by this mechanism with certain aquometal ions while failing to do so with others. This aspect is currently being investigated.

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The Volume of Activation in the Acid Hydrolysis of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$

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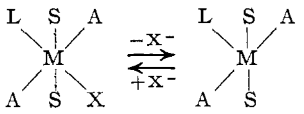
The volumes of activation for the acid hydrolysis of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$ have been determined by measurement of the effect of hydrostatic pressure on the reaction rates. The values of ΔV^* are, respectively, -17 and -14 ml/mole with an error of approximately 2 ml in each. The effect of pressure on the equilibrium constants is too small for reliable measurement and the volumes of reaction are therefore nearly zero. It is inferred that, in the transition state, the formation of two Pt–OH_2 bonds is nearly complete, and the Pt–Cl bond is nearly intact.

Introduction

In recent years the measurement of activation volume has proved to be a useful tool in the study of reaction mechanisms.[1] The aquation reactions of platinum(II) complexes appear to be well suited to investigation by this method because their reaction rates lie in a convenient range, accurate kinetic and equilibrium data at ordinary pressure are already recorded, and a variety of types of evidence support the postulation of a mechanistic pathway.[2,3]

It has been shown in previous studies that the substitution reactions of platinum(II) complexes can be divided into two classes. One class includes the reactions of the poor nucleophilic reagents whose rates are first order in complex, zero order in reagent, and approximately the same for all substitutions on a given complex. The other class includes the good nucleophilic reagents whose rates are higher than those of the first and are first order in both complex and reagent. It is believed that the square-planar complexes of Pt(II) possess, in addition to the four strong bonds to ligands in the plane of the complex, two weak bonds to solvent molecules above and below the plane of the complex. In the mechanistic path postulated for the first class of reactions a five-coordinated intermediate (resembling either a square pyramid or trigonal bipyramid) is formed when two solvent molecules move in closer to the complex and help displace the leaving group, *viz.*[2,3]



(1)

Since the theory of platinum(II) substitution reactions imputes such an important role to the solvent in the rate-determining step, it seemed desirable to measure first the volume of activation in the hydrolysis of one of the complexes. Determination of kinetic order is unable to reveal any participation of solvent in the formation of the activated complex, but measurement of activation volume has revealed the bimolecular nature of several hydrolysis reactions of organic substrates.[4]

The volume of activation can be attributed either to a change in the volume of the molecules in the activated state or in the volume of the solvent provided a change in the electrical polarization accompanies the formation of the activated complex.[1] The acid hydrolysis (first aquation) of $Pt(NH_3)Cl_3^-$ which is described by the reaction

$$Pt(NH_3)Cl_3^- + H_2O \underset{k_1}{\overset{k_{-1}}{\leftrightarrows}} Pt(NH_3)Cl_2(H_2O) + Cl^- \qquad (2)$$

seemed best suited for a volume of activation study since the charge type of reactant and product ions is the same, and consequently the volume change due to solvent effects should be negligible. In the acid hydrolysis of $PtCl_4^{2-}$ described by the reaction

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[1] (a) S. D. Hamann, "High Pressure Physics and Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1963, pp 163–205; (b) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworth and Co. Ltd., London, 1957; (c) S. D. Hamann, *Ann. Rev. Phys. Chem.*, **15**, 349 (1964); (d) E. Whalley, *Advan. Phys. Org. Chem.*, **2**, 93 (1964).

[2] R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960).

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 186–190.

[4] (a) J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, **55**, 815 (1959); (b) B. T. Baliga and E. Whalley, *Can. J. Chem.*, **42**, 1019 (1964).

$$PtCl_4^{2-} + H_2O \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} PtCl_3(H_2O)^- + Cl^- \tag{3}$$

the formation of two single negative ions from one double negative ion involves the dispersal of charge and a possible volume change due to solvent effects. It is therefore essential in this case and highly desirable in the first case to measure the over-all volume of reaction.

Experimental Section

Materials.—K_2PtCl_4 was prepared by the reduction of K_2PtCl_6 with hydrazine sulfate.[5] The product was washed with methanol and ether. *Anal.* Calcd for K_2PtCl_4: Pt, 47.0; Cl, 34.2. Found: Pt, 46.4; Cl, 33.7.

$KPt(NH_3)Cl_3$ was prepared from K_2PtCl_4 according to a procedure reported elsewhere.[6] *Anal.* Calcd forK $Pt(NH_3)Cl_3$: Pt, 54.6; Cl, 29.8. Found: Pt, 54.4; Cl, 29.8.

