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Temperature and Pressure Dependencies of the Anation of Pd(MeEt$_4$dien)OH$_2^{2+}$ by Chloride Ion in Acidic Aqueous Solution. A Mixing System for Studying the Kinetics of Moderately Fast Reactions under Pressure

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The kinetics of anation of Pd(MeEt$_4$dien)OH$_2^{2+}$ by chloride ion were studied under the following conditions: $0{,}011 \leq [Cl^-] \leq 0{,}081$ M; $15 \leq$ temperature ≤ 35 °C; $1 \leq$ pressure ≤ 1000 bar; $[H^+] = 2.5 \times 10^{-3}$ M (HClO$_4$) and ionic strength 0,1 M (NaClO$_4$). The $[Cl^-]$ and temperature dependencies of the reaction rate were investigated at 500 bar. A high pressure rapid mixing system was used in these studies and is described in detail. Mixing of the pressurized reactant solutions can be accomplished within five seconds so that reactions with half-lives in the order of ten seconds can be measured accurately. The activation parameters for the title reaction are considered as evidence for an associative mechanism, possibly of the I_a type.

Introduction

The study of the kinetics of irreversible reactions in solution under pressure (up to *ca.* 1,5 kbar) has mainly been restricted to slow reactions with half-lives in the order of 10 minutes or longer. In such conventional studies the reagents are mixed and transferred to a high pressure cell, which is then pressurized. Further time must be allowed for temperature and pressure equilibration before the reaction can be effectively monitored. Recently Heremans and co-workers [1] reported the construction of a high pressure stopped-flow apparatus in which fast reactions with half-lives ≥ 20 msec can be studied under pressure. In addition, the T-jump technique has been used successfully in high pressure investigations of reactions in the μsec range [2–4]. We have developed a simple method for studying the effect of pressure on moderately fast reactions with half-lives of ten seconds or more.

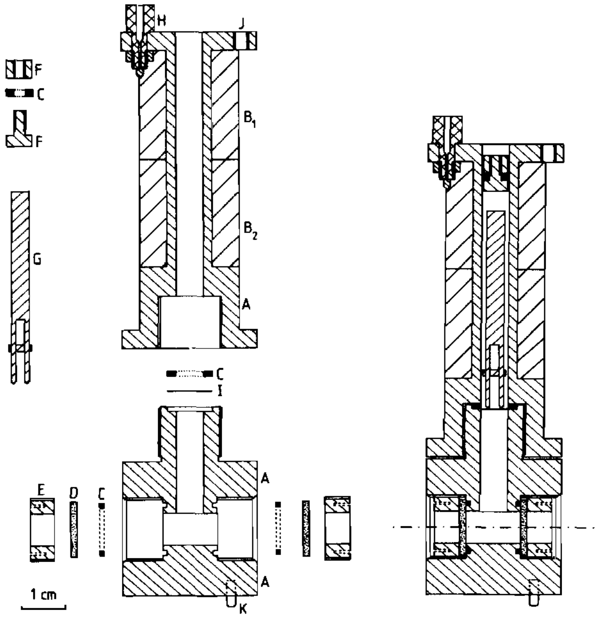

Figure 1. Detail drawing of the rapid mixing system. A, Kel F body; B, 2 coils; C, Teflon rings; D, window; E, Kel F ring screw; F, Kel F adjustable piston; G, soft iron mixing bar; H, electrical connecter; I, membrane; J, port for inserting rod; K, positioning pin.

The anation reactions of substituted diethylenetriamine palladium(II) complexes [5] have half-lives in the seconds range and thus require such a rapid mixing device to study their behaviour under high pressure. The anation of Pd(MeEt$_4$dien)OH$_2^{2+}$ by chloride ion (MeEt$_4$dien = 4-methyl-1,1,7,7-tetraethyldiethylenetriamine) was chosen since the rate of this reaction [6, 7] at convenient temperatures allows the effectiveness of the mixing system to be fully tested. It can therefore be regarded as the first of a series of studies in which the effect of pressure on such moderately fast reactions is investigated. Some details of the high pressure rapid mixing system will be emphasized.

