TABLE IX
RELATIVE RATES OF RELEASE OF Cl^- FROM
trans-$M(en)_2LCl^+$ (M = Rh, Ir)

L	Ratio of rates (L/Cl)	
	Rh^b (50°)	Ir (105°)
Cl^a	1	1
Br	5.3	3
I	1100	54
NO_2	250^c	36

[a] Divided by 2 for statistical effect. [b] From ref 2. [c] From ref 10.

than would the second-row transition metal rhodium. Certainly, this appears to be the case for substitution reactions of square-planar complexes where the *trans* effect in complexes of platinum(II) is larger than for corresponding palladium(II) and nickel(II) systems. Even this statement may not be entirely justified because of the scarcity of data in the latter two systems. Furthermore, the *trans* effect in octahedral systems may operate quite differently from that in square-planar complexes.

An important effect which is operating to diminish the relative kinetic *trans* effects is the high temperature (105°) at which the rates of substitution with different ligands in the *trans*-$Ir(en)_2LX^+$ complexes are compared. The slopes of the activation energy plots are such that the kinetic *trans* effect decreases with increasing temperature, and the rates of the analogous Rh(III) complexes shown in Table IX are compared at a much lower temperature (50°).

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The Reaction between 1,10-Phenanthroline and Platinum(II) Compounds. II. The Reaction of Potassium Tetrachloroplatinate(II) in Water–Ethanol and Other Mixed Solvents

BY JOHN V. RUND AND FRANK A. PALOCSAY

Received April 18, 1969

The reaction of K_2PtCl_4 and 1,10-phenanthroline to give $Pt(phen)Cl_2$, which is slow and second order in water, proceeds at a fast, nearly constant rate in aqueous ethanol solution. The rate is independent of the concentration of phenanthroline but depends on the concentration of ethanol and on the initial (but not the instantaneous) concentration of K_2PtCl_4. Potential catalysts that might be formed by K_2PtCl_4 in water–ethanol are tested for catalytic activity. Of these, only ethylene has a pronounced effect on the rate, but one that is too small to explain the kinetics. The role of solvolysis in promoting the reaction is examined. Several solvents produce the same kind of reaction as ethanol. The presence of phenanthroline is not necessary for a pseudo-zero-order reaction to occur. When added to an ethanolic solution of K_2PtCl_4 which has stood for some time, phenanthroline will immediately disappear to the same extent as if it had been present from the beginning of the reaction. It appears that a platinum compound which reacts rapidly and irreversibly with phenanthroline is formed at a constant rate as the result of three consecutive, pseudo-first-order solvolysis reactions. This labile intermediate is most likely of the form $PtS_2(OH)Cl$ (S = solvent).

Introduction

In the previous paper[1] we reported that reaction 1 (phen = 1,10-phenanthroline) was slow and second order in water solution. During the investigation, we

$$PtCl_4^{2-} + \text{phen} \longrightarrow Pt(\text{phen})Cl_2 + 2Cl^- \qquad (1)$$

found that if the reactants were mixed in 50% aqueous ethanol, the same product was formed much more rapidly. At 45°, a typical reaction in water with millimolar concentrations of reactants took some 10 days to come to 75% completion. The same reaction in 50% ethanol required only 3 hr. Furthermore, it proceeded at a nearly constant rate. This paper describes the kinetics of the ethanolic reaction, an investigation of possible catalysts formed by ethanol and K_2PtCl_4, and the role of solvolysis in promoting the fast reaction.

Experimental Section

The method of following reaction 1 spectrophotometrically has been described.[1] Aliquots of the reaction mixture were pipetted into iron(II) solutions. Red $Fe(phen)_3^{2+}$ formed rapidly, and the solution absorbance at 510 mμ was used to determine the concentration of phenanthroline that had not reacted with platinum. The reaction product was identified by comparison of its infrared spectrum with that of an authentic sample of $Pt(phen)Cl_2$ and by elemental analysis. *Anal.* Calcd for $Pt(C_{12}H_8N_2)Cl_2$: Pt, 43.72; C, 32.27; H, 1.79; Cl, 15.89. Found: Pt, 43.90; C, 32.22; H, 1.85; Cl, 15.92. The yield, beginning with 1 mmol each of K_2PtCl_4 and phenanthroline in 2 l. of 50% ethanol, was 431 mg (97%).

