(18) N. D. Chikanov, A. P. Palkin, and M. K. Bizyaeva, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **6**, 355 (1963).
(19) R. Huglen, F. W. Poulsen, G. Mamantov, R. Marassi, and G. M. Begun, *Inorg. Nucl. Chem. Lett.*, **14**, 167 (1978).
(20) G. L. Carlson, *Spectrochim. Acta*, **19**, 1291 (1962).
(21) H. A. Andreasen and N. J. Bjerrum, *Inorg. Chem.*, **17**, 3605 (1978).
(22) W. Bues, F. Demiray, and W. Brockner, *Spectrochim. Acta, Part A*, **32a**, 1623 (1976).

Contribution from the Institute of Physical Chemistry,
University of Frankfurt, D 6000 Frankfurt am Main, West Germany

Volumes of Activation for the Substitution Reactions of *cis*- and *trans*-$[PtL_2(Cl)X]$ with Pyridine in Various Solvents

M. KOTOWSKI,[1] D. A. PALMER,* and H. KELM*

Received March 9, 1979

The pressure dependence of the second-order rate constant for the substitution by pyridine in *trans*-$[Pt(py)_2(Cl)(NO_2)]$ was measured in the solvents nitromethane, methanol, ethanol, and dichloromethane. The respective $\Delta V^{\ddagger}_{\text{exptl}}$ values were calculated to be −6.2 ± 0.4 at 10 °C, −8.8 ± 0.6 at 25 °C, −13.1 ± 0.8 at 25 °C, and −19.8 ± 1.7 $cm^3\ mol^{-1}$ at 25 °C. The $\Delta V^{\ddagger}_{\text{exptl}}$ values for the corresponding reactions of *cis*-$[Pt(py)_2(Cl)\ (NO_2)]$ and *trans*-$[Pt(PEt_3)_2Cl_2]$ in methanol at 25 °C are −5.5 ± 0.5 and −13.6 ± 0.8 $cm^3\ mol^{-1}$, respectively. These $\Delta V^{\ddagger}_{\text{exptl}}$'s were found to be only slightly temperature dependent. The activation parameters $\Delta H^{\ddagger}_2$ and $\Delta S^{\ddagger}_2$ were also determined for each reaction. The volume change associated with the partial formation of the Pt–py bond was estimated to be −4 ± 1 $cm^3\ mol^{-1}$. A qualitative explanation of the solvent dependence of $\Delta V^{\ddagger}_{\text{exptl}}$ is also given.

Introduction

The rate of substitution in d^8 square-planar complexes is known to obey a two-term rate law:[2–6]

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][\text{nucleophile}]$$

The relative importance of the two terms is governed by various factors such as the nucleophilicity of the nucleophile and solvent, the degree of steric crowding within the substrate, the size of the nucleophile and solvent molecules, and the solvation of the reactants and transition states. Naturally some of these properties are interrelated. However, in the title reactions the k_1 term is virtually negligible in the solvents chosen so that only the k_2 path will be discussed here in detail. The mechanism of substitution is generally acknowledged[2–6] as being associative, with both the entering nucleophile and leaving ligand tightly bound in the transition state.

The volume of activation, $\Delta V^{\ddagger}_{\text{exptl}}$, provides a very effective criterion for characterizing reaction mechanisms, especially when the possibility exists to extract the volume changes, $\Delta V^{\ddagger}_{\text{intr}}$, arising from the variations in bond lengths and angles.[7] In the majority of cases this requires a knowledge of the origin and nature of solute–solvent interactions involved in the development of the transition state and their respective volume contributions to $\Delta V^{\ddagger}_{\text{exptl}}$.

The intimate reaction mechanism, operating in the present system, implies that only one bond is formed (viz., that between the nucleophile and the platinum center) in the rate-determining step. Thus the basic concept of $\Delta V^{\ddagger}_{\text{exptl}}$ dictates that $\Delta V^{\ddagger}_{\text{intr}}$ must be negative for this process.[7,8] However, it would be extremely valuable to determine the absolute value associated with bond formation.

The Menschutkin reaction,[9–11] which is perhaps the most studied reaction in the field of high-pressure kinetics, provides a good precedent for investigating the solvent dependence of substitution into transition-metal complexes.

Experimental Section

Materials. *trans*-$[Pt(py)_2(Cl)(NO_2)]$ was prepared by dissolving equimolar quantities (10 mmol) of *trans*-$[Pt(py)_2Cl_2]$[12] and $AgClO_4\cdot H_2O$ in a minimum amount of Me_2SO. The mixture was stirred for 1 h at 40 °C and then cooled to room temperature and filtered. After *p*-toluenesulfonic acid was dissolved in the filtrate (1 mmol), 10 mmol of $NaNO_2$ was added. Crystallization of the white *trans*-$[Pt(py)_2(Cl)(NO_2)]$ product occurred immediately. The precipitate was washed with water and ethanol and repeatedly recrystallized from boiling chloroform. Anal. Calcd for $C_{10}H_{10}ClN_3O_2Pt$: C, 26.6; H, 2.3; N, 9.7; Cl, 8.8. Found: C, 27.5; H, 2.4; N, 9.7; Cl, 7.7.

cis-$[Pt(py)_2(Cl)(NO_2)]$ was prepared from the *cis*-dichloro-compound by the same procedure. Anal. Found: C, 26.3; H, 2.2; N, 9.5.