Platinum was determined gravimetrically by reduction to the metal with hydrazine sulfate. The analysis for chloride as AgCl was made gravimetrically.

Equipment.—pH measurements were made with a Beckman Model 96 pH meter calibrated with standard buffer solution at pH 9. The high-pressure equipment consists of a Micro Series reactor from the American Instrument Co. Inc., Superpressure Division, Silver Springs, Md., and a hand pump and Bourdon gauge from Autoclave Engineering Inc., Erie, Pa. The high-pressure bomb was thermostated in an oil bath, and the temperature was controlled to ±0.2°.

Rate Measurements.—To prepare each 0.0166 *M* solution a sample of K_2PtCl_4 or $KPt(NH_3)Cl_3$ was weighed in a small test tube and 2 ml of freshly distilled water was added. The tube was filled to the brim with carbon tetrachloride which served as a liquid seal between the solution and the pressurizing fluid, and the tube was inverted inside a larger test tube which was then filled with carbon tetrachloride. Preliminary experiments showed that no acid titer was produced by carbon tetrachloride in blank runs at 1 atm or high pressure. Titration curves were obtained for both reactions in order to locate the end points. Each solution was quickly titrated to the end point with standard 0.01 *M* NaOH, and the number of equivalents of acid was calculated.

Partial Molar Volumes.—Densities of aqueous solutions of sodium maleate and sodium malate were measured to an accuracy of 1 part in 10,000 with a pycnometer, and apparent molar volumes were obtained from the equation

$$\phi(V) = \frac{1000(d_0 - d)}{cd_0} - \frac{M}{d_0} \tag{4}$$

in which c is the concentration of solute, d_0 the density of the solvent, d the density of the solution, and M the molecular weight of the solute. The partial molar volumes of sodium maleate (46.3 ml) and sodium malate (56.0 ml) were found by plotting the apparent molar volumes at 1.0, 0.4, and 0.1 *M* against $c^{1/2}$ and extrapolating to zero concentration.

Treatment of Data.—The course of acid hydrolysis (first aquation) of tetrachloroplatinate(II) ion and trichloroammineplatinate(II) ion was followed by titration of the acidic products $PtCl_3(H_2O)^-$ and $Pt(NH_3)Cl_2(H_2O)$, respectively, against standard alkali with a pH meter as described in earlier work.[6-8]

The equilibrium constants and the forward rate constants were measured first at 1 atm in order to check the recorded values. For a 0.0166 *M* K_2PtCl_4 solution with no added electrolyte at 25° we find that the hydrolysis reaction is 72 ± 2% complete at equilibrium ($K_c = 0.030 \pm 0.003$ *M*) and the value of the forward rate constant is 4.2×10^{-5} sec^{-1}. The recorded values are 72.5% ($K_c = 0.031$ *M*) for a 0.0163 *M* solution at $\mu = 0$,[6] and 3.9×10^{-5} sec^{-1} for a 0.0166 *M* solution at $\mu = 0.318$,[8] respectively. For a 0.0166 *M* $KPt(NH_3)Cl_3$ solution with no added electrolyte at 26° we find that the equilibrium constant is 0.018 ± 0.002 *M*, and the forward rate constant is 3.9×10^{-5} sec^{-1}. For a 0.0166 *M* $KPt(NH_3)Cl_3$ solution at $\mu = 0.318$, the recorded value of the equilibrium constant is 0.015 *M* at 26° and the forward constant is 3.6×10^{-5} sec^{-1} at 25° and 5.8×10^{-5} sec^{-1} at 30°.[5]

In the previous studies[6,8] the following differential equation was used

$$dx/dt = k_1(a - x) - k_{-1}(x)(b + x) \tag{5}$$

The solution of eq 5 is

$$\ln \left\{ \frac{(x - x_\infty)[x_0 - x_\infty + \sqrt{(b + K)^2 + 4Ka}]}{(x_0 - x_\infty)[x - x_\infty + \sqrt{(b + K)^2 + 4Ka}]} \right\} = k_{-1}t\sqrt{(b + K)^2 + 4Ka} \tag{6}$$

