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Effect of Pressure on the Substitution Reactions of $[Pt(dien)X]^+$ Complexes in Aqueous Solution[1]

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The effect of pressure on the substitution reactions of $[Pt(dien)X]^+$ complexes (dien = diethylenetriamine) with a number of nucleophiles, Y, have been studied in aqueous solution at 25°C and at an ionic strength of 0.2 M, where $X = Cl^-$, Br^-, I^-, N_3^- and $Y = OH^-$, I^-, N_3^-, NO_2^-, SCN^- and pyridine. The volumes of activation are all negative with the mean value for the nucleophile independent path being -18 ± 2 ml mol^{-1}. Partial molar volumes of the respective substrates and products were measured at 25°C. The data are discussed in terms of an associative mechanism for the nucleophile dependent path, while for the independent path both associative and dissociative mechanisms are considered.

Introduction

It is well known that square planar complexes of the heavier transition metals with d^8 electron configurations undergo ligand substitution of the type:

$$ML_3X + Y \rightleftharpoons ML_3Y + X \qquad (1)$$

which, as a rule, follows a two term rate law of the form[2–7]:

$$\text{Rate} = k_1[\text{complex}] + k_2[\text{complex}][Y] \qquad (2)$$

The reaction schemes (a) and (b), shown in Figure 1, have been proposed in accordance with the obtained rate expression (2). Both schemes include a direct attack by the nucleophile Y on the substrate, *i.e.* the k_2 path. The first order term, k_1 path, is rationalized in scheme (a) by a rate determining dissociation of the ligand X followed by a fast reaction of the reactive three-coordinate intermediate with the entering ligand Y. According to scheme (b) the same rate law is obtained when the k_1 path consists of a slow bimolecular substitution of X by a solvent molecule S, while the resulting solvent-containing complex reacts rapidly with Y.

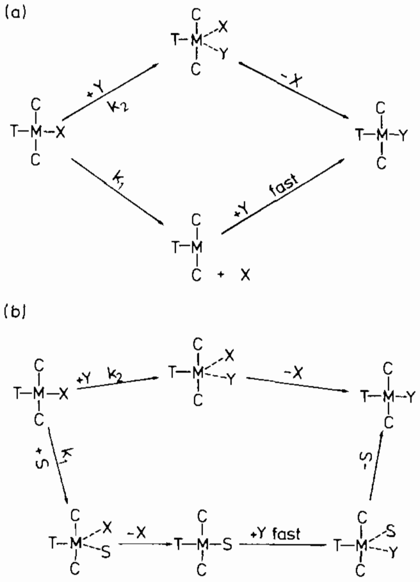

Figure 1. Alternative reaction schemes for reactions of Pt(II) complexes *via* a dissociative mechanism (a) or an associative mechanism (b).

Although the bulk of the kinetic evidence gives strong support for the associative mechanism in scheme (b), no direct proof of its existence has, as yet, been presented. Moreover, in the case of the substrate $[Pt(dien)X]^+$ Basolo, Gray and Pearson[8] proposed that the mechanism may possess some dissociative character depending on the nature of the leaving group X, *i.e.* some stretching of the Pt–X bond in forming the transition state.

During the last few years the volume of activation, $\Delta V^{\ddagger}$, derived from the pressure dependence of the rate constant of a reaction, has been used in several cases as a criterion in the discussion of mechanisms of complex ion reactions[9–11]. As pointed out[11] the most significant contribution to $\Delta V^{\ddagger}_{exp}$ stems from an intrinsic effect reflecting changes in bonding during the formation of the transition state, bond formation being expected to give a negative contribution to the

$\Delta V^{\ddagger}_{exp}$ and bond breaking a positive one. In many examples, especially when charged species are involved, the change in solvation during the development of the transition state results in an additional contribution which modifies the intrinsic effect. This additional effect calls for a special discussion in each particular case.

We had therefore hoped that an accurate determination of the $\Delta V^{\ddagger}_{exp}$ values and the partial molar volumes of the substrates for reactions of type (1) would provide both qualitative and quantitative information as to the nature of the transition state and therefore the mechanism of reaction.

Experimental

Materials

The preparation of [Pt(dien)X]X and [Pt(dien)X]NO_3 complexes are generally adequately described in the literature[8,12,13]. However the synthesis[12] of [Pt(dien)Br]Br, which was generally the starting material used to make the other complexes, was modified slightly. Solid NaOH was added to the mother liquor, formed by refluxing K_2PtCl_4 and dien·2HCl and then concentrating the solution on a rotary evaporator, to give a final pH of *ca.* 5, just prior to precipitating the complex by addition of solid NH_4Br. The resulting yield was *ca.* 65%. Calcd for [Pt(dien)Br]Br: C, 10.5; H, 2.9; N, 9.2; Br, 34.9. Found: C, 10.7; H, 2.9; N, 9.5; Br, 35.8%. The corresponding chloride and iodide complexes were prepared directly by the same method.

All other salts used were of reagent grade. The water was passed through an ion exchange column, then doubly distilled.

Rate Measurements

The reactions were followed spectrophotometrically using a Zeiss PMQ II spectrophotometer as part of a high pressure apparatus, the detailed design of which has been previously described[14]. A 1 cm quartz cell was used throughout. Reactions were studied over a pressure range of 1–1500 atm and at an ionic strength of 0.2*M* adjusted with $NaClO_4$. For the pressure dependence studies the temperature was maintained at 25 °C.

Each reaction studied is known[8,15,16] to proceed to completion and good pseudo first order rate plots were always obtained using the Guggenheim method fitted by a least squares program. All the rate constants shown are the mean result of at least three individual measurements. In the case of the hydrolysis of [Pt(dien)Br]$^+$ in alkaline solution, where the plot of $\ln k_1$ *versus* pressure is not linear, as shown in Figure 2a, a minimum of 7 runs were made at each pressure in order to determine most accurately the shape of the curve.