$[Pt(py)_3NO_2]ClO_4$ was prepared from *trans*-$[Pt(py)_2(Cl)(NO_2)]$ in methanol by a similar method. After the AgCl was filtered off, an excess of pyridine was added, and the resulting solution was stirred at 30 °C for 2 days. The solution was then evaporated to dryness on a rotary evaporator. The solid residue was dissolved in water and the solution filtered and again evaporated to dryness. The white precipitate was recrystallized twice from methanol. Anal. Calcd for $C_{15}H_{15}ClN_4O_6Pt$: C, 31.7; H, 2.6; N, 9.9. Found: C, 29.9; H, 2.7; N, 9.8.

trans-$[Pt(PEt_3)_2Cl_2]$ was prepared according to the method of Jensen.[13]

Pyridine was distilled a number of times as described previously.[14] All other salts used were of reagent grade.

The solvents (reagent grade or Uvasol product) used in the conductivity measurements were purified and dried according to standard procedures.[14,15] Purification was repeated until a constant, minimum conductivity was reached. The purity of each solvent was also monitored by density measurements.

Kinetic Measurements. Most of the reactions were followed conductometrically with a B-642 Autobalance Universal Bridge. A standard Pyrex-glass cell fitted with platinum electrodes was used for the kinetic runs at normal pressure. For measurements at higher pressures the conductivity cell shown in Figure 1 was constructed. Basically it consists of a Kel-F body, F, into which a flexible Teflon tube, H, is screwed. The cell is sealed at this joint, as well as at the remote end of the Teflon tube—where the cell can be filled by removing the Teflon screw, I— with Viton O-rings, G. The platinum electrodes, E, are fixed to the body of the cell by means of Teflon cones, C, through which tight-fitting platinum wire (0.8 mm) leads, D, pass; the Teflon cones are pressed in place by hollow cylindrical Kel-F screws, B. The cell itself fits into an aluminum holder, J, which in turn can be attached to the "plug", A, of the high-pressure bomb. The electrical leads consist of insulated copper wires which are sealed into the plug by a steel cone, K, seated in an epoxy-resin glue.[16] The plug is also fitted with a Viton O-ring. The bomb is enclosed in a cylindrical copper tubing jacket through which water is pumped from an external thermostat. The temperature inside the bomb can be controlled by

0020-1669/79/1318-2555$01.00/0

Table I. Rate Constants for the Substitution Reactions of $[PtL_2(Cl)X]$ with Pyridine as Function of Pyridine Concentration, Solvent, and Temperature

solvent	T, °C	[py], M	10^3k_{obsd}, s^{-1}	10^4k_1, s^{-1}	10^3k_2, M^{-1} s^{-1}
	trans-$[Pt(py)_2(Cl)(NO_2)] + py \rightarrow [Pt(py)_3NO_2]^+ + Cl^-$				
nitromethane	25.0	0.02	0.703	6 ± 1	5.8 ± 0.3
	25.0	0.05	0.832		
	25.0	0.10	1.35		
	25.0	0.20	1.86		
	25.0	0.30	2.20		
	25.0	0.40	2.96		
	25.0	0.50	3.60		
	33.6	0.05	1.44	9 ± 1	10.4 ± 0.5
	33.6	0.10	1.82		
	33.6	0.18	2.62		
	33.6	0.25	3.78		
	33.6	0.40	4.91		
	33.6	0.50	6.08		
	40.0	0.05	1.83	9 ± 1	18.1 ± 0.3
	40.0	0.10	2.57		
	40.0	0.20	4.52		
	40.0	0.30	6.24		
	40.0	0.38	7.75		
	44.6	0.05	2.36	6 ± 2	29.7 ± 1.2
	44.6	0.10	3.30		
	44.6	0.15	5.02		
	44.6	0.20	6.48		
	44.6	0.30	9.63		
methanol	29.8	0.01	0.132	0.7 ± 0.6	7.35 ± 0.09
	29.8	0.025	0.268		
	29.8	0.10	0.826		
	29.8	0.15	1.18		
	29.8	0.25	1.86		
	29.8	0.32	2.45		
	35.0	0.01	0.257	1.4 ± 0.5	11.1 ± 0.3
	35.0	0.05	0.696		
	35.0	0.10	1.31		
	35.0	0.16	1.83		
	35.0	0.25	2.96		
	40.0	0.025	0.476	1.4 ± 0.3	14.2 ± 0.2
	40.0	0.05	0.497		
	40.0	0.10	1.54		
	40.0	0.15	2.27		
	40.0	0.20	3.00		
ethanol	20.6	0.10	0.404	−0.3 ± 0.3	4.1 ± 0.1
	20.6	0.20	0.759		
	20.6	0.30	1.20		
	20.6	0.40	1.65		
	20.6	0.50	2.01		
	30.2	0.01	0.100	0.4 ± 0.3	8.18 ± 0.02
	30.2	0.10	0.885		
	30.2	0.20	1.65		
	30.2	0.28	2.36		
	30.2	0.35	2.88		
ethanol	40.1	0.05	0.990	1.95 ± 0.05	16.4 ± 0.2
	40.1	0.10	1.85		
	40.1	0.15	2.68		
	40.1	0.20	3.50		
	40.1	0.25	4.20		
	40.1	0.30	5.15		
acetone	10.0	0.005	0.641	90 ± 70	99 ± 3
	10.0	0.015	1.48		
	10.0	0.020	2.10		
	10.0	0.025	2.50		
	10.0	0.030	3.04		
	10.0	0.035	3.61		
	15.5	0.0025	0.578	160 ± 20	170 ± 1
	15.5	0.010	1.89		
	15.5	0.015	2.75		
	15.5	0.020	3.61		
	15.5	0.025	4.44		
	20.6	0.001	0.481	3100 ± 100	240 ± 4
	20.6	0.005	1.58		
	20.6	0.010	2.68		
	20.6	0.015	3.58		
	20.6	0.020	5.05		