where K is the equilibrium constant, a is the original concentration of K_2PtCl_4 or $KPt(NH_3)Cl_3$, b is the original concentration of Cl^-, x is the concentration of $PtCl_3(H_2O)^-$ or $Pt(NH_3)Cl_2(H_2O)$ at time t, x_∞ is the concentration of $PtCl_3(H_2O)^-$ or $Pt(NH_3)Cl_2(H_2O)$ at equilibrium, and x_0 is the value of x at $t = 0$. It seemed possible that a simpler expression involving only the forward reaction could be used if the measurements were made before hydrolysis had proceeded far enough for the back reaction to be important. The rate would then be expressible by

$$dx/dt = k_1(a - x) \tag{7}$$

and the solution would be

$$\ln [a/(a - x)] = k_1t \tag{8}$$

when $x = 0$ at $t = 0$.

The plot of $\ln [a/(a - x)]$ *vs.* time at 1 atm gave a straight line as far as 45% hydrolysis of $PtCl_4^{2-}$. Measurement of the equilibrium constant for both $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$ showed that an increase in pressure did not greatly affect the position of equilibrium. At 1 and 1200 atm, K_c for the former has values of 0.030 ± 0.003 and 0.024 ± 0.003 *M*, respectively. This difference corresponds to a volume change of +4 ml. For the latter the figures are 0.018 ± 0.002 and 0.019 ± 0.002. Since the objective of this research was to measure the variation in the rate constant with pressure rather than find its absolute value, it seemed desirable to determine all rate constants at the same stage of reaction so that systematic errors would be cancelled in the ratio of rates at ordinary and high pressure. It was decided, therefore, to analyze the reaction mixtures at approximately 45% conversion and calculate the rate constant from eq 8. In order to compare our results with the reported rate constants at atmospheric pressure, values of k were also calculated from eq 6 and were about 5% higher than those from eq 8. Both equations gave the same value of k_p/k_1 within 0.01% for all kinetic data.

A correction was made in each high-pressure rate constant for the fraction of reaction time at atmospheric pressure while the high-pressure apparatus was either being closed or opened. For example, if the reaction proceeded at atmospheric pressure 5% of the total reaction time, the apparent acceleration k_p'/k_1 (where k_p' is the apparent high-pressure rate constant and k_1 the constant at 1 atm) was multiplied by 1.05 to find the true acceleration. The true high-pressure rate constant, k_p, and $\ln (k_p/k_1)$ were then calculated from the corrected acceleration.

The volume of activation was determined graphically using a plot of $\ln (k_p/k_1)$ against pressure according to the expression

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^*}{RT} \tag{9}$$

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[5] Kh. I. Gil'dengershel and G. A. Shagisultanova, *Zh. Prikl. Khim.*, **26**, 222 (1953).

[6] T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **80**, 536 (1958).

[7] C. I. Sanders and D. S. Martin, Jr., *ibid.*, **83**, 807 (1961).

[8] L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., *ibid.*, **77**, 2965 (1955).

where ΔV^* is the molar volume change when the reactants are converted to an activated complex. From the graphs in Figures 1 and 2 the volumes of activation for the acid hydrolysis of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$ were found to be -17 ml/mole and -14 ml/mole, respectively. Kinetic data for these reactions are given in Table I.

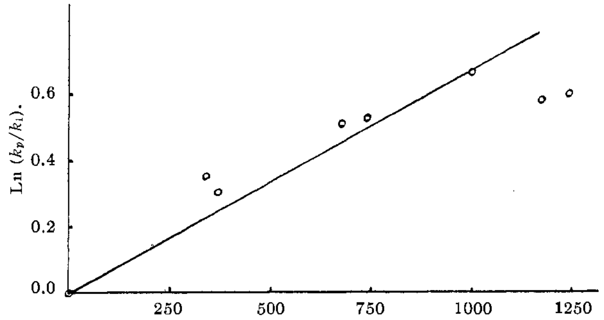

Figure 1.—Acid hydrolysis of $PtCl_4^{2-}$; plot of ln (k_p/k_1) *vs.* P (atm).

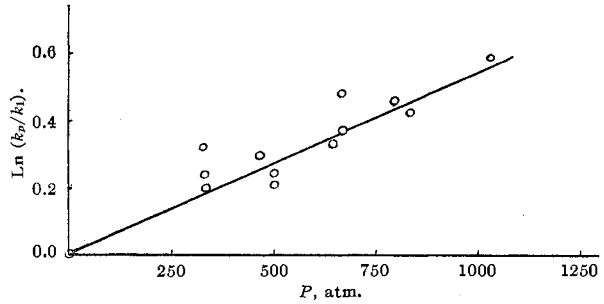

Figure 2.—Acid hydrolysis of $Pt(NH_3)Cl_3^-$; plot of ln (k_p/k_1) *vs.* P (atm).

