \pm 0.8$ kJ mol^{-1}, $\Delta S^{\neq} = -63 \pm 3$ J K^{-1} mol^{-1} and $\Delta V^{\neq} = -9.5 \pm 0.5$ cm^3 mol^{-1}, $\Delta V^{\neq}$ being independent of pressure, within experimental error, and therefore calculated from the usual linear treatment. Under the same conditions (*i.e.*, $\mu = 0.1$ *M*, 30 °C), Johnson *et al.* [9] reported a rate constant of 1.93×10^{-4} s^{-1} and a $\Delta H^{\neq}$ of 82.8 kJ mol^{-1} and a $\Delta S^{\neq}$ of -42 J K^{-1} mol^{-1}, in reasonable agreement with our findings.

TABLE V. Activation Parameters for the Isomerization of and the Bromide Substitution in $Pd(REt_4dien)SCN^+$ at 30 °C.

	μ, M	$\Delta H_1^{\neq}$ kJ mol^{-1}	$\Delta S_1^{\neq}$ J K^{-1} mol^{-1}	$\Delta V_1^{\neq}$ cm^3 mol^{-1}
		Isomerization		
$Pd(Et_4dien)SCN^+$	0.1	72.8 ± 1.7	−67 ± 5	−10.1 ± 0.3
	0.1	72.4 ± 2.1[22]	−70 ± 4[22]	
$Pd(MeEt_4dien)SCN^+$	0.5	67.8 ± 1.3	−85 ± 4	−10.8 ± 0.3
		Substitution		
$Pd(Et_4dien)SCN^+$	0.5	70.7 ± 2.7	−72 ± 9	−10.6 ± 0.4
	0.1	72.4 ± 2.1[22]	−70 ± 4[22]	
$Pd(MeEt_4dien)SCN^+$	0.5	75.3 ± 1.7	−64 ± 5	−10.5 ± 0.6

TABLE VI. Observed Pseudo-First-Order Rate Constants for the Anation of $Pd(REt_4dien)OH_2^{2+}$ by SCN^- (μ = 0.5 M; temp. = 10 °C; pH ~ 5).

$[SCN^-]$ M	10^2 k_{obs}, s^{-1}	
	$Pd(Et_4dien)OH_2^{2+}$	$PdMeEt_4dien)OH_2^{2+}$
0.005	4.6 ± 0.2	1.78 ± 0.05
0.010	10.3 ± 0.4	3.90 ± 0.28
0.015		8.13 ± 0.44
0.020	18.9 ± 0.5	11.3 ± 0.4
0.030	25.0 ± 1.5	16.2 ± 1.4
0.040	38.6 ± 4.5	25.2 ± 1.5

TABLE VII. Pseudo-First-Order Rate Constants for the Isomerization of $Pd(Et_4dien)SCN^+$ [a] in DMF.

Temperature, °C	Pressure, bar	μ M	$[SCN^-]$ M	10^4 k_{obs} s^{-1}
25	1	0.1[b]	0	1.16 ± 0.02
30				2.02 ± 0.02
35				3.33 ± 0.04
40				5.37 ± 0.10
30	1	0.1[c]	0	1.94 ± 0.03
	250			2.19 ± 0.10
	500			2.27 ± 0.10
	750			2.56 ± 0.05
	1000			2.80 ± 0.10
	1250			3.16 ± 0.01
	1500			3.61 ± 0.20
	2000			3.99 ± 0.20
30	1	0.5[c]	0	1.60 ± 0.10
			0.025	3.36 ± 0.16
			0.050	5.35 ± 0.13
			0.100	8.22 ± 0.10
			0.200	15.3 ± 0.2
			0.300	19.1 ± 0.4
			0.400	22.6 ± 1.5
			0.500	26.2 ± 4.1

[a]Used as $[Pd(Et_4dien)SCN]PF_6$ salt. [b]$NaClO_4$ [c]$KClO_4$.

Discussion

The rate parameters, either $\Delta H_1^{\neq}$ or $\Delta S_1^{\neq}$, given in Table V for the isomerization and bromide substitution of $Pd(Et_4dien)SCN^+$ are virtually equal, merely substantiate the earlier observations of Basolo *et al.* [8] and confirm their concept that these reactions involve a common intermediate. These findings have now been extended to include the parameter, $\Delta V_1^{\neq}$. Furthermore, although the agreement is not nearly as good, the activation parameters for the corresponding reactions of the substrate $Pd(MeEt_4dien)SCN^+$ are at least similar to those of the tetraethyl derivative. This similarity between all the respective activation parameters strongly suggests a common mechanism. Thus the same hydrolysis mechanism for substitution, which was shown to be of the associative interchange (I_a) type, must also apply to the linkage isomerization reaction.

The rate constant k_1 for the $Pd(MeEt_4dien)SCN^+$ species is *ca.* 2.3 times smaller than the tetraethyl analog at 30 °C, in good agreement with the factor of *ca.* 2.5 reported for the hydrolysis rate constants for the chloro complexes [14]. The reduced reactivity of the 4-methyl substituted dien complex was thought to be due to increased steric hindrance brought about by this substituent; presumably it affects the free rotation of the ethyl groups and is therefore only a secondary effect, although the *trans* effect of the 4-methyl group could also explain the slower hydrolysis rate.