Table I (*Continued*)

solvent	T, °C	[py], M	10^3k_{obsd}, s^{-1}	10^4k_1, s^{-1}	10^3k_2, M^{-1} s^{-1}
dichloromethane	29.8	0.10	0.036	0.06 ± 0.01	0.150 ± 0.004
	29.8	1.00	0.131		
	29.8	2.00	0.313		
	29.8	3.00	0.453		
	29.8	4.00	0.060		
	36.9	1.07	0.435	0.3 ± 0.2	0.244 ± 0.007
	36.9	2.00	0.435		
	36.9	3.00	0.710		
	36.9	4.00	0.947		
	36.9	5.00	1.20		
	39.8	0.50	0.122	0.3 ± 0.1	0.315 ± 0.003
	39.8	1.00	0.296		
	39.8	2.00	0.580		
	39.8	3.00	0.909		
	39.8	4.00	1.24		
	39.8	5.00	1.54		
cis-$[Pt(py)_2(Cl)(NO_2)] + py \rightarrow [Pt(py)_3NO_2]^+ + Cl^-$					
methanol	25.0	0.05	0.017	0.12 ± 0.05	0.181 ± 0.005
	25.0	0.20	0.045		
	25.0	0.50	0.110		
	25.0	0.75	0.154		
	25.0	1.00	0.186		
	25.0	1.25	0.241		
	25.0	1.50	0.281		
	30.1	1.00	0.283		
	35.0	1.00	0.385		
	40.0	1.00	0.482		
trans-$[Pt(PEt_3)_2Cl_2] + py \rightarrow$ *trans*-$[Pt(PEt_3)_2(Cl)(py)]^+ + Cl^-$					
methanol	25.0	1.00	0.260		
	30.0	0.05	0.029	−0.1 ± 0.1	0.53 ± 0.02
	30.0	0.07	0.040		
	30.0	0.10	0.053		
	30.0	0.30	0.126		
	30.0	0.50	0.222		
	30.0	0.75	0.402		
	30.0	1.00	0.529		
	35.0	1.00	0.624		
	40.0	1.00	0.825		

Table II. Pressure Dependencies of the Pseudo-First-Order Rate Constants and Volumes of Activation for the Substitution Reactions $[PtL_2(Cl)X] + py \rightarrow [PtL_2(py)X]^+ + Cl^-$

				10^4k_{obsd}, s^{-1}							
				pressure, bar							
substrate	solvent	T, °C	[py], M	1	250	500	750	1000	1250	1500	$\Delta V^{\ddagger}_{exptl}$, cm^3 mol^{-1}
trans-$[Pt(py)_2(Cl)(NO_2)]$	methanol	10	0.30	7.06	7.73	8.88	10.1	11.7	12.9		−11.6 ± 0.3
	methanol	25	0.05	2.98	3.32	3.80	4.31	5.19	5.60	6.08	−12.2 ± 0.6
	methanol	25	0.10	6.42	7.19	7.94	8.63	9.92	11.7	12.8	−11.6 ± 0.6
	methanol	40	0.02	4.72	5.31	5.78	7.22	7.93	8.88		−12.0 ± 0.5
	methanol	40	0.03	6.12	6.90	7.50	8.88	10.6	12.1		−13.1 ± 0.6
	nitromethane	10	0.05	3.26	3.52	3.94	4.09	4.53	5.11	5.63	−8.3 ± 0.4
	nitromethane	10	0.10	5.36	6.04	6.50	7.43	8.25	8.81		−8.7 ± 0.3
	ethanol	25	0.01	1.36	1.78	2.00	2.42	2.63	3.25		−16.3 ± 0.8
	ethanol	25	0.02	2.02	2.46	2.87	3.55	3.92	5.02	4.95	−15.4 ± 0.7
	dichloromethane	25	1.00	1.21	1.63	1.93	2.44	3.09	3.85	4.62	−20.5 ± 0.4
	dichloromethane	25	3.00	3.81	5.20	7.32	9.25	12.8	13.7		−23.9 ± 1.1
cis-$[Pt(py)_2(Cl)(NO_2)]$	methanol	25	0.50	1.10	1.20	1.32	1.40	1.57	1.70	1.80	−8.3 ± 0.2
	methanol	25	1.00	1.86	2.12	2.21	2.61	2.64	3.10	3.21	−8.9 ± 0.5
trans-$[Pt(PEt_3)_2Cl_2]$	methanol	25	0.50	1.54	1.93	2.31	2.72	3.30	3.72	4.62	−16.6 ± 0.7
	methanol	25	1.00	2.44	3.04	3.37	3.83	5.03	5.77		−16.8 ± 0.8
	methanol	30	0.20[a]	1.59	2.26	2.84	4.16	5.72	7.05	8.25	−28.4 ± 1.0

[a] Br^- was used as a nucleophile instead of py.

this means to within ±0.1 °C. *n*-Heptane was used as the pressure-transmitting liquid. The conductivity cell[17] proved to be leak resistant up to 1.5 kbar, and no attempt was made to extend the pressure range further.