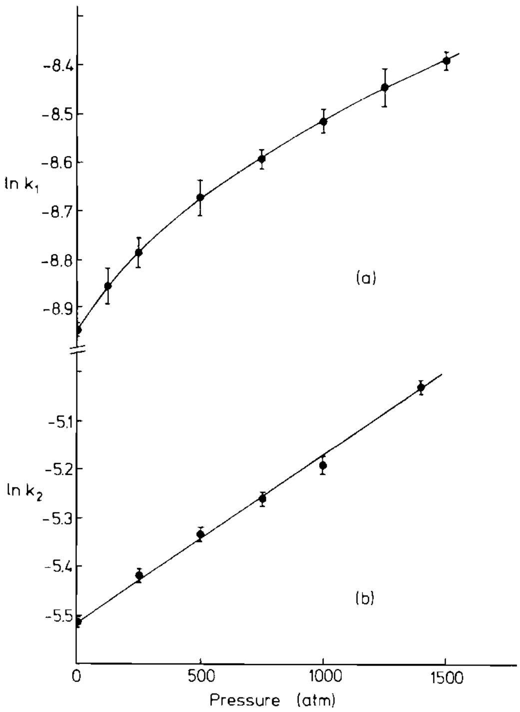

Figure 2. Pressure dependence plots for the reactions: (a) $[Pt(dien)Br]^+ + OH^- \rightarrow [Pt(dien)OH]^+ + Br^-$ (k_1 path); (b) $[Pt(dien)N_3]^+ + SCN^- \rightarrow [Pt(dien)SCN]^+ + N_3^-$ (k_2 path).

Density Measurements

The density measurements were carried out at 25.000 ± 0.005 °C using a vibrating capillary apparatus. The apparent molar volume of each platinum complex was determined at a minimum of 4 different concentrations in the range 1.9 to $6.6 \times 10^{-3} M$ which encompasses the range of concentrations used in the rate studies. No attempt was made to adjust the ionic strength of these solutions.

The apparent molar volume of KN_3 was determined at 9 concentrations and shows only a slight linear dependence on concentration up to the maximum concentration studied of 0.1354*M*.

Results

The principal reaction, as described by equation (1) for the substrate [Pt(dien)X]$^+$, was studied with 8 different combinations of X and Y. For each of these reactions, except for the "base hydrolysis"[17], the function $k_{obs} = k_1 + k_2[Y]$ was established at 6 to 8 different pressures within the range 1–1500 atm and at 2–5 different concentrations of Y. One particular reaction, $[Pt(dien)Br]^+ + N_3^-$, was studied more intensively in an attempt to obtain the intercept on the

k_{obs} axis, k_1, as accurately as possible and thereby an accurate, independent value for $\Delta V^{\ddagger}_{exp}$ (1) for comparison with the directly determined value of $\Delta V^{\ddagger}_{exp}$ (1) for $[Pt(dien)Br]^+ + OH^-$. The plot of $\ln k_{obs}$ as a function of $[N_3^-]$ is shown in Figure 3 at the various applied pressures. The reaction of $[Pt(dien)Br]^+$ with NO_2^- was investigated because the direct attack of nitrite ion on the substrate is relatively slow, thus causing k_1 to be the dominant contribution to k_{obs} and allowing a more accurate evaluation of $\Delta V^{\ddagger}_{exp}$ (1). All the pressure dependence rate data are summarized in Table I.

In order to make a comparison between the volumes and entropies of activation the available literature values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were supplemented by studying the reaction of the bromo complex with NO_2^- as a function of temperature. These data are given in Table III.

It should be noted that for this reaction the k_2 value at one atmosphere pressure is significantly smaller than that given in the literature; *i.e.* $1.44 \times 10^{-3} M^{-1}$ sec^{-1} at 25°C, *cf.* $3.7 \times 10^{-3} M^{-1}$ sec^{-1} [15]. Apparently this results from the use of higher nitrite concentrations in our study which eliminates the contribution of the reverse reaction, a factor which is already discussed by Gray[15].

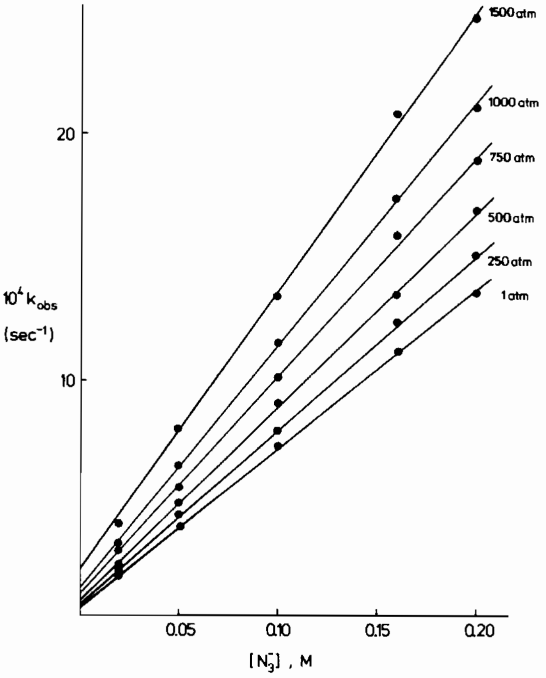

Figure 3. Pressure dependence of k_{obs} for the reaction of $[Pt(dien)Br]^+$ with azide ion at 25°C.

TABLE I. Pressure Dependence of the Rate Constants of the Reactions (μ = 0.2*M*, 25°C).

