CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY, SOCORRO, NEW MEXICO 87801

The Volume of Activation in the Substitution Reaction of *trans*-Dichlorobis(triethylphosphine)platinum(II) with Bromide Ion

BY T. TAYLOR AND L. R. HATHAWAY

Received April 4, 1969

Determination of the effect of hydrostatic pressure upon the reaction rates of *trans*-$Pt(P(C_2H_5)_3)_2Cl_2$ with Br^- in methanol and methanol–water (60 mol % H_2O) systems yields volumes of activation (ΔV_2^*) for the bimolecular nucleophilic substitution reaction pathway of -27 ± 3 and -28 ± 3 ml/mol, respectively, and a value of -28 ± 3 ml/mol for the volume of activation (ΔV_1^*) for the solvolytic path of the reaction. The values of ΔV_2^* and ΔV_1^* show bond formation is the dominant feature for both transition states. It is inferred that formation of a Pt–Br bond and a Pt–solvent bond in the bimolecular nucleophilic reaction pathway and two Pt–solvent bonds in the solvolytic pathway are nearly complete in the respective transition states, and the Pt–Cl bond is nearly intact in each case.

Introduction

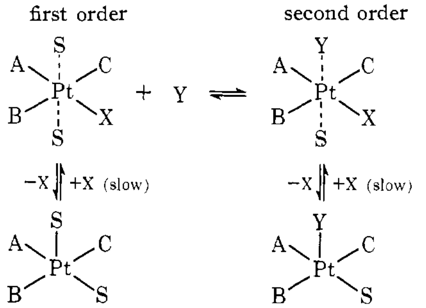
The usefulness of activation volume measurements in studies of reaction mechanisms has been well documented in the literature in recent years.[1,2] The general applicability of this method to the investigation of substitution reactions of Pt(II) complexes[3] has been demonstrated in the studies of activation volumes for the acid hydrolysis of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$.

Rates of substitution reactions of Pt(II) complexes are recognized to follow a two-term rate law[4]

$$Rate = k_1(\text{complex}) + k_2(\text{complex})(\text{reagent}) \qquad (1)$$

where k_1 is the first-order rate constant for the solvolytic path of the reaction and k_2 is the second-order rate constant for the bimolecular nucleophilic substitution path of the reaction.

The mechanistic model proposed by Basolo, *et al.*,[5] for substitution reactions of the square-planar complexes of Pt(II) suggests that solvent molecules aid in displacing the leaving group in substitution reactions of Pt(II) complexes exhibiting both first-order and second-order kinetics, *viz.*



(2)

The role of the solvent in the first-order substitution reactions has been demonstrated[3] by the activation volume measurements made for the acid hydrolysis of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$. However, data have not been reported for substitution reactions of Pt(II) complexes exhibiting second-order kinetic behavior which allow the importance of the solvent in the formation of the activated complex to be ascertained for these cases.

The volume of activation can be attributed either to a change in volume of the molecules in the activated complex or to a change in the volume of the solvent produced by a change in electrical polarization upon formation of the activated complex. The reaction of *trans*-$Pt(P(C_2H_5)_3)_2Cl_2$ with bromide ion in methanol exhibits second-order kinetics at moderate bromide ion concentrations (0.1 *M*).[6] Furthermore, the rate-determining step of the reaction sequence

$$trans\text{-}Pt(P(C_2H_5)_3)_2Cl_2 + Br^- \xrightarrow{\text{slow}} trans\text{-}Pt(P(C_2H_5)_3)_2BrCl + Cl^- \qquad (3)$$

is of a type well suited for a volume of activation study since the charge types of reactant and product species are the same; consequently, volume changes due to electrostrictive effects should be negligible.

Experimental Section

Materials.—*trans*-$Pt(P(C_2H_5)_3)_2Cl_2$ was prepared according to the method of Jensen.[7] The observed melting point was 142–143° as compared to the reported value of 143°. Platinum was determined gravimetrically following reduction to the metal with hydrazine sulfate. *Anal.* Calcd for $Pt(P(C_2H_5)_3)_2Cl_2$: Pt, 38.0. Found: Pt, 38.8.

Tetrabutylammonium bromide, from Eastman Organic Chemicals, was used as the source of bromide ion without further purification. The methanol used as the solvent was purified by distillation from $Mg(OCH_3)_2$.[8]

Equipment.—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 Engineers Inc., Erie, Pa. The reaction vessel consisted of a 5-cm^3 ground-glass syringe outfitted with a rubber sleeve cover for sealing the tip of the syringe. The high-pressure bomb was thermostated in an oil bath at a

---

[1] S. D. Hamann, "High Pressure Physics and Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1963, pp 163–205.