The reaction of *trans*-$[Pt(PEt_3)_2Cl_2]$ with bromide in methanol was followed on a Cary 15 spectrophotometer equipped with a high-pressure cell, the detailed design of which has been described previously.[18]

Pseudo-first-order conditions were maintained for each system by using at least a tenfold excess of nucleophile (within the concentration range 1×10^{-3}–5.0 M) compared to a complex concentration range of 5×10^{-5}–5×10^{-4} M. The pseudo-first-order rate constants k_{obsd} were calculated from the slopes of plots of $\ln (A_\infty - A_t)$ vs. time, where A_t and A_∞ represent the conductivities (absorbances) at time t and infinity, respectively. Except for the results for acetone, these plots were linear for at least 3 half-lives over a pressure range of 1–1500 bar. The values of k_{obsd} are given in Tables I and II as a function of temperature and pressure, respectively.

The volumes of activation were derived from a linear least-squares treatment of the $\ln k_{obsd}$ vs. pressure data.

Density Measurements. Density measurements of the pure solvents

Table III. Rates and Activation Parameters for the Substitution Reactions of $[PtL_2(Cl)X]$ with Pyridine in Different Solvents at 30 °C

substrate	solvent	10^3k_2, $M^{-1}\,s^{-1}$	$\Delta H^{\ddagger}_2$, kJ mol^{-1}	$\Delta S_2^{\ddagger}$,[e] J K^{-1} mol^{-1}	$\Delta V^{\ddagger}_{exptl}$,[f] cm^3 mol^{-1}
trans-$[Pt(py)_2(Cl)(NO_2)]$	CH_3NO_2	7.38 ± 0.08	55.6 ± 5.0	−75 ± 12	−6.2 ± 0.4[a]
	CH_3OH	7.35 ± 0.09	49.3 ± 0.8	−94 ± 3	−8.8 ± 0.6[b]
	C_2H_5OH	8.18 ± 0.02	51.8 ± 0.4	−88 ± 3	−13.1 ± 0.8[b]
	$(CH_3)_2CO$	457 ± 4[c]	54.8 ± 7.8	−43 ± 15	
	CH_2Cl_2	0.150 ± 0.001	55.2 ± 3.8	−110 ± 10	−19.8 ± 1.7[b]
cis-$[Pt(py)_2(Cl)(NO_2)]$	CH_3OH	0.28 ± 0.01	46.8 ± 3.8	−129 ± 10	−5.5 ± 0.5[b]
trans-$[Pt(PEt_3)_2Cl_2]$	CH_3OH	0.53 ± 0.02	53.9 ± 8.4	−100 ± 31	−13.6 ± 0.8[b]
	CH_3OH[d]	0.16 ± 0.01			−25.3 ± 0.8

[a] At 10 °C. [b] At 25 °C. [c] This value has been extrapolated to 30 °C. [d] In this reaction Br^- was the nucleophile rather than py. [e] These values were calculated from the corresponding k_2 values converted into mole fractions. [f] These values have been corrected for the compressibilities of the solvents.

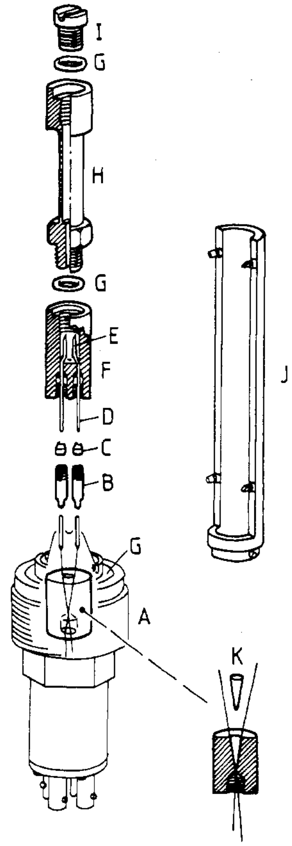

Figure 1. Exploded view of the high-pressure conductivity cell.

and their solutions were made with a digital densitometer DMA 02C, Anton Paar K.G. The temperature was controlled to within ±0.002 °C. The apparent molar volumes, ϕ_i, were determined from the well-known equation

$$\phi_i = \frac{M}{d_0} - \frac{10^3(d_i - d_0)}{c_i d_0}$$

where M is the molecular weight of the solute, d_0 and d_i are the densities of the solvent and solution, respectively, and c_i is the molar concentration of the solute. As ϕ_i did not appear to be concentration dependent within experimental error, the partial molar volume, $\bar{V}_i$, was assumed to be equal to the average value of Φ_i.