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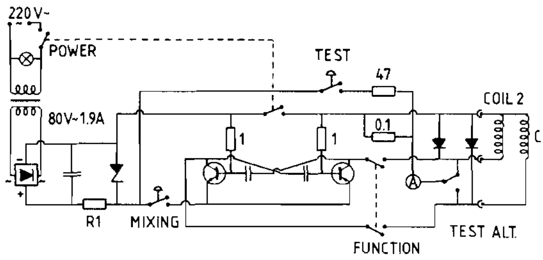

Figure 2. Circuit diagram of the control unit. Resistance is quoted in kΩ unless otherwise specified. Components: R1-82Ω, 50 W, rectifier – B125 C350, capacitors – 100μF, Zener diode – ITT ZL22 (on cooling surface), transistors – 2N2061 A, diodes – 1N4007, Amp. meter – 50 μA, coils – *ca.* 2000 windings, *ca.* 110Ω.

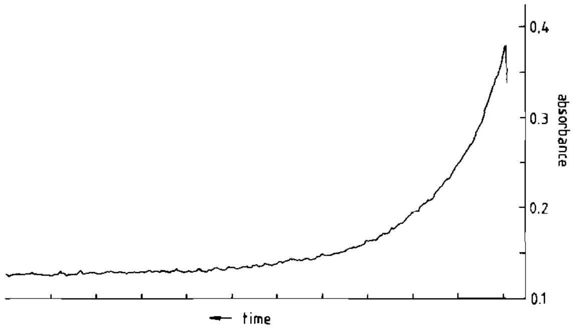

Figure 3. A typical absorbance *versus* time plot obtained with the rapid mixing system. Temp. = 34.5 °C, pressure = 500 bar, $[Cl^-]$ = 0.011 *M*, ionic strength = 0.1 *M*, wavelength = 325 nm, [complex] = 10^{-3} *M*, time scale = 10 sec/div.

Experimental

Description of the High Pressure Rapid Mixing System

A detailed drawing of the mixing device is given in Fig. 1. It consists of two main sections A, made from Kel F, which are separated by a membrane I, usually aluminium foil. The lower section is constructed in such a way that the light beam of a spectrophotometer, in our case a Zeiss DMR 10, can pass through the cell. Around the upper section, which contains the mixing bar G, are wound two separate electric coils B. The reagents are screened from the surrounding pressurizing medium (water) by the adjustable piston F, which also acts as a pressure transmitting device. On filling the mixing system care should be taken to omit air bubbles. The volumes of the two compartments are equal (1.25 cm^3).

With the aid of a rod screwed into port J, the filled mixing system is lowered into a thermostatted high pressure cell, the construction of which has been reported previously [8]. It is seated into position within the cell as determined by the pin K. Insulated electrical leads, connected to the three contacts H, are fed through the top of the high pressure cell by means of insulated conical connectors. The pressurized system is allowed to reach temperature and pressure equilibrium for 20 to 30 minutes prior to mixing.

The circuit diagram of the control unit is outlined in Fig. 2. With the power on, a direct current of 24 V flows through the unit. The electrical contact to coils B_1 and B_2 within the high pressure vessel, can be checked when the "Function" switch is in the "Test" position. When in the "Mixing" position, the multivibrator is activated by the press-switch "Mixing" inducing a periodically changing magnetic field in the mixing system. The soft iron bar, G, is oscillated at ca. 7 Hz thereby forcing its way through the membrane and mixing the reagent solutions. When the power is switched off, the mixing bar comes to rest in the lower section of the system. The reaction may then be followed spectrophotometrically as only a small fraction of the incident light is blocked by the mixing bar.

A typical absorbance *versus* time plot is illustrated in Fig. 3. Adequate mixing is obtained within 5 to 7 seconds. Calculations show that when mixing is carried out for 10 seconds, a maximum increase in temperature of 0.05 °C around the electric coils can be expected.

Materials

The complex $[Pd(MeEt_4dien)Cl]PF_6$ was prepared according to standard procedures [9]. Analyses were in agreement with theoretical values and the absorption spectra agreed with that reported in the literature [9]. The complex, $Pd(MeEt_4dien)OH_2^{2+}$, was obtained in solution by converting the chloro complex to the corresponding hydroxo complex in 0.01 *M* NaOH at *ca.* 50 °C for one hour. The pH of this stock solution was adjusted to 10 (the pK_a of the aquo species is 7.5 [5, 6]. The kinetic runs were initiated by mixing this solution with acidic $NaCl/NaClO_4$ mixtures resulting in a final acid concentration of 2.5 × 10^{-3} *M*. The complex concentration was kept constant at 1 × 10^{-3} *M*, while the chloride concentration was varied over the range 0.011 to 0.081 *M*. The ionic strength was adjusted to 0.1 *M* using $NaClO_4$. Concentrations quoted are those obtained after mixing.