[2] (a) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworth and Co. Ltd., London, 1957; (b) S. D. Hamann, *Ann. Rev. Phys. Chem.*, **15**, 349 (1964); (c) E. Whalley, *Advan. Phys. Org. Chem.*, **2**, 93 (1964); (d) W. J. le Noble, *J. Chem. Educ.*, **44**, 729 (1967).

[3] E. Brower, L. Hathaway, and K. R. Brower, *Inorg. Chem.*, **5**, 1899 (1966).

[4] H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962).

[5] (a) D. Banerjea, F. Basolo, and R. G. Pearson, *ibid.*, **79**, 4055 (1957); (b) R. G. Pearson, H. B. Gray, and F. Basolo, *ibid.*, **82**, 787 (1960); (c) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1958, pp 186–190.

[6] U. Belluco, L. Cattaini, F. Basolo, R. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

[7] K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **229**, 225 (1936).

[8] H. Lund and K. Bjerrum, *Ber.*, **64**, 210 (1931).

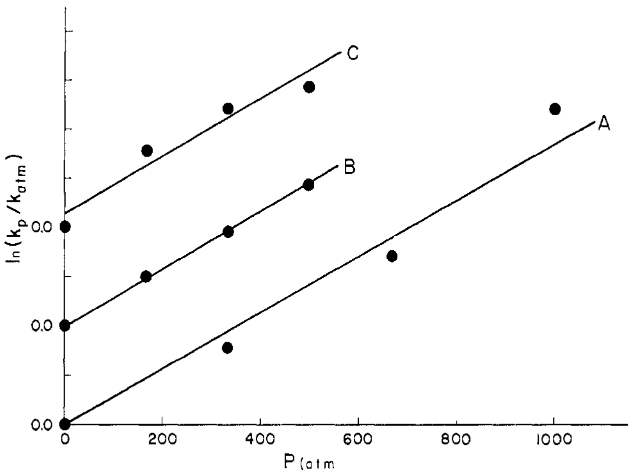


Figure 1.—Plot of ln (k_p/k_{atm}) *vs.* P (atm): curve A, k_2 data of the methanol system; curve B, k_2 data of the methanol–water system; curve C, least-squares fit of k_1 data of the methanol–water system. Ordinate divisions have a value of 0.2.

temperature of 25.0 ± 0.1°. The reactions were followed spectrophotometrically in the ultraviolet region with both a Beckman DU and a Beckman DB-G.

Rate Measurements.—Stock solutions of *trans*-$Pt(P(C_2H_5)_3)_2Cl_2$ and $(n\text{-}C_4H_9)_4NBr$ in methanol were used to prepare all test solutions used. The studies performed in pure methanol as the solvent had substrate and reagent concentrations of 2.0×10^{-4} and 0.1 M, respectively.

Reactions studied in the methanol–water system (60 mol % H_2O) had a substrate concentration of 2.0×10^{-4} M and reagent concentrations of 0.01, 0.02, and 0.03 M. Solutions for the mixed solvent system studies were maintained at a constant ionic strength of 0.1 by the addition of $LiClO_4$. It was observed in the methanol–water system that the solubility of *trans*-$Pt(P(C_2H_5)_3)_2Cl_2$ was greatly diminished if the water content was much greater than 60 mol %.

The reaction was followed in both solvent systems by measuring changes in the optical density of the solutions at 267 mμ. Preliminary experiments showed a loss of 1% transmittance at all complex concentrations and high pressures used, which results from a slight amount of leakage of the pressurizing oil into the reaction vessel at high pressure.

Treatment of Data.—The use of an excess of reagent for reaction 3 allows the determination of the pseudo-first-order rate constant, k_{obsd}. The relationship of this rate constant to k_1 and k_2 of eq 1 is given by

$$k_{obsd} = k_1 + k_2(Br^-) \qquad (4)$$

Pseudo-first-order behavior was observed for the reaction at atmospheric pressure up to 40% conversion in pure methanol for 0.1 M Br^- and up to 34% conversion in methanol–water for 0.01 M Br^-. Since the purpose of this study was to determine the variation in the rate constant with pressure, it seemed desirable to determine the pseudo-first-order rate constants at the same degree of conversion in each solvent system studied so systematic errors would cancel when ratios of rates at high pressure to atmospheric pressure were calculated. The measurements were made at times corresponding to 30% reaction in pure methanol and 28% reaction in methanol–water.