Results and Discussion

Chemical analysis of the products and potentiometric titration of the liberated chloride ion established that, with the pyridine concentrations used in this research, the title reaction proceeds to completion and may be written as

$$cis\text{- or } trans\text{-}[PtL_2(Cl)X] + py \rightarrow cis\text{- or } trans\text{-}[PtL_2(py)X]^+ + Cl^-$$

This applies to L = py or PEt_3 and $X^- = Cl^-$ or NO_2^- for the solvents nitromethane, methanol, ethanol, and dichloromethane.

In acetone, however, the reaction of *trans*-$[Pt(py)_2(Cl)(NO_2)]$ with pyridine reaches an equilibrium. From potentiometric titrations of the equilibrated reaction solutions at various [py], an equilibrium constant of (7.6 ± 0.8) × 10^{-4} was derived. This value was found to be independent of temperature within the range 10–25 °C. Comparable equilibria have also been reported for reactions involving *trans*-$[Pt(PEt_3)_2R(Cl)]$ and pyridine in ethanol[19] and methanol,[20] where R = phenyl, *o*-tolyl, and mesityl. The rate constants listed in Table I for acetone are, therefore, composite values of the forward and reverse rate constants. Furthermore, Ricevuto et al.[20] reported a nonlinearity of the pseudo-first-order kinetic plots for these reactions when followed conductometrically. We observed a similar behavior for the above reaction in acetone and conclude that this is the result of ion-pair formation between the product ions. It is well documented that most electrolytes are generally highly associated in acetone.[21,22] As a consequence, we believe that both equlibrium and ion-pairing effects are operative in acetone, and, therefore, no attempt was made to investigate the pressure dependence of the rate constants in this solvent. Ion-pair formation between $[Pt(py)_3NO_2]^+$ and Cl^- was not detected in CH_2Cl_2, despite its low dielectric constant.

From the data given in Table II it can be seen that the same volumes of activation are obtained, within experimental error, for a given reaction in the same solvent at different [py]. This substantiates earlier findings[2,3] on similar systems where $k_2[Y]$ was found to far exceed k_1. In addition, the $\Delta V^{\ddagger}_{exptl}$ values are insensitive to temperature within the limits shown in Table II so that all these values may be freely compared.

The rate constants and averaged activation parameters for all the reactions studied here are summarized in Table III. The rate constants for the reaction of *trans*-$[Pt(py)_2(Cl)(NO_2)]$ in the dipolar aprotic solvent CH_3NO_2 and the protic solvents CH_3OH and C_2H_5OH are similar, which is consistent with the findings of Parker,[23] who suggested that due to the basicity of the transition state in platinum chemistry, the various solvent effects tend to counteract each other. Nevertheless, in the remaining two dipolar aprotic solvents the reaction rate varies significantly, indicating that specific solute–solvent interactions are also important.

The conventional activation parameters, $\Delta H^{\ddagger}_2$ and $\Delta S^{\ddagger}_2$, show no marked variation with solvent or with the character of the substrate. The $\Delta H^{\ddagger}_2$ values are relatively small, compensating for the highly negative $\Delta S^{\ddagger}_2$ values, both of which have been considered in the past as characteristic of an associative reaction.[24] The negative entropies of activation were qualitatively ascribed to an increase in coordination number in the transition state, rather than being due to solvation effects.[24] However, no quantitative explanation of the magnitude of these values could be made; i.e., no cor-

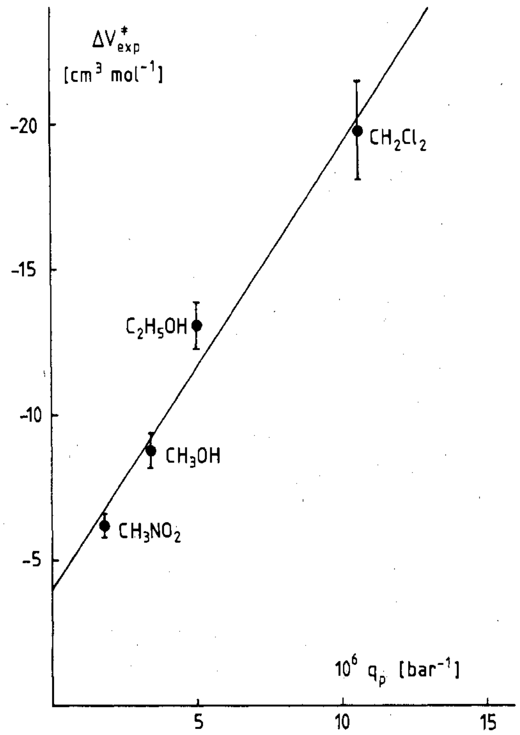

Figure 2. Plot of $\Delta V^{\ddagger}_{\mathrm{exptl}}$ (cm³ mol⁻¹) vs. the solvent electrostriction parameter, q_p (bar⁻¹).

relation between $\Delta S^{\ddagger}$ and the nature of the reactants, their charges, or the nature of the medium appears to exist. The trends shown in $\Delta V^{\ddagger}_{\mathrm{exptl}}$ (Table III) are, on the other hand, clear and very significant, especially when the greater experimental certainty of these values, as compared to the corresponding $\Delta S^{\ddagger}_2$ values, is taken into account. It is therefore apparent that the type of linear relationship between $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ postulated[25] for various reactions of octahedral complexes does not exist here and that, potentially, $\Delta V^{\ddagger}_{\mathrm{exptl}}$ contains more explicit information as to the intimate nature of the reaction mechanism and the associated interactions than does $\Delta S^{\ddagger}_2$.