The solvolysis of K_2PtCl_4 was studied in a similar way. The reaction was found to give an intermediate which reacted immediately and irreversibly with phenanthroline. The progress

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[1] F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, **8**, 524 (1969).

of the solvolysis to give the labile intermediate was followed by withdrawing portions of the reaction mixture at intervals and pipetting them into solutions of phenanthroline. Within 1 min, the phenanthroline had reacted with all of the labile platinum. Iron(II) solution was then added to the sample, transforming the unreacted phenanthroline into $Fe(phen)_3^{2+}$, the concentration of which was determined spectrophotometrically. The acidity and conductivity of the solvolysis reaction solutions were also determined as functions of time. These measurements were made with a Leeds and Northrup 7401 pH meter equipped with a glass pH electrode and a calomel reference electrode and with an Industrial Instruments Inc. RC16B2 conductivity bridge.

The solvent kinetic isotope effect could not be measured practically by the method described in the first paragraph of this section. Instead, the reaction of K_2PtCl_4 with the disulfonate derivative of 4,7-diphenyl-1,10-phenanthroline (G. Frederick Smith Chemical Co.) was employed. These materials gave a soluble product, and the reaction was monitored by direct spectrophotometry of the reaction mixture at 245 mμ in deuterated and nondeuterated 50% aqueous ethanol solutions.

The chemicals used in this study were the same as previously described,[1] except for the solvents. These were boiled to free them from oxygen and were kept under nitrogen. Immediately before being used, dioxane and diglyme were distilled from sodium, and tetrahydrofuran was distilled from lithium aluminum hydride.

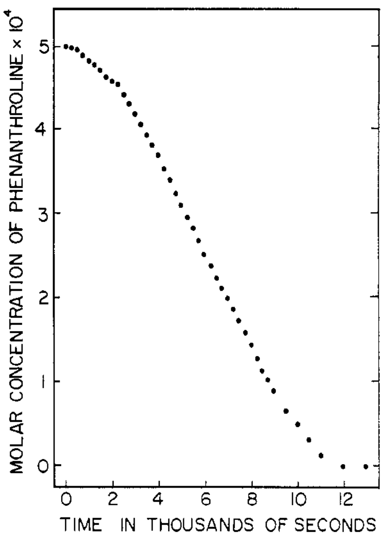

Figure 1.—Sample kinetic run for reaction 1 in 50% ethanol. $[PtCl_4^{2-}] = 1.0 \times 10^{-3}\ M$, $[phen] = 5.0 \times 10^{-4}\ M$, $[Cl^-] = 5.83 \times 10^{-3}\ M$, $[H^+] = 2.4 \times 10^{-3}\ M$, $\mu = 0.0194\ M$, and temperature is 45°.

Results and Discussion

Kinetics.—When K_2PtCl_4 and phenanthroline were dissolved in aqueous ethanol, they reacted to form $Pt(phen)Cl_2$ at a nearly constant rate until the reagent in the smaller concentration was used up. Figure 1 shows a sample graph of phenanthroline concentration *vs.* time, from which zero-order rate constants were determined. All reactions had induction periods and tended to become slower near the end. In those having more $PtCl_4^{2-}$ than phenanthroline, metallic platinum formed after all the phenanthroline had reacted.

In zero-order rate constants for the reaction under various conditions are listed in Table I. Figure 2 shows the rate constants as functions of different initial concentrations of K_2PtCl_4 and ethanol. It is apparent that the reaction is first order in these concentrations. There is some nonlinearity in the ethanol data, but this is not surprising, for there should be changes in the general character of the solvent as its composition is varied from 0 to 75% ethanol.