A correction was made for each high-pressure pseudo-first-order rate constant for the fraction of the reaction time at atmospheric pressure while the high-pressure apparatus was being closed or opened. Thus if the reaction proceeded at atmospheric pressure 10% of the total reaction time, the apparent acceleration k'_p/k_{atm} (where k'_p is the apparent high-pressure rate constant and k_{atm} the atmospheric rate constant) was multiplied by 1.10 to find the true acceleration. This value was then used to calculate the true high-pressure rate constant, k_p, and the ratio ln (k_p/k_{atm}).

The reaction of *trans*-$Pt(P(C_2H_5)_3)_2Cl_2$ with bromide ion was found to be first order in both complex and reagent, with k_2 being 4.7×10^{-4} M^{-1} sec^{-1} at 25° and $[Br^-] = 0.1$ M. This observation is consistent with reported values of k_1 and k_2 at 30° of $\sim 10^{-7}$ sec^{-1} and 9.3×10^{-4} M^{-1} sec^{-1}, respectively.[6] The reaction in the methanol–water system exhibited mixed first- and second-order behavior with values of k_1 and k_2 at 25° and $\mu = 0.1$ being 4.7×10^{-5} sec^{-1} and 9.3×10^{-4} M^{-1} sec^{-1}, respectively.

The volumes of activation were determined graphically from plots of ln (k_p/k_{atm}) *vs.* pressure according to the expression

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^*}{RT} \qquad (5)$$

where ΔV^* is the molar volume change when reactants are converted to an activated complex. Curves A and B of Figure 1 yield volumes of activation (ΔV_2^*) of −27 ml/mol in methanol and −28 ml/mol in methanol–water for the bimolecular nucleophilic substitution path of the reaction. Curve C of Figure 1 represents a least-squares treatment of k_1 data for the methanol–water system which gives a volume of activation (ΔV_1^*) of −28 ml/mol for the solvolytic path of the reaction. Kinetic data are given in Tables I and II.

Table I

Second-Order Rate Constants in Methanol at 25°

Pressure, atm	10^4k_2,[a] M^{-1} sec^{-1}	ln (k_p/k_{atm})
1	4.7	0
333	6.4	0.31
667	9.3	0.68
1000	16.9	1.28

[a] Values at each pressure represent an average for three to five runs.

Table II

Rate Constants in Methanol–Water at 25° and $\mu = 0.1$

First-Order Rate Constants

Pressure, atm	10^5k_1,[a] sec^{-1}	ln (k_p/k_{atm})
1	4.7	0
167	6.4	0.31
333	7.6	0.48
500	8.3	0.57

Second-Order Rate Constants

Pressure, atm	10^4k_2,[a] M^{-1} sec^{-1}	ln (k_p/k_{atm})
1	9.3	0
167	11.4	0.20
333	13.7	0.38
500	16.4	0.57

[a] Values for each pressure obtained from plots of k_{obsd} *vs.* Br^- (according to eq 4) for triplicate runs made at each of the three Br^- concentrations used (0.01, 0.02, and 0.03 M Br^-).

The mean deviation of duplicate rate measurements is about 5%. Pressures were controlled to ±20 atm. The error in the volume of activation is 3 ml/mol in each of the three cases and arises almost entirely from the uncertainty in ln (k_p/k_{atm}).

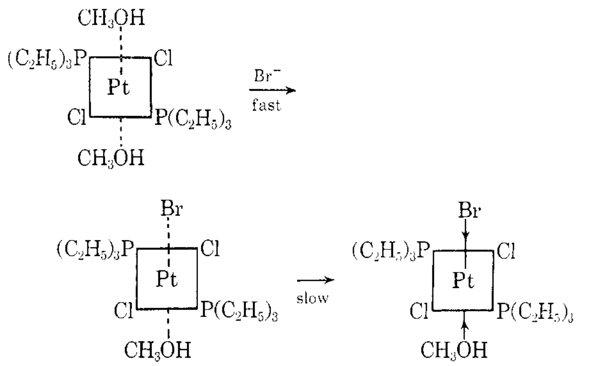
Discussion

Volume of activation values measured for bimolecular reactions between ions and neutral molecules, in which the charge type of the reaction remains the same throughout the course of the reaction, have a mean value of −9 ± 2 ml/mol and have been interpreted in terms of the formation of a new bond between the reactant species in the transition state.[1] The larger negative values of the activation volumes in the acid hydrolysis of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$ have been viewed in terms of the formation of two Pt–OH_2 bonds in the transition state.[3]