The $\Delta V^{\ddagger}_{\mathrm{exptl}}$ values for the reaction of *trans*-$[Pt(py)_2(Cl)(NO_2)]$ with pyridine were measured in four solvents: CH_3NO_2, CH_3OH, C_2H_5OH, and CH_2Cl_2. It should be noted that the range of solvents amenable to this study was restricted mainly by the poor solubility of the complex in the more nonpolar solvents and in H_2O and by the occurrence of a stable solvent-containing complex in many of the polar solvents, such as Me_2SO and DMF. The difficulties encountered with acetone as the reaction medium have already been outlined. These restrictions notwithstanding, the data may be treated within the concept[7] that $\Delta V^{\ddagger}_{\mathrm{exptl}} = \Delta V^{\ddagger}_{\mathrm{intr}} + \Delta V^{\ddagger}_{\mathrm{solv}}$, where $\Delta V^{\ddagger}_{\mathrm{intr}}$ represents the mechanistically diagnostic term involving changes in bond lengths and angles (in this case, the formation of the Pt–py bond) during the activation step, while $\Delta V^{\ddagger}_{\mathrm{solv}}$ results from the concurrent changes in solvation. Given a parameter, $f(\mathrm{solv})$, which successfully describes $\Delta V^{\ddagger}_{\mathrm{solv}}$, a simple plot of $\Delta V^{\ddagger}_{\mathrm{exptl}}$ vs. $f(\mathrm{solv})$ will yield an intercept of $\Delta V^{\ddagger}_{\mathrm{intr}}$, i.e., the volume change in a hypothetical nonsolvating medium. The solvent parameter most widely used in organic chemistry[10,11] is obtained from the pressure derivative of the Kirkwood equation,[26] in other words, the parameter q_p which basically describes the solvent in terms of the pressure dependence of its dielectric constant ($\delta\epsilon/\delta P$). Although another "empirical" parameter—the pressure derivative of the solvatochromic shift of various zwitterions—has been used on several occasions,[27,28] this treatment was recently criticized.[29]

The plot of $\Delta V^{\ddagger}_{\mathrm{exptl}}$ vs. q_p $(=(3/(2\epsilon + 1)^2)(\delta\epsilon/\delta P)_T)$ is illustrated in Figure 2. The relationship is indeed linear with an intercept, $\Delta V^{\ddagger}_{\mathrm{intr}}$, of -4 ± 1 cm³ mol⁻¹ which, from the standpoint of the sign alone, is indicative of an associative process. The absolute value, corresponding to Pt–py bond formation, is slightly less than the general order of magnitude anticipated for bond formation of −5 to −10 cm³ mol⁻¹ for this type of reaction.[7]

An oversimplified way of calculating $\Delta V^{\ddagger}_{\mathrm{intr}}$ is to consider the volume swept out by the Pt(II) metal center and the nitrogen of the pyridine as they approach one another from a distance corresponding to the sum of their van der Waals radii[31] to a distance of closest approach, namely, the sum of their covalent radii.[32] This rather crude model results in a $\Delta V^{\ddagger}_{\mathrm{intr}}$ of −6.8 cm³ mol⁻¹ for complete bond formation in the transition state. Although it may be argued that the volume swept out should also include carbon atoms 2 and 6, this treatment at least provides a minimum value for $\Delta V^{\ddagger}_{\mathrm{intr}}$. Thus the Pt–py bond appears to be partially formed in these reactions, corresponding to an asynchronous process with the transition state lying between the reactants and the five-coordinate intermediate having the highest energy.

In the analogous reaction or $[Pt(dien)Br]^+$ with pyridine in water,[30] where the ordered structure of water and the effect of electrostriction exerted by the complex may be expected to minimize the solvation contributions, $\Delta V^{\ddagger}_{\mathrm{exptl}}$ was found to be -7.7 ± 0.5 cm³ mol⁻¹, which is in keeping with the above value of $\Delta V^{\ddagger}_{\mathrm{intr}}$.

The values of $\Delta V^{\ddagger}_{\mathrm{solv}}$ can now be estimated to be −2, −5, −9, and −16 cm³ mol⁻¹ for the reaction of *trans*-$[Pt(py)_2(Cl)(NO_2)]$ with pyridine in CH_3NO_2, CH_3OH, C_2H_5OH, and CH_2Cl_2, respectively. Thus, contrary to the conclusions drawn from the $\Delta S^{\ddagger}_2$ values, solvation does play an important role in these reactions. The compliance of these $\Delta V^{\ddagger}_{\mathrm{solv}}$ contributions with the Kirkwood correlation establishes that either a large change in polarity or charge formation occurs during the activation step. However, as both reactant species are uncharged and because the dipole moment of the trans complex must be small, possibly 2–3 D, it must be concluded that the transition state is highly polar. Consequently, assuming that the solvation effects stem from an increase in dipole–solvent interaction, the five-coordinate transition state must be a distorted trigonal bipyramid with the direction of dipole corresponding to the resultant of the NO_2–Pt–Cl angle within the trigonal plane.