Pressure atm	Nucleophile *M*	$10^4 \times k_{obs}$ sec^{-1}	$10^4 \times k_1$ sec^{-1}	$10^3 \times k_2$ M^{-1} sec^{-1}
$[Pt(dien)Br]^+ + N_3^- \rightarrow [Pt(dien)N_3]^+ + Br^-$				
1	0.02	2.15 ± 0.06	0.89 ± 0.03	6.40 ± 0.02
	0.05	4.04 ± 0.01		
	0.10	7.37 ± 0.04		
	0.16	11.2 ± 0.3		
	0.20	13.6 ± 0.2		
250	0.02	2.45 ± 0.05	0.97 ± 0.07	7.08 ± 0.06
	0.05	4.45 ± 0.15		
	0.10	7.99 ± 0.03		
	0.16	12.4 ± 0.4		
	0.20	15.1 ± 0.2		
500	0.02	2.56 ± 0.08	1.06 ± 0.13	7.89 ± 0.10
	0.05	5.03 ± 0.16		
	0.10	9.11 ± 0.11		
	0.16	13.5 ± 0.1		
	0.20	16.9 ± 0.3		
750	0.02	3.17 ± 0.08	1.33 ± 0.18	8.93 ± 0.14
	0.05	5.68 ± 0.01		
	0.10	10.2 ± 0.2		
	0.16	15.9 ± 0.0		
	0.20	19.0 ± 0.4		

TABLE I. (Cont.)

Pressure atm	Nucleophile *M*	$10^4 \times k_{obs}$ sec^{-1}	$10^4 \times k_1$ sec^{-1}	$10^3 \times k_2$ M^{-1} sec^{-1}
1000	0.02	3.41 ± 0.15	1.60 ± 0.14	9.82 ± 0.11
	0.05	6.56 ± 0.09		
	0.10	11.6 ± 0.2		
	0.16	17.4 ± 0.3		
	0.20	21.1 ± 0.4		
1500	0.02	4.21 ± 0.06	2.2 ± 0.3	11,5 ± 0.2
	0.05	8.08 ± 0.47		
	0.10	13.8 ± 0.1		
	0.16	20.9 ± 0.3		
	0.20	24.8 ± 0.7		
$[Pt(dien)Br]^+ + py \rightarrow [Pt(dien)py]^{2+} + Br^-$				
1	0.10	3.04 ± 0.03	2.7 ± 0.6	2.77 ± 0.02
	0.31	8.92 ± 0.05		
	0.52	14.6 ± 0.4		
250	0.10	3.35 ± 0.17	4.6 ± 0.7	2.89 ± 0.02
	0.31	9.38 ± 0.12		
	0.52	15.2 ± 0.2		
500	0.10	3.65 ± 0.04	3.8 ± 0.8	3.27 ± 0.02
	0.31	10.6 ± 0.3		
	0.52	17.3 ± 0.5		
750	0.10	4.06 ± 0.11	5.6 ± 2.7	3.56 ± 0.08
	0.31	11.8 ± 0.3		
	0.52	18.9 ± 0.5		
1000	0.10	4.38 ± 0.13	4.7 ± 4.0	4.01 ± 0.11
	0.31	13.2 ± 0.2		
	0.52	21.1 ± 0.4		
1500	0.10	4.94 ± 0.12	3.2 ± 0.3	4.57 ± 0.01
	0.31	14.5 ± 0.3		
	0.52	24.0 ± 0.5		
$[Pt(dien)Br]^+ + NO_2^- \rightarrow [Pt(dien)NO_2]^+ + Br^-$				
1	0.05	1.98 ± 0.11	1.22 ± 0.05	1.44 ± 0.07
	0.10	2.76 ± 0.02		
250	0.05	2.28 ± 0.01	1.47 ± 0.07	1.62 ± 0.10
	0.10	3.09 ± 0.04		
500	0.05	2.53 ± 0.01	1.68 ± 0.16	1.73 ± 0.24
	0.10	3.41 ± 0.01		
750	0.05	2.85 ± 0.03	1.96 ± 0.06	1.79 ± 0.09
	0.10	3.75 ± 0.01		
1000	0.05	3.12 ± 0.04	2.17 ± 0.05	1.90 ± 0.07
	0.10	4.07 ± 0.03		
1500	0.05	3.78 ± 0.02	2.60 ± 0.20	2.36 ± 0.28
	0.10	4.96 ± 0.03		

TABLE I. (Cont.)

Pressure atm	Nucleophile M	$10^4 \times k_{obs}$ sec^{-1}	$10^4 \times k_1$ sec^{-1}	$10^3 \times k_2$ M^{-1} sec^{-1}
$[Pt(dien)Cl]^+ + N_3^- \rightarrow [Pt(dien)N_3]^+ + Cl^-$				
1	0.05	2.33 ± 0.01	1.07 ± 0.01	2.53 ± 0.01
	0.10	3.61 ± 0.03		
	0.20	6.13 ± 0.05		
250	0.05	2.72 ± 0.01	1.13 ± 0.25	3.07 ± 0.20
	0.10	4.16 ± 0.05		
	0.20	7.30 ± 0.05		
500	0.05	2.99 ± 0.02	1.21 ± 0.10	3.47 ± 0.07
	0.10	4.62 ± 0.03		
	0.20	8.18 ± 0.03		
750	0.05	3.24 ± 0.03	1.38 ± 0.05	3.76 ± 0.04
	0.10	5.18 ± 0.03		
	0.20	8.88 ± 0.06		
1000	0.05	3.52 ± 0.07	1.40 ± 0.29	4.08 ± 0.22
	0.10	5.44 ± 0.07		
	0.20	9.60 ± 0.15		
1500	0.05	3.87 ± 0.02	1.55 ± 0.27	4.53 ± 0.18
	0.10	6.01 ± 0.09		
	0.20	10.63 ± 0.20		
$[Pt(dien)I]^+ + N_3^- \rightarrow [Pt(dien)N_3]^+ + I^-$				
1	0.05	2.43 ± 0.03	–0.02 ± 0.32	5.23 ± 0.23
	0.10	5.36 ± 0.10		
	0.15	8.05 ± 0.15		
	0.20	10.25 ± 0.15		
250	0.05	2.92 ± 0.04	–0.03 ± 0.42	5.83 ± 0.26
	0.10	5.65 ± 0.15		
	0.15	8.98 ± 0.15		
	0.20	11.73 ± 0.20		
500	0.05	3.31 ± 0.10	0.48 ± 0.52	6.06 ± 0.34
	0.10	6.74 ± 0.10		
	0.15	9.77 ± 0.15		
	0.20	12.50 ± 0.30		
750	0.05	3.63 ± 0.03	0.64 ± 0.43	6.61 ± 0.28
	0.10	7.19 ± 0.15		
	0.15	10.98 ± 0.25		
	0.20	13.66 ± 0.30		
1000	0.05	4.02 ± 0.03	0.31 ± 0.31	7.68 ± 0.21
	0.10	8.10 ± 0.15		
	0.15	11.71 ± 0.15		
	0.20	15.70 ± 0.30		
1500	0.05	4.82 ± 0.05	0.32 ± 0.37	8.98 ± 0.57
	0.10	9.25 ± 0.35		
	0.15	14.27 ± 0.20		
	0.20	18.22 ± 0.40		