TABLE I

Pressure, atm	Rate constant, 10^5k sec^{-1}	$\ln(k_p/k_1)$	Pressure, atm	Rate constant, 10^5k sec^{-1}	$\ln(k_p/k_1)$
0.0166 *M* K_2PtCl_4 at 25°			0.0166 *M* $K(Pt(NH_3)Cl_3$ at 26°		
1	4.2	0	1	3.9	0
367	5.6	0.29	333	4.8	0.19
333	5.9	0.34	333	5.0	0.23
733	7.1	0.52	333	5.4	0.31
667	6.8	0.49	500	4.8	0.20
1000	8.1	0.66	500	4.9	0.22
1167	7.5	0.58	467	5.2	0.28
1200	7.6	0.60	667	6.3	0.47
			667	5.6	0.35
			658	5.4	0.32
			800	6.0	0.42
			833	6.0	0.41
			1067	6.9	0.55

The deviation of the points at highest pressure in Figure 2 is probably due to experimental difficulties rather than pressure dependence of ΔV^*. In no case recorded in the literature is there a definite indication of curvature for an aqueous reaction in the range of pressure from zero to 1000 atm. However that may be, the datum of interest is the instantaneous slope at zero pressure.

The mean deviation of duplicate rate measurements is about 5%. Pressures were controlled to ±20 atm. The error in the volume of activation is 2 ml/mole, and it arises almost entirely from the 10% uncertainty in ln (k_p/k_1).

Discussion

The interpretation of activation volumes has been amply discussed elsewhere[1] and will be only briefly reviewed here. A complication which must always be considered is that reactions which involve the generation or destruction of ionic charges in water with no change in the total number of particles, *e.g.*, proton transfers to and from acids and bases, are accompanied by volume changes up to 28 ml/mole.[1a] The reactions under discussion here were selected because they do not entail a change in the number of ionic charges. Although it would be difficult in this case to provide experimental support, it seems reasonable to suppose that the transition state has the same charge type as reactants. For a group of organic reactions which do not change their course when the solvent is changed, it has been found that electrostriction effects are predictable on the basis of the charge types of reactants and products.[9] It is also reassuring that a wide variety of reactions of the same type we think we have here ($ion_1 + neutral_1 \rightarrow ion_2 + neutral_2$) do not show capriciously variable activation volumes, but rather ΔV^* lies in the range of -5 to -13 ml with a mean of -9 ml and a mean deviation of 2 ml.[10] The decrease of volume is ascribed to the coalescence of two separate particles into one.

The activation volumes for the hydrolysis of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$ are -17 ± 2 and -14 ± 2 ml/mole. Rather than attempt to estimate volume changes on an absolute basis, it is safer to interpret these results by analogy to measured volume differences in model compounds and volumes of activation for analogous reactions of firmly established mechanism. It is posible, of course, to propose any number of imaginative mechanisms which would be consistent with the results of a single measurement, and we will restrict our attention to a pathway which has been proposed on other grounds by Basolo, Pearson, *et al.*[2,3] Some of the features of this pathway are shown by eq 1.

It is easy to obtain volume differences for real or hypothetical reactions in which water combines with an unsaturated compound to give a stable adduct. Table II shows representative data which are based on recorded densities of the various pure liquids. It can be seen that the "hydrates" have molar volumes

TABLE II

VOLUMES OF HYDRATION

Reagents	Molar vol., ml/mole	Vol. of hydration, ml/mole
Acetone	73.2	−12.5
2-Methoxyethanol	78.7	
Allyl alcohol	68.0	−12.8
Propylene glycol	73.2	
2-Pentene	108	−8.0
Ethyl propyl ether	118	
Styrene	115	−7.0
Phenetole	126	

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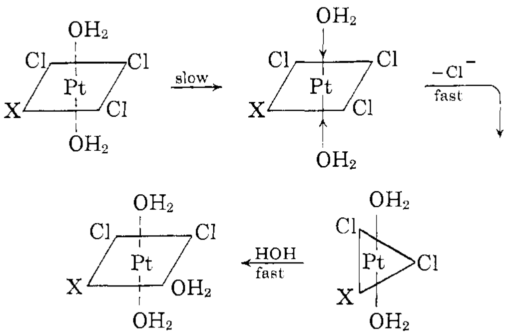
(9) K. R. Brower, *J. Am. Chem. Soc.*, **85**, 1401 (1963).

