

Evidence for a Dual Mechanism in Reactions of $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]^+$ Complexes

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The kinetics of Pt(II), Pd(II) and Ni(II)^{1,2} generally follow a typical two term rate law, $k_{\text{obs}} = k_1 + k_2[\text{Y}]$, where Y represents the incoming nucleophile. Substitution reactions of $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]^+$ complexes (Et₄dien = 1,1,7,7-tetraethyldiethylenetriamine) therefore aroused interest when the rates were found to be independent of nucleophile concentration³⁻⁵. This was attributed simply to steric crowding of the axial positions, or potential reaction sites, of the complex by the terminal ethyl groups of the dien. Only in a few cases was a k_2 path found in non-aqueous solvents^{6,7}.

Our present study of the effects of applied pressure on this type of reaction necessitated employing higher nucleophile concentrations than those previously used⁵ and in the majority of these cases the traditional two term rate law was, in fact, found to apply.

Experimental

Complexes of the type $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]\text{X}$, where X = Cl⁻, Br⁻, I⁻, N₃⁻, -SCN⁻, and -NCS⁻, were prepared by standard methods.^{3,8} Chemical analysis confirmed the composition of these complexes. Their absorption maxima are compared with those reported by

TABLE I. Absorption Maxima of $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]^+$.

Complex, X	This Work λ_{max} (nm)	ϵ (cm ² mol ⁻¹)	λ_{max} (nm)	Literature ϵ (cm ² mol ⁻¹)
Cl	345	800	346	815
Br	356	720	358	690
I	392	660	387	654
N ₃	320	1850	320	1780
-SCN	ca. 380	440		
-NCS	327	1340	325	1360

Baddley and Basolo³ in Table I. All other salts used were of reagent grade.

The kinetics were followed spectrophotometrically in aqueous solution using either a ZEISS PMQ II or a CARY 15 spectrophotometer. The ionic strength was adjusted to 0.5M using NaClO₄. In reactions involving high concentrations of free azide the pH was adjusted to 7 - 8 with NaClO₄. The observed rate constant for the reaction of N₃⁻ with $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$ at 25 °C and $[\text{N}_3^-] = 0.05\text{M}$ showed only a slight dependence on ionic strength, as shown in Table II, which is consistent with the previous work of Roulet and Gray.⁵ This result, together with the observed linearity of the k_{obs} versus $[\text{Y}]$ plots, strongly suggest that contributions to the mechanism from conceivable ion pairing are negligible despite the high nucleophile concentrations employed. All rate constants given in this work represent the mean value of two or more runs.

It should be noted that decomposition of these complexes was not observed at high bromide or iodide concentrations as reported earlier.⁴ However, for certain very strong nucleophiles such as cyanide and thiourea rapid decomposition was observed even at low concentrations.

Results and Discussions

Basolo *et al.*⁴ found that $[\text{Pd}(\text{Et}_4\text{dien})\text{Br}]^+$ exhibits a two term rate law for reactions with S₂O₃²⁻ and OH⁻. The hydroxide ion dependence was effectively explained in terms of a S_N2CB mechanism and was substantiated by the absence of this dependence for $[\text{Pd}(\text{MeEt}_4\text{dien})\text{Br}]^+$ (MeEt₄dien = 4-methyl-1,1,7,7-tetraethyldiethylenetriamine). However, they offered no definite explanation for the case of

TABLE II. Ionic Strength Dependence for $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+ + \text{N}_3^-$ at 25 °C using NaClO₄.

Ionic Strength (M)	10 ³ k_{obs} (sec ⁻¹)
0.05	2.63 ± 0.01
0.15	2.55 ± 0.03
0.25	2.47 ± 0.03
0.35	2.39 ± 0.03
0.45	2.30 ± 0.05
0.50	2.27 ± 0.01