TABLE I. (Cont.)

Pressure atm	Nucleophile *M*	$10^4 \times k_{obs}$ sec^{-1}	$10^4 \times k_1$ sec^{-1}	$10^3 \times k_2$ M^{-1} sec^{-1}
$[Pt(dien)N_3]^+ + I^- \rightarrow [Pt(dien)I]^+ + N_3^-$				
1	0.05	1.79	0.27 ± 0.19	3.21 ± 0.14
	0.10	3.60		
	0.20	6.64		
250	0.05	2.00	0.05 ± 0.05	3.91 ± 0.01
	0.10	3.96		
	0.20	7.86		
500	0.05	2.22	–0.06 ± 0.01	4.46 ± 0.08
	0.10	4.34		
	0.20	8.89		
750	0.05	2.52	0.03 ± 0.06	5.04 ± 0.05
	0.10	5.11		
	0.20	10.1		
1000	0.05	2.94	–0.02 ± 0.03	5.97 ± 0.03
	0.10	5.96		
	0.20	11.9		
1500	0.05	3.57	0.23 ± 0.05	7.56 ± 0.03
	0.10	7.30		
	0.20	14.9		
$[Pt(dien)N_3]^+ + SCN^- \rightarrow [Pt(dien)SCN]^+ + N_3^-$				
1	0.05	1.75	–0.03 ± 0.11	3.65 ± 0.09
	0.10	3.70		
	0.20	7.25		
250	0.05	2.02	–0.04 ± 0.06	4.06 ± 0.04
	0.10	3.99		
	0.20	8.10		
500	0.05	2.23	0.01 ± 0.01	4.46 ± 0.01
	0.10	4.47		
	0.20	8.92		
750	0.05	2.51	0.11 ± 0.04	4.85 ± 0.03
	0.10	4.98		
	0.20	9.79		
1000	0.05	2.74	0.13 ± 0.03	5.24 ± 0.03
	0.10	5.39		
	0.20	10.61		
1500	0.05	3.28	0.14 ± 0.03	6.26 ± 0.02
	0.10	6.38		
	0.20	11.95		
$[Pt(dien)Br]^+ + OH^- \rightarrow [Pt(dien)OH]^+ + Br^-$				
1	0.01	1.31 ± 0.02	1.31 ± 0.02	–
125	0.01	1.44 ± 0.07	1.44 ± 0.07	–
250	0.01	1.55 ± 0.07	1.55 ± 0.07	–
500	0.01	1.75 ± 0.09	1.75 ± 0.03	–
750	0.01	1.91 ± 0.05	1.91 ± 0.05	–
1000	0.01	2.08 ± 0.07	2.08 ± 0.07	–
1250	0.01	2.25 ± 0.11	2.25 ± 0.11	–
1500	0.01	2.39 ± 0.06	2.39 ± 0.06	–

TABLE II. Partial Molar Volumes of Salts and Ions in Water at 25°C.

Salt	$\bar{V}$ ml mol^{-1}	Ion	$\bar{V}$ ml mol^{-1}	Ref.
$[Pt(dien)Br]NO_3$	153.6 ± 1.0	$[Pt(dien)Br]^+$	120.3 ± 1.0	This Work
$[Pt(dien)Cl]NO_3$	147.5 ± 0.4	$[Pt(dien)Cl]^+$	114.2 ± 0.4	This Work
$[Pt(dien)I]I$	170.9 ± 0.4	$[Pt(dien)I]^+$	129.9 ± 0.4	This Work
$[Pt(dien)N_3]ClO_4$	172.2 ± 0.6	$[Pt(dien)N_3]^+$	121.5 ± 0.6	This Work
$[Pt(dien)SCN]NO_3$	175.0 ± 1.0	$[Pt(dien)SCN]^+$	141.7 ± 1.0	This Work
$[Pt(dien)py](NO_3)_2$	258.1 ± 1.1	$[Pt(dien)py]^{2+}$	191.5 ± 1.2	This Work
$[Pt(dien)NO_2]NO_3$	155.8 ± 2.2	$[Pt(dien)NO_2]^+$	122.5 ± 2.2	This Work
KN_3	36.3 ± 0.1	N_3^-	31.8 ± 0.2	This Work
KSCN	44.7	SCN^-	40.2	22
KNO_3	37.8	NO_3^-	33.3	22
$KClO_4$	55.2	ClO_4^-	50.7	22
KI	45.5	I^-	41.0	22
KBr	33.9	Br^-	29.4	22
KCl	26.3	Cl^-	21.8	22
$NaNO_2$	25.0	NO_2^-	30.7	22
		K^+	4.5	23
		Na^+	-5.7	22
(pyridine)	77.1 ± 0.3			This Work