It is reasonable that the over-all reaction rate depended on ethanol concentration but individual reactions proceeded at a constant rate, because ethanol was present in large amounts, and its concentration could not have diminished much during the course of a reaction. This is not so for $PtCl_4^{2-}$. The reaction could be followed while $PtCl_4^{2-}$ fell to one-fourth or less of its original concentration with little change in the observed rate. Thus the reaction had the peculiar property of depending on the initial, but not the instantaneous, $PtCl_4^{2-}$ concentration.

TABLE I[a]

CONDITIONS AND PSEUDO-ZERO-ORDER RATE CONSTANTS FOR THE REACTION

$$PtCl_4^{2-} + phen \rightleftharpoons Pt(phen)Cl_2 + 2Cl^-$$

% ethanol	$10^4[PtCl_4^{2-}]$, M	10^4 [phen], M	10^2 $[Cl^-]$, M	10^3 $[H^+]$, M	$10^2\mu$, M	10^8k, M/sec
25	10.0	5.00	2.00	2.0	2.3	2.04 ± 0.01
37.5	10.0	5.00	2.00	2.0	2.3	3.60 ± 0.01
50	10.0	5.00	2.00	2.0	2.3	4.88 ± 0.14
75	10.0	5.00	2.00	2.0	2.3	6.80 ± 0.01
50	2.50	5.00	2.00	2.0	2.3	1.11 ± 0.01
50	5.00	5.00	2.00	2.0	2.3	2.36 ± 0.01
50	7.50	5.00	2.00	2.0	2.3	3.58 ± 0.01
50	10.0	10.0	2.00	2.0	2.3	4.79 ± 0.04
50	5.00	5.00[b]	2.30	2.0	2.6	2.15 ± 0.14
50	5.00	5.00[c]	2.30	2.0	2.6	2.14 ± 0.04
50	5.00	5.00	5.00	2.0	5.3	1.80 ± 0.01
50	5.00	5.00	10.0	2.0	10.3	1.10 ± 0.01
50	5.00	10.00	0.10	2.0	10.3	5.85 ± 0.07
50	10.0	10.0	1.00	2.0	10.3	4.80 ± 0.14
50	10.0	10.0	2.00	2.0	10.3	3.80 ± 0.14
50	10.0	10.0	5.00	2.0	10.3	2.65 ± 0.07
50	10.0	10.0	10.0	2.0	10.3	2.25 ± 0.10
50	5.00	5.00	2.30	2.0	2.6	2.05 ± 0.11
50	5.00	5.00	2.30	0.5	2.6	2.11 ± 0.04
50	5.00	5.00	2.30	0.02	2.6	2.33 ± 0.06
50	5.00	5.0	2.30	0.01	2.6	2.24 ± 0.04
50	10.0	10.0	2.00	2.0	5.3	4.25 ± 0.02
50	10.0	10.0	2.00	2.0	10.3	3.70 ± 0.14
50	10.0	5.00	2.00	2.0	2.3	14.3 ± 0.1

[a] All temperatures are 45° except for the final one, which is 55°. [b] 5,6-Dimethyl-1,10-phenanthroline. [c] 4,7-Dimethyl-1,10-phenanthroline.

The rate was independent of the concentration and basicity of the phenanthroline. The basicity dependence was tested by running the reaction with the 5,6-dimethyl and 4,7-dimethyl derivatives of 1,10-phenanthroline, which are, respectively, one-tenth and ten times as basic as the unsubstituted ligand. The insensitivity of the ethanolic reaction to phenanthroline was unlike the result obtained in water solution. This suggested that the ethanol was producing a fundamental change in the mechanism rather than a simple dielectric constant effect. As in water, variation in the pH over a range wide enough to make substantial changes in the amounts of free phenanthroline and phenanthrolinium ion did not cause a significant rate change. Also as in water, an increase in ionic strength caused a decrease in the rate. In this case, however, the calculated charge product of the reactants was only −0.35. Although