Kinetic Experiments

According to the visible absorption spectra of $Pd(MeEt_4dien)OH_2^{2+}$ and $Pd(MeEt_4dien)Cl^+$ [5, 6, 9], the anation reaction was studied at 325 nm where a substantial decrease in absorbance is observed. Plots of $\ln(A_t - A_\infty)$ *versus* t, where A_t and A_∞ are the absorbances at time t and infinity, respectively, were linear for at least three to four half-lives and the observed first order rate constant was calculated in the usual way. All reported rate constants

TABLE I Observed Rate Constant as a Function of [Cl^-] at 15 °C and 500 bar

[Cl^-] M	$k_1 \times 10^2$ sec^{-1}	k_2 M^{-1} sec^{-1}
0 011	1 00 ± 0 06	0 914 ± 0 063
0 021	2 14 ± 0 12	1 02 ± 0 06
0 041	3 88 ± 0 15	0 945 ± 0 037
0 061	6 05 ± 0 26	0 992 ± 0 043
0 081	8 22 ± 1 61	1 01 ± 0 20
	Average	0 976 ± 0 045

represent the mean value of at least two kinetic runs

Results

The chloride concentration dependence of the observed pseudo first order rate constant k_1 was studied at 500 bar and the results are summarized in Table I The data obeys the equation $k_1 = k_2 [Cl^-]$ The temperature and pressure dependencies of k_1 are reported in Table II The second order rate constant k_2 was calculated from $k_1/[Cl^-]$ and corrected for the compressibility [10] of the solvent (H_2O) $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated from the temperature dependence of $k_2^{corrected}$ at 500 bar The plot of $\ln k_2^{corrected}$ *versus* pressure was linear within experimental error limits and the activation volume, $\Delta V^{\neq}$, was calculated from the slope of this line

Discussion

The results in Tables I and II show that a high reproducibility was obtained with the developed mixing system Typical mixing times were between 5 and 7 seconds and reactions with half-lives of 10 seconds or longer could be studied very accurately Reactions with half-lives in the order of the mixing time could also be studied, however, the error then became meaningful (see last entry in Table I)

From the data in Table I it is concluded that, within the experimental error limits, no significant intercept is obtained for the plot of k_1 *versus* [Cl^-] This is in accord with results of similar investigations recently performed in this laboratory [6, 7, 11] and elsewhere [5], but in disagreement with that reported [12] for anation reactions of $Pt(dien)OH_2^{2+}$ The values of k_2 for various similar systems are summarized in Table III It can be seen that for the chloride anation of $Pd(MeEt_4dien)OH_2^{2+}$ our value for k_2 of 0 77 M^{-1} sec^{-1} is in good agreement with the reported value [7] for this reaction measured under second order conditions using conventional techniques The smaller value of k_2 for anation reactions of $Pd(MeEt_4dien)OH_2^{2+}$ when compared to the corresponding reactions of $Pd(Et_4dien)OH_2^{2+}$, is ascribed to additional steric hindrance caused by the 4-methyl group on the dien ligand

The $\Delta H^{\neq}$ value in Table II complies with values generally reported for substitution reactions of Pd(II) and Pt(II) dien complexes [6, 7, 13, 14] complexes The latter reactions, and those referred to in Table III, are all believed to proceed via associative, A, or associative interchange, I_a, mechanisms depending on the extent of steric crowding at the reaction center The virtually zero value for $\Delta S^{\neq}$ in Table II emphasizes the I_a character of the sterically hindered anation reaction studied

On the basis of an I_a mechanism one would anticipate some curvature in the k_1 *versus* [Cl^-] plot resulting from a precursor ion-pair, formation equilibrium As no curvature was observed within experimental error, we must conclude that the ion-pair formation constant is relatively small This phenome-