Various authors[18, 19] have proposed a variety of equations to "best fit" the lnk *versus* P plots in those cases where $\Delta V^{\ddagger}_{exp}$ is dependent on pressure. The k_1 path for the substitution reactions of $[Pt(dien)X]^+$ complexes offers such an example. In the case of $[Pt(dien)Br]^+ + OH^-$ we attempted to obtain the exact empirical form of the curve drawn in Figure 2a by conducting many runs. As has been pointed out previously[20], in discussion of mechanisms one is primarily interested in the value of $\Delta V^{\ddagger}_{exp}$ at 1 atm and hence the need is for accurate data at lower pressures. Here, in view of the experimental limits, the lowest pressure that we were able to obtain was 125 atm. However, despite these low pressure studies and the large number of runs conducted, the curvature at lower pressures was so acute that no satisfactory fit of these data could be obtained using the proposed methods and equations[9, 18, 19], with the exception of the higher order polynomials. The success of the higher order polynomial equations is obviously not surprising and the real significance of their parameters must be treated with utmost caution. Therefore in these cases where a high degree of curvature is found, we prefer to use a simple graphic method which will give at least a minimum value of $\Delta V^{\ddagger}_{exp}$. The $\Delta V^{\ddagger}_{exp}$ (2) for the corresponding k_2 path proved to be independent of pressure in the range studied. An example of this is shown in Figure 2b.

Apparent molar volume data φ_i were obtained from precision density measurements using the known equation[21]

$$\varphi_i = \frac{M_i}{d_o} - 1000\frac{d_i - d_o}{d_o c_i} \qquad (3)$$

in which d_i and d_o are the densities of the solution and solvent respectively; M_i is the molecular weight of the dissolved species; and c_i its molar concentration. No definite trend in the apparent molar volume data was observed over the range of concentrations studied, *i.e.* 7×10^{-4} to $1.2 \times 10^{-1} M$. Therefore, as a first approximation, the φ_i values may be taken as equivalent to the partial molar volumes. The results of these measurements, together with a number of relevant partial molar volumes taken from the literature[22], are given in Table II. This table also contains the partial molar volumes of individual ions obtained on the assumption that the partial molar volume of K^+ is 4.5 ml mol^{-1} [23].

From the data presented in Table I one can determine the volume of activation, $\Delta V^{\ddagger}_{exp}$, according to the equation of Evans and Polanyi[24]:

TABLE III. Temperature Dependence of the Rate Constant for the Substitution Reaction $[Pt(dien)Br]^+ + NO_2^- \rightarrow [Pt(dien)NO_2]^+ + Br^-$

Temp. °C	$10^4 \times k_1$ sec^{-1}	$10^3 \times k_2$ $M^{-1}\,sec^{-1}$
19.8	0.60 ± 0.04	1.09 ± 0.09
32.4	2.27 ± 0.07	3.89 ± 0.04
37.1	3.54 ± 0.09	4.78 ± 0.05
40.0	4.90 ± 0.04	6.88 ± 0.03

$\Delta H^{\ddagger}_1 = 17.9 \pm 0.8$ kcal mol^{-1}; $\Delta S^{\ddagger}_1 = -15.9 \pm 2.5$ e.u.
$\Delta H^{\ddagger}_2 = 17.1 \pm 1.1$ kcal mol^{-1}; $\Delta S^{\ddagger}_2 = -13.5 \pm 3.5$ e.u.

TABLE IV. Volumes of Activation and Reaction for the Substitution Processes: $[Pt(dien)X]^+ + Y^{(-)} \rightarrow [Pt(dien)Y]^{+,(2+)} + X^-$ in Aqueous Solutions at 25°C.

Substrate $[Pt(dien)X]^+$	Nucleophile Y	$\Delta V^{\ddagger}_{exp}$ (1) ml mol^{-1}	$\Delta V^{\ddagger}_{exp}$ (2) ml mol^{-1}	$\Delta \bar{V}$ ml mol^{-1}
$[Pt(dien)Br]^+$	N_3^-	-15 ± 1	-8.5 ± 0.2	-1.2 ± 1.0
$[Pt(dien)Br]^+$	py	neg.[a]	-7.7 ± 0.5	$+23.5 \pm 1.2$
$[Pt(dien)Br]^+$	NO_2^-	-18 ± 1	-6.4 ± 0.7	$+0.9 \pm 2.2$
$[Pt(dien)Cl]^+$	N_3^-	-17 ± 2[b]	-8.2 ± 1.3	-2.7 ± 1.0
$[Pt(dien)I]^+$	N_3^-	-18 ± 2[b]	-8.2 ± 0.7	$+0.8 \pm 0.6$
$[Pt(dien)N_3]^+$	I^-	neg.[a]	-12.2 ± 0.1	-0.8 ± 0.6
$[Pt(dien)N_3]^+$	SCN^-	neg.[a]	-7.3 ± 0.1	$+11.8 \pm 1.0$
$[Pt(dien)Br]^+$	$OH^-(H_2O)$	-18.0 ± 2.0		

[a] k_1 values were not accurate enough to calculate $\Delta V^{\ddagger}_{exp}$ (1), only its pressure dependence trend was taken. [b] In these cases k_{obs} at the lowest nucleophile concentration, *i.e.* 0.05*M*, was taken to calculate $\Delta V^{\ddagger}_{exp}$ (1) approximately.

$$\frac{d\ln k}{dP} = -\frac{\Delta V^{\ddagger}_{exp}}{RT} - \Delta\nu\varkappa RT \qquad (4)$$

If one uses molarity concentrations for the calculations of the rate constants, the correction term ($-\Delta\nu\varkappa$ RT) of equation (4) has to be applied including $\Delta\nu$, the algebraic sum of the stoichiometric coefficients during the formation of the transition state, and $\varkappa$, the compressibility of the solvent. On the other hand one can correct the rate constants obtained at individual pressures for the compression effect of the liquid system. Either method leads in our examples to a constant correction term of +1.2 ml mol^{-1} for all activation volumes obtained from the second order rate constants. The corrected values of $\Delta V^{\ddagger}_{exp}$ are summarized in Table IV together with the volumes of reactions, $\Delta \bar{V}$.