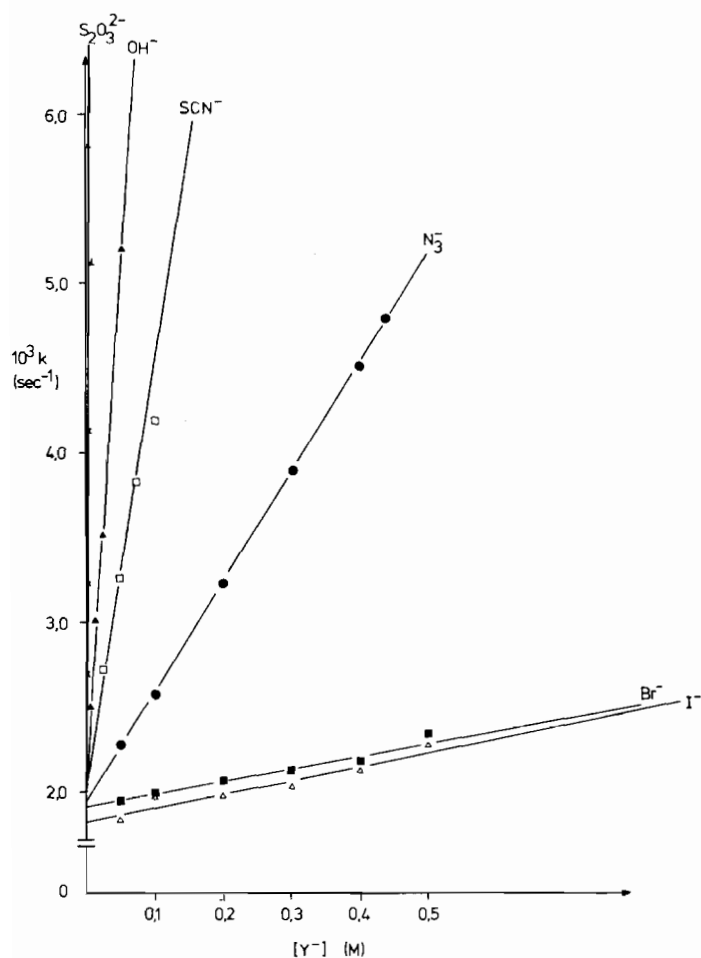


Fig. 1. The rate dependence for the reaction of $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$ with various nucleophiles at 25°C and $\mu = 0.5M$.

thiosulphate, other than its strong nucleophilicity.

Figure 1 shows the rate dependence for the reaction of $[\text{Pd}(\text{Et}_4\text{dien})\text{Cl}]^+$ with $\text{S}_2\text{O}_3^{2-}$, OH^- , SCN^- , N_3^- , Br^- , and I^- at 25°C and $\mu = 0.5$. The second order rate constants decrease in the order $\text{S}_2\text{O}_3^{2-} > \text{SCN}^- > \text{N}_3^- > \text{Br}^- \cong \text{I}^-$ ($5.6:2.23 \times 10^{-2}:6.44 \times 10^{-3}:8.18 \times 10^{-4}:7.96 \times 10^{-4} M^{-1} \text{sec}^{-1}$, resp.), whereas the order for decreasing n_{Pt} values is $\text{S}_2\text{O}_3^{2-} > \text{SCN}^- > \text{I}^- > \text{Br}^- > \text{N}_3^-$ (e.g. rate constants $9:0.18:0.107:3.7 \times 10^{-3}:1.55 \times 10^{-3} M^{-1} \text{sec}^{-1}$ resp., for *trans*- $[\text{Pt}(\text{py})_2\text{Cl}_2]$ in methanol at 30°C^1). Obviously the order and the relative rates in the known sequence of nucleophilicities have been significantly modified for these sterically hindered complexes. Thus the overall size of the potential nucleophile imposes this modifying restraint on its inherent nucleophilic strength. This effect is particu-

larly apparent for iodide as it appears practically unable to interact directly with the metal center. A further example is the virtual equivalence of N_3^- and $-\text{NCS}^-$ as nucleophiles. The effectiveness of steric hindrance in these complexes is well known from the observed linkage isomerization⁹ of $[\text{Pd}(\text{Et}_4\text{dien})\text{SCN}]^+$ to give the less hindered N-bonded isothiocyanate complex despite the greater Pd-S bond strength.