TABLE II Observed Rate Constant as a Function of Temperature and Pressure[a]

Temp 0 °C	Pressure bar	$k_1 \times 10^2$ sec^{-1}	k_2 M^{-1} sec^{-1}	$k_2^{corrected}$ M^{-1} sec^{-1}	Activation Parameter
15	500	1 00 ± 0 06	0 914 ± 0 063	0 894 ± 0 062	
20 3	500	1 60 ± 0 05	1 45 ± 0 04	1 42 ± 0 04	$\Delta H^{\neq}$ = 70 2 ± 1 7 kJ mol^{-1}
25 7	500	2 95 ± 0 01	2 68 ± 0 01	2 62 ± 0 01	
29 8	500	4 21 ± 0 00	3 83 ± 0 00	3 74 ± 0 00	$\Delta S^{\neq}$ = −1 2 ± 5 4 J K^{-1} mol^{-1}
34 5	500	6 84 ± 0 56	6 22 ± 0 51	6 08 ± 0 50	
15	1	0 846 ± 0 019	0 769 ± 0 017	0 769 ± 0 017	
15	250	0 954 ± 0 040	0 867 ± 0 036	0 857 ± 0 036	
15	500	1 00 ± 0 06	0 914 ± 0 063	0 894 ± 0 062	$\Delta V^{\neq}$ = −7 7 ± 0 5 cm^3 mol^{-1}
15	750	1 11 ± 0 01	1 01 ± 0 01	0 981 ± 0 013	
15	1000	1 23 ± 0 15	1 12 ± 0 14	1 07 ± 0 13	

[a] [Cl^-] = 0 011 M

TABLE III. A Comparison of the Values of k_2 at Atmospheric Pressure for Anation Reactions of Pt(II) and Pd(II) Dien Complexes.

Complex Ion	Entering Ligand	Ionic Strength *M*	k_2[a] M^{-1} sec^{-1}	Reference
$Pd(Et_4dien)OH_2^{2+}$	Cl^-	0.02	7.36(25°)	5
	Br^-	0.02	4.18(25°)	5
	I^-	0.02	5.42(25°)	5
	SCN^-	0.5	9.36(10°)	6
$Pd(MeEt_4dien)OH_2^{2+}$	Cl^-	0.05	0.89(15°)	7
	Cl^-	0.1	0.77(15°)	This work
	Br^-	0.05	0.86(15°)	7
	I^-	0.05	1.37(15°)	7
	SCN^-	0.5	5.02(10°)	6
$Pt(dien)OH_2^{2+}$	Cl^-	–	1.0 (25°)	12
	NO_2^-	–	0.56(25°)	12

[a] Temperature is quoted in brackets.

non has been observed previously for analogous Pd(II) complexes [5].

For an associative anation process involving oppositely charged ions, two contributions to the observed $\Delta V^{\neq}$ may be expected. The accompanying partial neutralization of charge, which must result in a relaxation of the surrounding solvation shells, leads to a positive contribution to $\Delta V^{\neq}$, whereas bond making manifests itself in a negative volume change. Conversely stretching of the $Pd–OH_2$ bond does not involve significant changes in electrostriction and must result in a positive $\Delta V^{\neq}$ value. Clearly the measured value for $\Delta V^{\neq}$ of –7.7 ± 0.5 cm^3 mol^{-1} allows us to immediately reject the possibility of a basically dissociative mechanism.

Within the context of an associative type mechanism, Le Noble [15] has shown that sterically hindered reactions result in larger negative contributions to $\Delta V^{\neq}$ stemming from bond making. Thus it is likely that these intrinsic effects outweigh volume changes due to electrostriction effects. The magnitude of the reported $\Delta V^{\neq}$ is in close agreement with that found for similar substitution reactions [6, 7, 13] for which exist strong arguments in favour of associative type mechanisms.