Discussion

As mentioned in the introduction, for liquid systems the values of $\Delta V^{\ddagger}_{exp}$ primarily consist of two contributions: the intrinsic part, $\Delta V^{\ddagger}_{intr}$, and the solvation part, $\Delta V^{\ddagger}_{solv}$. In principle, this applies to $\Delta V^{\ddagger}_{exp}$ derived for the k_1 path, $\Delta V^{\ddagger}_{exp}$ (1), as well as for the k_2 path, $\Delta V^{\ddagger}_{exp}$ (2). By assuming a basically associative mechanism[2–7] for both paths one can exclude any electrostriction effects contributing to $\Delta V^{\ddagger}_{exp}$ (1) as, in the first approximation, the mechanism merely involves the formation of a $Pt{-}OH_2$ bond. The values of $\Delta V^{\ddagger}_{exp}$ (1) are, in fact, independent of the nature of the potential leaving groups and lie between −15 and −18 ml mol^{-1}. Although this is consistent with either an A or I_a mechanism, the absolute values are far larger than would be expected for the simple formation of a $Pt{-}OH_2$ bond, where only the $\Delta V^{\ddagger}_{intr}$ (1) term is involved. This is particularly apparent when one considers that partial bonding is known to occur between solvent water molecules occupying the axial positions and the Pt(II) center of such square planar complexes. Furthermore, $\Delta V^{\ddagger}_{exp}$ (1) is certainly more negative than the corresponding values found for the water exchange reactions of complexes of the type, $[M(NH_3)_5OH_2]^{3+}$ (where M = Cr(III)[25], Rh(III)[25], and Ir(III)[26]), and $[Cr(OH_2)_6]^{3+}$[27], for which an I_a, or possibly an A, mechanism is proposed. Here the most negative value of $\Delta V^{\ddagger}_{exp}$ obtained was for the latter reaction, *i.e.* -9.3 ± 0.3 ml mol^{-1}.

In addition, in the reaction with hydroxide ion, where k_1 could be accurately determined, a plot of $\ln k_1$ against pressure shows an extremely sharp curvature, particularly at relatively low pressures (see Figure 2a), whereas the plots for the k_2 paths (see Figure 2b for example) are linear within experimental error as are those for the water exchange reactions mentioned above[25, 26]. In other words, the volume of activation, $\Delta V^{\ddagger}_{exp}$ (1), exhibits a marked pressure dependence, while $\Delta V^{\ddagger}_{exp}$ (2) values remain essentially independent of pressure up to our measured limit of 1500 atm.

Two other studies on the effect of pressure on substitution reactions of Pt(II) complexes exist in the literature[28, 29]. Although these authors reported a linear dependence for their $\ln k_1$ *versus* pressure plots we feel that a curve would better describe their data. Therefore, in view of these differences between the two paths, we prefer to discuss them individually.

Experimental results and theoretical considerations have shown that for a hypothetical, unsolvated species in solution, the intrinsic volume of activation is pressure independent[30] as long as small to moderate pressures are applied. Some workers[31, 32] have proposed a model in which the species under consideration is placed in a spherical cavity within a continuous medium. The cavity is considered to be both expandable and compressible and has a dielectric constant of unity. In the case of complex ions the cavity is occupied by a strongly bound, highly-ordered first coordination sphere. Estimations of its compressibility, $\varkappa$, from the observed pressure dependence of the electronic absorption bands of crystalline complex salts[33] yielded values of *ca.* 1 to 2×10^{-6} atm^{-1} for bivalent ions. This in turn gives rise to contributions to $\Delta V^{\ddagger}_{\mathrm{intr}}$ in the order of 0.1 ml mol^{-1}. Without doubt, these values become more significant for singly charged ions, but it is unlikely that the overall effect of compression of the unsolvated moiety will exceed the errors incurred in measuring $\Delta V^{\ddagger}_{\mathrm{exp}}$ values.

$\Delta V^{\ddagger}_{\mathrm{solv}}$, on the other hand, representing the difference in solvation between the initial and transition states, may well be pressured dependent inasmuch as the solvation of both states is differently influenced by pressure. This appears to be the case for the k_1 path, but not for the k_2 path. It is significant that curvature of the $\ln k_1$ plot in Figure 2a virtually ceases at 1500 atm, which is unfortunately the maximum pressure attainable with our high pressure apparatus.

Several authors[9,18,34,35] have been able to interpret the curvature of lnk *versus* pressure plots in terms of an interchange mechanism involving solvent molecules in solvation sheaths of differing compressibilities around the reaction center. Kruse and Taube[36] originally proposed that for $(\partial\Delta V^{\ddagger}_{\mathrm{exp}}/\partial P)_T$ values greater than the compressibility of bulk water, *ca.* 7×10^{-4} ml atm^{-1} mol^{-1}, would be expected for aquation or water exchange reactions involving an A mechanism. Notwithstanding our difficulties in determining $(\partial\Delta V^{\ddagger}_{\mathrm{exp}}/\partial P)_T$ with any accuracy, a value of 3×10^{-1} ml atm^{-1} mol^{-1} can be approximated. This value is far too large to fit the type of treatment used by these workers[9,18,34,35] and indicates further that the curvature has another origin, although it does not presuppose that an A mechanism is not involved here.