Interpretation of the large negative values of ΔV_2^* for the bimolecular nucleophilic path of the reaction between *trans*-$Pt(P(C_2H_5)_3)_3Cl_2$ and bromide ion requires a consideration of potential contributions of electrostriction effects, bond stretching, and bond formation to the activation volume. Brower[9] has observed that the volume of activation measured for a series of organic reactions in which ionic charges are created in the transition state show a marked dependence upon the solvent used, reflecting the varying ability of the charges to constrict solvent molecules surrounding the activated complex. The fact that ΔV_2^* values are the same within limits of experimental error for both the methanol and methanol–water systems suggests that gross electrostrictive forces are not present in the transition state for this path of the reaction.

Specific information regarding the volume change resulting from stretching of the Pt–Cl bond is not available. The activation volume for the decomposition of CCl_3^- into CCl_2 and Cl^- is reported to be +16 ml/mol[10] and other unimolecular decompositions of univalent ions have positive values averaging about 10 ml/mol.[11] This suggests the stretching and rupture of the Pt–Cl bond should produce a positive volume change of the order of 10 ml/mol. In view of the strongly negative values of ΔV_2^* and the insensitivity of these values to solvent change, it seems apparent that the Pt–Cl bond is virtually intact in the transition state of this course of the reaction.

A value of −12 ml/mol is reported for the isotopic exchange of bromide ion with propyl bromide.[12] Considering the larger negative values of ΔV_2^* and a maximum coordination number of 6 for Pt in accordance with the mechanistic sequence of Basolo, *et al.*, the additional volume change should be attributable to the formation of a Pt–solvent bond in the transition state. It appears likely that the coordinated solvent molecule will be a methanol molecule even in the methanol–water system in view of the difficult solubility of the complex in water. Volume changes for some real or hypothetical reactions in which methanol combines with an unsaturated compound to give a stable adduct can be calculated from recorded densities of the various pure liquids. It can be seen from the data of Table III that the "methanol adducts" have molar volumes which are 13–20 ml less than those of the starting materials. Estimates of the value of ΔV_2^* based upon the assumption that a bromide ion and a methanol molecule are bound to *trans*-$Pt(P(C_2H_5)_3)_2Cl_2$ in the transition state are in good agreement with the measured values of ΔV_2^*. It seems reasonable that initially two methanol molecules may be loosely coordinated to the neutral complex species since methanol is more abundant than bromide ion in the system.



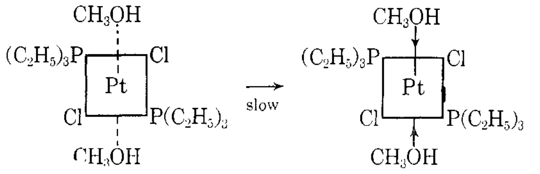
(6)

TABLE III

VOLUMES FOR CH_3OH ADDITION TO $CH_2{=}CHCH_2OH$

Product	Vol of CH_3OH addn, ml/mol
1,2-Butanediol	−19.8
1,4-Butanediol	−19.7
1,3-Butanediol	−17.7
1-Methoxy-2-propanol	−14.7
Trimethylene glycol methyl ether	−12.7

The data regarding the solvolytic reaction path are not extensive enough within themselves to provide a very clear-cut interpretation of the ΔV_1^* value. However, in view of the large negative value of ΔV_1^*, it would appear that elongation or rupture of the Pt–Cl bond is not an important feature of the transition state. If electrostrictive effects are no greater than those believed operative in the transition states for the acid hydrolysis of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$ and ΔV_2^* of this study, then ΔV_1^* can be considered in terms of the formation of two Pt–solvent (methanol) bonds in the transition state in a manner analogous to that of the $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$ systems. Thus, an important role for the solvent in the formation of the transition state is inferred not only for the portion of the reaction following first-order kinetics but also for that part exhibiting a second-order kinetic behavior.



(7)

Acknowledgments.—The authors are indebted to Dr. K. R. Brower for his helpful discussions and to the National Science Foundation, which supported this work through Grant G-7020.

---

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

(10) W. J. le Nobel and M. Duffy, *ibid.*, **86**, 4512 (1964).

(11) K. R. Brower, B. Gay, and T. L. Konkol, *ibid.*, **88**, 1681 (1966).

(12) J. Koskikallio and E. Whalley, *Can. J. Chem.*, **37**, 783 (1959).