Finally, using the recently determined value [7] of $\Delta V^{\neq}$ for the aquation reaction of $Pd(MeEt_4dien)Cl^+$ of –17.5 ± 0.3 cm^3 mol^{-1}, as well as the partial molar volume of this substrate [7], a volume profile for the entire system may be constructed, as shown in Fig. 4. This profile leads to a calculated value of 240.7 ± 1.7 cm^3 mol^{-1} for the partial molar volume of $Pd(MeEt_4dien)OH_2^{2+}$ which could not be measured directly [7]. From a comparison of the partial molar volumes for a series of $Pd(MeEt_4dien)X^+$ and $Pd(Et_4dien)X^+$ complex ions [7], we conclude that the "4-CH_3 group" on the dien ligand contributes *ca.* 13 cm^3 mol^{-1} to the partial molar volume. Høiland *et al.* [18] quote a value of 16 cm^3 mol^{-1} for the addition of a CH_2 group to an organic chain molecule in aqueous solution. From a combination of these two values with that calculated from the volume profile for $Pd(MeEt_4dien)OH_2^{2+}$, we estimate a value of between 228 ± 2 and 225 ± 2 cm^3 mol^{-1} for the volume of $Pd(Et_4dien)OH_2^{2+}$. These values are indeed very close to that reported [13] for $Pd(Et_4dien)NH_3^{2+}$, viz. 225.1 ± 0.7 cm^3 mol^{-1}, and demonstrate the validity of the volume profile.

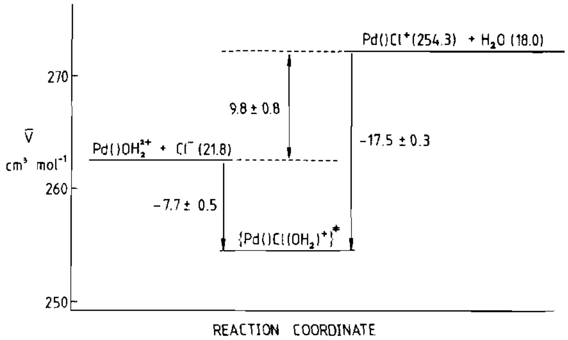

Figure 4. Volume profile diagram for the reaction: $Pd(MeEt_4dien)OH_2^{2+} + Cl^- \rightleftarrows Pd(MeEt_4dien)Cl^+ + H_2O$ ( ) = $MeEt_4$-dien.

The fact that the transition state is more compact than either the reactants or products signifies further that the reaction is associative in character. On the basis of one reaction, however, it is not possible to distinguish with any certainty between an A and I_a mechanism. Thus it is our intention to investigate a series of such reversible reactions using the newly developed *in situ* mixing device for a variety of nucleophiles, in order to establish quantitatively the exact associative character of the mechanism operating in reactions of sterically hindered Pd(II) complexes.

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References

1 K. Heremans, J. Snauwaert and J. Rijkenberg, *Proc. 6th AIRAPT High Pressure Conf.*, Boulder (U.S.A.) (1977).
2 E. F. Caldin, J. E. Crooks and B. H. Robinson, *J. Phys. E, 4,* 165 (1971).
3 A. D. Yu, M. D. Waissbluth and R. A. Greiger, *Rev. Sci. Instrum., 44,* 1390 (1373).
4 A. Jost, *Ber. Bunsenges. physik. Chem., 79,* 850 (1975).
5 J. B. Goddard and F. Basolo, *Inorg. Chem., 7,* 936 (1968).
6 M. Mares, *Ph.D. Thesis,* Frankfurt/Main (1977).
7 M. Kotowski, *Ph.D. Thesis,* Frankfurt/Main (1977).
8 F. K. Fleischmann, E. G. Conze, D. R. Stranks and H. Kelm, *Rev. Sci. Instrum., 45,* 1427 (1974).
9 W. H. Baddley and F. Basolo, *J. Am. Chem. Soc., 88,* 2944 (1966).
10 T. W. Swaddle and P. C. Kong, *Can. J. Chem., 48,* 3223 (1970).
11 D. A. Palmer and H. Kelm, unpublished results.
12 H. B. Gray and R. J. Olcott, *Inorg. Chem., 1,* 484 (1962).
13 D. A. Palmer and H. Kelm, *Inorg. Chim. Acta, 14,* L27 (1975).
14 D. A. Palmer and H. Kelm, *Inorg. Chim. Acta, 19,* 117 (1976).
15 W. J. Le Noble and T. Asano, *J. Am. Chem. Soc., 97,* 1778 (1975).
16 H. Høiland and E. Vikingstad, *Acta Chem. Scand., A30,* 182 (1976).