Why $\Delta V^{\ddagger}_{\mathrm{solv}}$ (1) is pressure dependent, and not $\Delta V^{\ddagger}_{\mathrm{exp}}$ (2), is difficult to explain, if we continue the discussion within the framework of a basically associative mechanism. Here we can merely propose that the transition state for the k_1 path is strongly solvated, possibly enhanced by the increase in acidity of the incoming water molecule, to give an overall relatively incompressible structure. Conversely, one could argue that the complex in the initial state is surrounded by a loosely structured solvation sheath. However, this explanation would equally well apply to the k_2 path, giving rise to some pressure dependence of $\Delta V^{\ddagger}_{\mathrm{exp}}(2)$.

In order to consider all possible origins of the unique behaviour of $\Delta V^{\ddagger}_{\mathrm{exp}}$ (1) let us consider briefly the k_1 path in terms of a dissociative mechanism, as shown in Figure 1a. In general terms, this should lead to a positive value for $\Delta V^{\ddagger}_{\mathrm{intr}}$ (1) of about 5 ml mol^{-1} [37] which must then be compensated by a $\Delta V^{\ddagger}_{\mathrm{solv}}$ (1) value of *ca.* −23 ml mol^{-1} to obtain the observed $\Delta V^{\ddagger}_{\mathrm{exp}}$ (1) of -18 ± 2 ml mol^{-1}. Such a large value for $\Delta V^{\ddagger}_{\mathrm{solv}}$ (1) appears incompatible with the formation of doubly and singly charged ions resulting from the dissociation of the leaving group. At first glance, $\Delta V^{\ddagger}_{\mathrm{exp}}$ (1) would be expected to be strongly dependent on the nature of the leaving group for a dissociative mechanism[18] and, as shown in Table IV, this is not the case. However, this argument can be examined quantitatively by considering the "volume equation" treatment proposed earlier[11]:

$$\bar{V}_{([Pt(dien)X]^+)} + \Delta V^{\ddagger}_{\mathrm{exp}}(1) = \bar{V}_{([Pt(dien)]^{2+})} + \bar{V}_{(X^-)} \qquad (5)$$

The calculated partial molar volumes, given in Table III, for [Pt(dien)X]$^+$ and X$^-$ permit the calculation of the intermediate, *i.e.* $\bar{V}_{([Pt(dien)]^{2+})}$, using equation (5). Application of this treatment to the three substrates, for which reasonably accurate values of $\Delta V^{\ddagger}_{\mathrm{exp}}$ (1) are available, yields the values shown in Table V. A mean value for $\bar{V}_{([Pt(dien)]^{2+})}$ of 73 ± 2 ml mol^{-1} covers all three theoretical reactions and, in fact, if one assumes a $\Delta V^{\ddagger}_{\mathrm{exp}}$ (1) value of -18 ± 2 ml mol^{-1} for the substrates [Pt(dien)NO$_2$]$^+$ and [Pt(dien)N$_3$]$^+$ one obtains 74 and 72 ml mol^{-1}, respectively, for $\bar{V}_{([Pt(dien)]^{2+})}$. For the cases of X = SCN and pyridine $\Delta V^{\ddagger}_{\mathrm{exp}}$ would have to equal −29 and −41 ml mol^{-1}, respectively, to fit into this picture. The latter four reactions are too slow to measure with our present techniques. The surprising consistency of the data in Table III must be treated with some caution as a rough linear relationship between $\bar{V}_{([Pt(dien)X]^+)}$ and $\bar{V}_{(X^-)}$ exists, which is in strong contrast with the corresponding values for [M(NH$_3$)$_5$X]$^{2+}$ complexes[38], where M = Co(III) and Cr(III). In other words, the more "open" structure of the square planar complexes enables the potential leaving group ligands to be partially solvated as if they were free ions, *i.e.* the ligands possess some of their free ion character in the coordinated form[39].

In terms of a dissociative mechanism the pressure dependence of $\Delta V^{\ddagger}_{\mathrm{exp}}$ (1) can be readily explained

TABLE V. Partial Molar Volumes of Individual Ions and the Hypothetical Intermediate, [Pt(dien)]$^{2+}$, in ml mol^{-1} at 25 °C. Calculated according to Equation (5).

X	$\bar{V}_{([Pt(dien)X]^+)}$	$\bar{V}_{(X^-)}$	$\Delta V^{\ddagger}_{\mathrm{exp}}$ (1)	$\bar{V}_{([Pt(dien)]^{2+})}$
Cl	114.2 ± 0.4	21.8 ± 0.5	−17. ± 2.	75. ± 3.
Br	120.3 ± 1.0	29.4 ± 0.5	−18. ± 2.	73. ± 3.
I	129.9 ± 0.4	41.0 ± 0.5	−18. ± 2.	71. ± 3.

by the difference in compressibilities of the ground and transition state (intermediate). This difference can now be attributed to the structural change in going from a square planar, singly charged ground state with loosely bound water molecules in axial positions to a doubly charged, virtual trigonal bipyramid with well developed metal–water bonds.

We now turn to the k_2 path, the mechanism for which is also believed to be associative[2,3,6], as supported by such criteria as: the rate law; the dependence of the rate on the nucleophilicity of the entering group; and the large, negative values of $\Delta S^{\ddagger}$ [2–4]. The expected contributions to the $\Delta V^{\ddagger}_{exp}$ (2) values call for a negative value for $\Delta V^{\ddagger}_{intr}$ (2) as a consequence of bond formation between Pt and Y, and generally for a positive $\Delta V^{\ddagger}_{solv}$ (2) due to the partial charge neutralization. The latter contribution appears to be small, as no major difference in $\Delta V^{\ddagger}_{exp}$ (2) can be detected for the reactions of the bromo complex with either pyridine, azide, or nitrite ions. Thus the $\Delta V^{\ddagger}_{intr}$ (2) part essentially determines the observed experimental values of $\Delta V^{\ddagger}_{exp}$ (2).