(10) W. J. Le Noble and M. Duffy, *ibid.*, **86**, 4512 (1964).

from 7 to 13 ml less than those of the starting materials. In order to provide a more detailed model, we have measured the partial molar volumes of sodium maleate and sodium malate and thereby obtained a value of −8.3 ml for the hydration of an unsaturated divalent ion. Several activation volumes for reactions involving the combination of an ion with a water molecule are available, and they lie in the range from −6 to −10 ml. Examples are the hydrolysis of epoxides[4a] and the hydration of olefins.[4b] The theoretical implications of these results are discussed in the references cited.

Another piece of information needed for the interpretation of the results is a knowledge of the volume change which would result from stretching of the Pt–Cl bond. Although specific information about this bond is not available, the activation volume for the decomposition of CCl_3^- into CCl_2 and Cl^- is reported to be +16 ml/mole.[10] Other unimolecular decompositions of univalent ions have positive values ranging up to 19 ml and averaging about 10 ml.[11]

In order to complete the formulation of a transition-state model it is necessary to postulate that the following physical processes are involved in greater or less degree. (1) One or more water molecules move inward and contribute to the formation of the Pt–OH_2 bond found in the product. (2) One of the Pt–Cl bonds elongates. We also postulate that the transition state has the same net charge as the original complex and constricts the same volume of solvent. It seems clear at the outset that the contribution of (2) is small since the activation volume is strongly negative. If the coordination number of the Pt is not to rise above 6, the contribution of (1) is limited to an extreme of twice −8.3 ml (the volume of hydration of maleate ion), and this is nearly equal to the observed activation volume. If the previously mentioned dissociative mechanism is correct, then a structural representation of the mechanism which would be consistent with our data is as follows (X = NH_3 or Cl)



Other recent evidence which has a bearing on the transition-state structure is the determination of activation energies and entropies for these complexes.[12] The entropies for $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$ are −16 and −23 eu. These values are consistent with a transition state in which increased bonding to the nucleophile is the dominant feature.

Acknowledgment.—The authors are indebted to the National Science Foundation, which supported this work through Grant G-19144.

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[11] K. R. Brower, B. Gay, and T. L. Konkol, *J. Am. Chem. Soc.*, **88**, 1681 (1966).

[12] U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

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The Dissociation Equilibria of Trioxochlorochromate(VI) and Chromic Acid

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The equilibrium quotients of the reactions

$$CrO_3Cl^- + H_2O = HCrO_4^- + Cl^- + H^+$$
$$H_2CrO_4 = HCrO_4^- + H^+$$

were determined spectrophotometrically at the wavelengths 320, 330, and 340 mμ at 15.0, 25.0, and 35.0° in solutions of unit ionic strength containing lithium perchlorate, lithium chloride, perchloric acid, and hydrochloric acid. The ΔH and ΔS of the dissociation of CrO_3Cl^- are −1.13 kcal and −8.6 eu, respectively. The ΔH and ΔS of the dissociation of H_2CrO_4 are −8.5 kcal and −26 eu, respectively.

The existence of trioxochlorochromate(VI) ion, CrO_3Cl^-, in solids has been known for many years. X-Ray studies have been reported on $KCrO_3Cl$[1,2] and on NH_4CrO_3Cl.[3] The reactions of $KCrO_3Cl$ have been investigated in liquid ammonia.[4–6] Chloro complexes have been postulated in the mechanism of oxidation of iso-

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[1] S. Gawrych, *Roczniki Chem.*, **19**, 413 (1939).

[2] L. Helmholz and W. R. Foster, *J. Am. Chem. Soc.*, **72**, 4971 (1950).

[3] F. Hanic and J. Madar, *Chem. Zvesti*, **10**, 82 (1956).

[4] H. H. Sisler, *Trans. Kansas Acad. Sci.*, **46**, 136 (1943).

[5] H. H. Sisler and F. E. Jirik, *J. Am. Chem. Soc.*, **66**, 1344 (1944).

[6] S. I. Tannenbaum, R. S. Drago, and H. H. Sisler, *ibid.*, **79**, 1815 (1957).