The two negative $\Delta V^{\neq}$ values for $Pd(Et_4dien)SCN^+$ show no effect from variations in ionic strength within their experimental uncertainty limits and are, furthermore, very similar to the $\Delta V_1^{\neq}$ value for substitution into $Pd(Et_4dien)NCS^+$ of −10.3 ± 0.2 cm^3 mol^{-1} at 40 °C and μ = 0.2 M [10]. Similarly, $\Delta H_1^{\neq}$ (75.2 ± 1.7 kJ mol^{-1}) and $\Delta S_1^{\neq}$ (−67 ± 6 J K^{-1} mol^{-1}) for the latter reaction are in close agreement with the corresponding values in Table V. One can draw the conclusion that the bulkiness of the leaving

group is not an important factor in determining the rate or mode of activation (*viz.* the degree of dissociation in the transition state) because the more 'bulky' S-bonded ligand, which provides the driving force for the isomerization, would otherwise be expected to be more labile. Indeed, as suggested earlier [10], reactivity as a function of the leaving group appears to be directly proportional to the Pd–X bond strength.

There also appears to be no significant solvent effect because the activation parameters for the solvolysis path in DMF are virtually indistinguishable from those in Table V (*i.e.*, $\Delta H_1^{\neq} = 76.6 \pm 0.8$ kJ mol^{-1}, $\Delta S_1^{\neq} = -63 \pm 3$ J K^{-1} mol^{-1} and $\Delta V_1^{\neq} = -9.5 \pm 0.5$ cm^3 mol^{-1}). However, because the solvent is involved both as the reactant and as the solvating medium, one cannot distinguish between these two contributions to the activation parameters. They may in fact compensate each other. In view of the widely differing solvation properties of protic *versus* aprotic solvents, one can safely assume that strong solvation changes are not involved in the activation step [11]. This is also consistent with the concept of an I_a mechanism and with the pressure independence of $\Delta V_1^{\neq}$.

The thiocyanate dependent pathway involves the associative attack of the SCN^- nucleophile on the $Pd(Et_4dien)SCN^+$ substrate [15], but it is difficult to distinguish between an I_a and an A mechanism on the basis of the $\Delta V_3^{\neq}$ value alone. However, a comparison of this value (-10.3 ± 1.1 cm^3 mol^{-1}) with those obtained for the bimolecular reaction of SCN^- with $Pd(Et_4dien)Cl^+$ and $Pd(Et_4dien)Br^+$ at 25 °C and $\mu = 0.5$ *M* ($\Delta V_3^{\neq}$ of -2.6 ± 0.5 and -10.1 ± 0.1 cm^3 mol^{-1}, respectively [10] demonstrates that $\Delta V_3^{\neq}$ is dependent on the leaving group. This leads to the inevitable conclusion that the mechanisms must also be I_a. Indeed, it is only logical that the mechanism should be the same whether the incoming group is a water molecule or a thiocyanate anion.

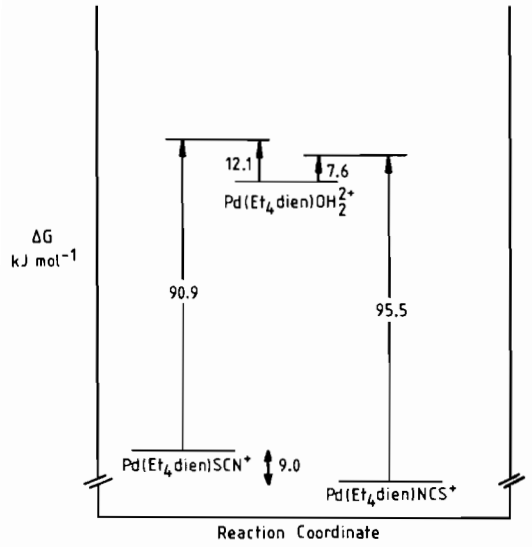

Fig. 2. Energy Profile Diagram for the Hydrolysis Path of the Isomerization of $Pd(Et_4dien)SCN^+$.

A final aspect of the isomerization of $Pd(Et_4dien)SCN^+$ concerns the overall free energy profile (Fig. 2), which can be calculated from the known $\Delta G^{\neq}$ values for the hydrolysis of both isomers and from the temperature dependence and product ratio of the anation of the aquo intermediate. This treatment serves to affirm that the N-bonded isomer is thermodynamically more stable by *ca.* 9 kJ mol^{-1}, which is in very good agreement with the value "most unlikely to be more than about 2 kcal mol^{-1}" as quoted from Hewkin and Poë [13]. The figure also more clearly distinguishes between the kinetically controlled distribution of isomers as obtained from the anation of the aquo intermediate and the final thermodynamic equilibrium.

Acknowledgments

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