In principle, both the Pt–Y bond formation process and the bond breaking of Pt–X contribute to $\Delta V^{\ddagger}_{intr}$ (2). However, the nearly identical values of $\Delta V^{\ddagger}_{exp}$ (2) shown in Table IV for the reactions between azide ion and the chloro-, bromo-, and iodo-complexes indicate that bond making is predominant, underlining the prevailing evidence for an I_a mechanism for this path.

As mentioned previously, all plots of $\ln k_2$ *versus* pressure show a linear correlation. Thus the change in solvation of the products and transition state is either comparable or negligible. This leads to the possible assumption that the entering nucleophile Y is already weakly coordinated to the complex in the ground state, causing a solvation situation which is similar in the initial and transition states. Such a behaviour corresponds to an ion-pair pre-equilibrium. So far no strong evidence, such as a nonlinear dependence of k_{obs} on the free nucleophile concentration, has been found to substantiate an ion-pairing mechanism. Only some spectral evidence for the existence of a five coordinate intermediate $[Pt(NH_3)_2(NO_2)_2Cl]^-$ has been reported[40] in the reaction of $[Pt(NH_3)_2(NO_2)Cl]$ with nitrite ion.

A comparison of the volume of activation, $\Delta V^{\ddagger}_{exp}$ (2), with the overall volume of reaction, $\Delta\bar{V}$, as given in the last column of Table IV, shows that in all cases $\Delta V^{\ddagger}_{exp}$ (2) is more negative than $\Delta\bar{V}$. In other words, the transition states are more compact than the products, which also supports the concept of an associative mechanism for this path.

With the deduced criteria for an essentially A type mechanism for the k_2 path and the indication that no major changes in solvation occur during the development of the transition state, one can use the partial molar volume of the reactants to calculate the volume of the transition state, [Pt(dien)XY], $\bar{V}_{\ddagger}$, as demonstrated by equation 6:

$$\bar{V}_{\ddagger} = \bar{V}_{(\text{complex ion})} + \bar{V}_{(\text{nucleophile})} + V^{\ddagger}_{exp}(2) \qquad (6)$$

The validity of this treatment can be verified by considering the reaction:

$$[Pt(dien)I]^+ + N_3^- \rightleftharpoons [Pt(dien)N_3]^+ + I^-$$

Application of equation 6 for the forward and reverse reactions must then result in the same value for $\bar{V}_{\ddagger}$. Figure 4 shows the complete volume profile diagram. The common transition state differs by only 3.2 ml mol^{-1}, amounting to a mean value for $\bar{V}_{\ddagger}$ of 151.9 ± 1.5 ml mol^{-1}. The agreement is very good considering the number of parameters involved. This combined approach gives further strong support for an associative mechanism for the direct substitution processes. It does not, however, exclude minor stretching of the Pt–X bond leading to an I_a mechanism as suggested by Basolo *et al.*[16]

Several attempts[41] have been made to correlate volumes and entropies of activation, mainly because both can be considered to include intrinsic and solvation contributions. A large amount of data on the activation enthalpies and entropies for the reactions studied here are available in the literature[16,42]. The actual comparison of these results does not reveal any correspondence between $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$, apart from the overall sign. Such trends as the significantly more negative volumes of activation for the k_1 path are not confirmed by the entropy data. This may be taken as a point in favour of an associative mechanism for the k_1 path (Table VI).

Although this study has provided more quantitative evidence for an associative mechanism for the k_2 path it has raised more questions as to the character of the k_1 path. The $\Delta V^{\ddagger}_{exp}$ (1) values presented here appear

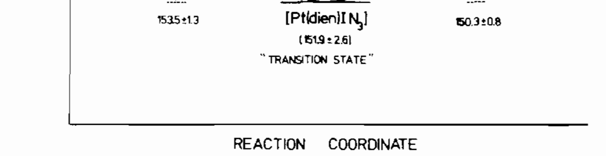

Figure 4. Volume profile diagram for the reaction: $[Pt(dien)I]^+ + N_3^- \rightleftharpoons [Pt(dien)N_3]^+ + I^-$.

TABLE VI. Enthalpies and Entropies of Activation for Substitution Processes:[a] $[Pt(dien)X]^+ + Y^{(-)} \rightarrow [Pt(dien)Y]^{2+,(+)} + X^-$

Substrate $[Pt(dien)X]^+$	Nucleophile Y	$\Delta H^{\ddagger}_1$ kcal mol^{-1}	$\Delta S^{\ddagger}_1$ e.u.	$\Delta H^{\ddagger}_2$ kcal mol^{-1}	$\Delta S^{\ddagger}_2$ e.u.	Ref.
$[Pt(dien)Br]^+$	N_3^-			15.5	–17	16
$[Pt(dien)Br]^+$	py			11.1	–32.5	8
$[Pt(dien)Br]^+$	NO_2^-	17.9	–15.9	17.1	–13.5	This Work
$[Pt(dien)Cl]^+$	N_3^-			16.0	–17	16
$[Pt(dien)I]^+$	N_3^-			15.5	–16	16
$[Pt(dien)N_3]^+$	I^-			14.5	–19	16
$[Pt(dien)N_3]^+$	SCN^-			14.0	–22	16
$[Pt(dien)Br]^+$	OH^-	19.5	–17			16

[a] The average error in $\Delta H^{\ddagger}$ is ± 1 kcal mol^{-1}, in $\Delta S^{\ddagger}$ ± 3 e.u.

to favour a dissociative mechanism for this path as do investigations[43,44] of the aquation reactions of $[PtA_2Cl_2]$ (A_2 = $2NH_3$ or en) and $[PdLCl]^+$ (L = dien, Et_4dien) in mixed aqueous solvents employing correlations with solvent dielectric constants or the Winstein–Grunwald parameter. A recent study[45] of the substitution reaction of an equilibrium mixture of $[PtCl_4]^{2-}$ and $[Pt(OH_2)Cl_3]^-$ with SCN^-, for which no k_1 path could be detected, also shows that the reactions of Pt(II) complexes are more complicated than commonly believed.

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