The slope of the line in Figure 2 is given by $-(N_L\sum\mu_i^2/\sum r_i^3)$, where N_L is Loschmidt's number, $\sum\mu_i$ is the sum of the dipole moments of the transition state and reactants, and $\sum r_i$ is the sum of the corresponding radii. As a first approximation the bulk volume of the species $[Pt(py)_3(Cl)(NO_2)]$ can be estimated from molecular models to be 212 Å³, for which an average radius of 3.7 Å for a spherical body can be calculated. From the given slope and radius the dipole moment of the transition state can be determined at ca. 11 D. In keeping with this concept of the origin of $\Delta V^{\ddagger}_{\mathrm{solv}}$, the *cis*-$[Pt(py)_2(Cl)(NO_2)]$ complex can be expected to possess a large dipole moment (cf. dipole moment for *cis*-$[Pt(PEt_3)_2Cl_2]$ is 10.7 D[13]) so that the change in this property should be minimal. $\Delta V^{\ddagger}_{\mathrm{solv}}$ must, therefore, be small and certainly far less negative than that which was observed for the corresponding trans isomer. As shown in Table III, $\Delta V^{\ddagger}_{\mathrm{exptl}}$ in methanol is -5.5 ± 0.5 cm³ mol⁻¹, whereby the $\Delta V^{\ddagger}_{\mathrm{solv}}$ contribution is only 1.5 ± 1.5 cm³ mol⁻¹. The *trans*-$[Pt(PEt_3)_2Cl_2]$ complex, on the other hand, has no dipole moment,[13] implying that $\Delta V^{\ddagger}_{\mathrm{solv}}$ for the reaction with pyridine would be more negative than that for the reaction involving *trans*-$[Pt(py)_2(Cl)(NO_2)]$. $\Delta V^{\ddagger}_{\mathrm{exptl}}$ for the former is -13.6 ± 0.8 cm³ mol⁻¹; i.e., $\Delta V^{\ddagger}_{\mathrm{solv}} = -9.6 \pm 1.8$ cm³ mol⁻¹.

Perhaps the most surprising result listed in Table III is the value of $\Delta V^{\ddagger}_{\mathrm{exptl}}$ of -25.3 ± 1.0 cm³ mol⁻¹ for the reaction of *trans*-[$Pt(PEt_3)_2Cl_2$] with Br^- in methanol. This particular reaction was studied earlier by Taylor and Hathaway[33] in absolute methanol and methanol–water (60% water) for which $\Delta V^{\ddagger}_{\text{exptl}}$ values of −27 ± 3 and −28 ± 3 $cm^3\ mol^{-1}$, respectively, were reported, in obvious agreement with our datum. Although $\Delta V^{\ddagger}_{\text{intr}}$ for this reaction may be somewhat more negative than −4 $cm^3\ mol^{-1}$ because of the larger radius of the bromide ion, it must be assumed that $\Delta V^{\ddagger}_{\text{solv}}$ is mainly responsible for such a large negative $\Delta V^{\ddagger}_{\text{exptl}}$ value. We must conclude that in the partially formed Pt–Br bond the bulk of the negative charge resides on the bromide ligand thereby considerably enhancing the dipole moment of the activated species giving rise to a large negative $\Delta V^{\ddagger}_{\text{solv}}$ term. The loosely bound bromide presumably exerts an electrostrictive influence on the solvent comparable to that of the free ion. Otherwise, a reduction in the degree of electrostriction around the bromide would offset the large increase in the solvation of the substrate. This explanation of $\Delta V^{\ddagger}_{\text{exptl}}$ is preferred over the proposed argument[33] that the reaction mechanism involves simultaneous Pt–Br bond formation and strengthening of a Pt–MeOH bond. The latter postulate involves a six-coordinate transition state which, among other properties, would not show the same correlation with the Kirkwood treatment as was observed here; i.e., the formation of a Pt–py bond to give a six-coordinate transition state would not lead to a significant change in the dipole moment of the substrate or in any other property which could account for the solvent dependence of $\Delta V^{\ddagger}_{\text{exptl}}$.

A general feature of all these reactions is that $\Delta V^{\ddagger}_{\text{exptl}}$ is pressure independent at least up to 1.5 kbar. This is consistent with a process involving merely a contraction of the existing solvation layers rather than a complete rearrangement of the solvent as was the case in the Menschutkin reaction for example.[10,11]

Finally, although these Pt(II) complexes and their reaction products were generally too insoluble to allow accurate measurements of their partial molar volumes to be made, a value could be obtained for *trans*-[$Pt(py)_2(Cl)(NO_2)$] in dichloromethane of 196.8 ± 1.2 $cm^3\ mol^{-1}$ at 25 °C. Thus, with the measured partial molar volume of pyridine in CH_2Cl_2 at 25 °C of 80.8 ± 1.1 $cm^3\ mol^{-1}$ and the appropriate $\Delta V^{\ddagger}_{\text{exptl}}$ value, the partial molar volume of the transition state, [$Pt(py)_3(Cl)(NO_2)$], can be calculated[30] to be 255.4 ± 4.0 $cm^3\ mol^{-1}$. Naturally it would be of considerable interest to obtain the partial molar volume of the transition state in the remaining solvents as we have proposed that the solvation effects are virtually all to be seen in the transition state. At the present time, it can only be stated that the partial molar volume of pyridine varies only slightly with the solvent; e.g., in CH_3NO_2, CH_3OH, C_2H_5OH, and CH_2Cl_2 the respective volumes are 78.0 ± 0.5, 78.6 ± 0.5, 79.0 ± 0.5, and 80.8 ± 1.1 $cm^3\ mol^{-1}$.