In Table III, which contains all the determined rate constants and activation parameters, one observes that the k_1 and ΔH^\ddagger_1 values are relatively constant for a given substrate considering errors involved in determining rate constants from intercepts. The corresponding ΔS^\ddagger_1 values are also consistent and uniformly negative, with the exception of the substrate $[\text{Pd}(\text{Et}_4\text{dien})\text{NCS}]^+$. In

TABLE III. Summary of Rate Constant and Activation Parameter Data for $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]^+ + \text{Y}^-$.

X	Y	T (°C)	$10^3 k_1$ (sec^{-1})	$10^3 k_2$ ($M^{-1}\text{sec}^{-1}$)	ΔH^\ddagger_1 (kcal mol^{-1})	ΔS^\ddagger_1 (e.u.)	ΔH^\ddagger_2 (kcal mol^{-1})	ΔS^\ddagger_2 (e.u.)
Cl	$\text{S}_2\text{O}_2^{2-}$	25	1.83 ± 0.22	5600 ± 360				
	SCN^-	25	2.07 ± 0.10	22.3 ± 1.7	16.3 ± 1.4	-21.0 ± 2.4	13.5 ± 1.6	-19.2 ± 2.7
	N_3^-	25	1.93 ± 0.10	6.44 ± 0.03	15.6 ± 0.2	-17.6 ± 0.8	13.8 ± 0.5	-22.4 ± 1.8
	I^-	25	1.87 ± 0.25	0.90 ± 0.06	16.5 ± 0.5^5	-16.5 ± 0.5^5		
	Br^-	25	1.89 ± 0.09	0.82 ± 0.02	16.5 ± 0.5^5	-16 ± 2^5		
Br	N_3^-	25	1.57 ± 0.05	6.40 ± 0.17	15.6 ± 0.7	-17.8 ± 2.3	13.8 ± 1.0	-22.4 ± 2.3
	I^-	40.2	5.50^5		17.6 ± 0.5^5	-13 ± 2^5	13.8 ± 1.0	-22.4 ± 2.3
I	N_3^-	25	0.346 ± 0.021	2.17 ± 0.07	17.0 ± 0.3	-16.5 ± 0.8	15.1 ± 0.9	-20.1 ± 2.5
	Br^- or Cl^-	40	1.4^5		18.5 ± 0.5^5	-13 ± 2^5		
N_3	I^-	25	3.96^a		17.1 ± 0.2	-16.9 ± 0.5		
SCN	Br^-	30	0.545 ± 0.009	0.475 ± 0.024	17.3 ± 0.5^9	-16.8 ± 1.0^9		
	I^-	25	$0.413 \pm 0.018^{a,b}$		17.6 ± 0.4	-14.9 ± 1.4		
	N_3^-	30	0.30 ± 0.10	9.7 ± 0.5				
NCS	N_3^-	30	0.175 ± 0.005	1.51 ± 0.02				
	I^-	30	0.201 ± 0.006^a		17.9 ± 0.4	2.3 ± 1.2		
	Br^-	35	0.51^9		25.8 ± 0.5^9	7.0 ± 1.0^9		

^a No attempt was made to measure the second order rate constant and therefore these reactions were conducted at nucleophile concentrations which were low enough to neglect any contribution from the second order term. ^b Ionic strength = 0.1 M.

this case the large discrepancy between the ΔH^\ddagger_1 and ΔS^\ddagger_1 values for Br^- ⁹ and I^- (this work) is not reconcilable with the above data. However, under the conditions described by Basolo *et al.*⁹ we found that the substitution does not proceed to completion and thus it is possible that their data are complicated by inclusion of the reverse reaction. Nevertheless, the ΔS^\ddagger value is slightly positive, a fact which we are unable to rationalize at this time. On the other hand, by measuring the volumes of activation for this whole series of substrates it should be possible to determine if this positive ΔS^\ddagger can be related to a change in mechanism.

Although some stretching of the Pd-X bond during the formation of the transition state is likely, in view of the consistency of the relative ΔH^\ddagger_1 and ΔS^\ddagger_1 values, we conclude that the reactions are basically associative in character involving the direct attack of a water molecule on the Pd center. This conclusion concurs with a similar postulate proposed by Gray *et al.*⁵

The activation parameters for the k_2 path are too few to allow any definite conclusions other than they are consistent with a basically associative mechanism.

Acknowledgements

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