Acknowledgment. The authors are grateful for the financial support of the Deutsche Forschungsgemeinschaft and the Max Buchner Forschungsstiftung.

Registry No. *trans*-[$Pt(py)_2(Cl)(NO_2)$], 70774-90-2; *cis*-[$Pt(py)_2(Cl)(NO_2)$], 70812-17-8; *trans*-[$Pt(PEt_3)_2Cl_2$], 15692-07-6; [$Pt(py)_3NO_2$]ClO_4, 70749-51-8; *trans*-[$Pt(py)_2Cl_2$], 14024-97-6; *cis*-[$Pt(py)_2Cl_2$], 15227-42-6.

References and Notes

(1) On leave from the Institute "Rudjer Boskovic", Zagreb, Yugoslavia.
(2) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1968; Chapter 5.
(3) Tobe, M. L. "Inorganic Reaction Mechanisms"; Nelson: London, 1972.
(4) Cattalini, L. "Reaction Mechanisms in Inorganic Chemistry"; Tobe, M. L., Ed.; University Park Press: Baltimore, MD, 1972; Chapter 7.
(5) Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974.
(6) Ibne-Rasa, K. M.; Edwards, J. O.; Rogers, J. L. *J. Solution Chem.* **1975**, *4*, 609.
(7) Hamann, S. D. "Physico-Chemical Effects of Pressure"; Butterworths: London, 1957; Chapter 9.
(8) Palmer, D. A.; Kelm, H. "High Pressure Chemistry"; Kelm, H., Ed.; Reidel: Dordrecht, 1978.
(9) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407.
(10) Hartmann, H.; Brauer, H.-D.; Kelm, H.; Rinck, G. *Z. Phys. Chem. (Frankfurt am Main)* **1968**, *61*, 53.
(11) Brauer, H.-D.; Kelm, H. *Z. Phys. Chem. (Frankfurt am Main)* **1971**, *76*, 53.
(12) Kauffman, G. B. *Inorg. Synth.* **1960**, *7*, 249.
(13) Jensen, K. A. *Z. Anorg. Allg. Chem.* **1936**, *229*, 225.
(14) "Organikum"; VEB Deutscher Verlag der Wissenschaften: Berlin, 1976.
(15) Mann, Ch. K. *Elektroanal. Chem.* **1969**, *3*, 57.
(16) Bloger, L. G.; Young, H. S. *Rev. Sci. Instrum.* **1962**, *33* 1007.
(17) The cell constant was determined over the pressure range 1–1500 bar and varied from 0.36 ± 0.02 to 0.58 ± 0.01. These values usually remained constant over a period of about 1 month with continuous use of the cell.
(18) Fleischmann, F. K.; Conze, E. G.; Stranks, D. R.; Kelm, H. *Rev. Sci. Instrum.* **1974**, *45*, 1427.
(19) Basolo, F.; Chatt, J.; Gray, H. B.; Pearson, R. G.; Shaw, B. L. *J. Chem. Soc.* **1961**, 2207.
(20) Ricevuto, V.; Romeo, R.; Trozzi, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1857.
(21) Reynolds, M. B.; Kraus, C. H. *J. Am. Chem. Soc.* **1948**, *70* 1709.
(22) Savedoff, L. G. *J. Am. Chem. Soc.* **1966**, *88*, 664.
(23) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1.
(24) Reference 2, p 405.
(25) Twigg, M. V. *Inorg. Chim. Acta* **1977**, *24*, L84.
(26) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351.
(27) Tamura, K.; Ogo, Y.; Imoto, T. *Bull Chem. Soc. Jpn.* **1973**, *46*, 2988.
(28) Tamura, K.; Imoto, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 369.
(29) von Jouanne, J.; Palmer, D. A.; Kelm, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 463.
(30) Palmer, D. A.; Kelm, H. *Inorg. Chim. Acta* **1976**, *19*, 117.
(31) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(32) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960; p 221.
(33) Taylor, T.; Hathaway, L. R. *Inorg. Chem.* **1969**, *8*, 2135.

Contribution from the Facultés Universitaires Notre-Dame de la Paix,
Laboratoire de Spectroscopie Electronique, B-5000 Namur, Belgique

ESCA and EPR Studies of Monomer, Dimer, and Polymer Iron Phthalocyanines: Involvements for the Electrocatalysis of O_2 Reduction

SERGE MAROIE, MICHEL SAVY, and JACQUES J. VERBIST*

Received January 26, 1979

Core- and valence-level X-ray photoemission spectra of three iron phthalocyanines (monomer, dimer, and polymer) are interpreted and related with the catalytic activity of these compounds in the electrochemical reduction of oxygen. EPR data are also reported for the three species. The iron spin and oxidation state, the electron delocalization in the organic ligand, and the covalent character of the Fe–O_2 bond are found to be important factors in the catalytic process.

I. Introduction

The questions raised by the reactivity with oxygen of phthalocyanine or hemoglobin structures are of interest to biochemistry as well as to electrochemistry concerned with air cathodes. In this way, Collman[1] reported that the free enthalpy change during oxygen adsorption on hemoglobin was 16 kcal

0020-1669/79/1318-2560$01.00/0