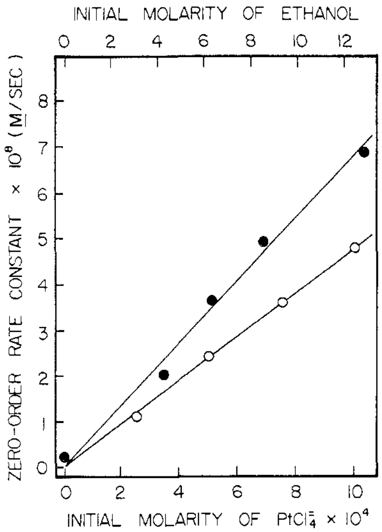

Figure 2. Dependence of the observed zero-order rate constants on the initial concentrations of K_2PtCl_4 (O) and ethanol (●). The point at $[C_2H_5OH] = 0$ indicates the initial rate of the second-order reaction in aqueous solution.

such calculations are not always reliable,[1] the small value suggested that a neutral molecule, probably the solvent, was playing a prominent part in controlling the rate. The kinetic isotope effect was further suggestive of the importance of the solvent. The reaction went 2.2 ± 0.1 times as fast in 1:1 D_2O–C_2D_5OD as in 1:1 H_2O–C_2H_5OH. Few temperature dependence data are included in the table, for it will be shown that the rate of phenanthroline disappearance is not controlled by a single chemical reaction.

Catalysis.—In an effort to account for the rate increase caused by alcohol, we investigated the action of some potential catalysts that might have been formed by K_2PtCl_4 and ethanol. These were basically of two kinds: those that might cause labilization by an oxidation–reduction mechanism and those that might cause labilization by the *trans* effect. Several substitution reactions of transition metal compounds are catalyzed by traces of the same metal in a different oxidation state.[2] Ethanol might have reduced a small amount of K_2PtCl_4 to a platinum(0) compound, and, having ten d electrons, this compound should be labile to substitution. Alternatively, ethanol might have formed an ethylene or hydride complex with K_2PtCl_4, which would be more easily substituted by phenanthroline as a result of the strong *trans*-labilizing ability of these ligands.

Redox labilization was tested by adding a platinum(0) compound, $Pt(OP(C_2H_5)_3)_4$, to an aqueous solution of K_2PtCl_4 and phenanthroline. The compound was handled in a dry nitrogen atmosphere and dissolved in carefully dried solvents that were free of oxidizing agents. Introduced as an ethanolic solution to give a concentration of 0.8×10^{-5} *M*, it gave no increase in rate. Added as a diglyme solution that contained an equivalent amount (1.3×10^{-5} *M*) of phenanthroline, it gave a slight increase in the second-order rate constant, probably because of the combined labilizing effects of diglyme and released phosphite. The fact that phenanthroline reacted with the platinum(0) was indicated by the immediate development of a deep yellow color when the two were mixed.

We had observed[1] that $Pt(C_2H_4)Cl_3^-$ reacts immediately with phenanthroline to give $Pt(phen)Cl_2$. If ethanol was being changed into ethylene, the catalysis might have occurred through an ethylene complex. When an aqueous solution with $[PtCl_4^{2-}] = [phen] = 5 \times 10^{-4}$ *M* was made 5×10^{-5} *M* in ethylene, a marginal increase in rate was observed. The same amount of ethylene was also added as $KPt(C_2H_4)Cl_3$ with the same result, except that a small quantity of product was generated immediately. In 2.4×10^{-3} *M* ethylene, a first-order reaction ensued, giving $Pt(phen)Cl_2$ with $k_1 = 5.6 \times 10^{-4}$ sec^{-1}. From this number we calculate that in order to achieve the rate of the ethanolic reaction, several moles of ethylene would have to be produced with every mole of product in the early part of the reaction. The requirement would drop to less than 1 mol during the middle of the reaction and then rise again as the reaction continued. This mechanism seems untenable. An examination of the free energies of formation and solution of ethylene and ethanol eliminates a mechanism in which ethylene was being produced by an independent reaction catalyzed by platinum.

Hydride ion was tested as the ethanolic reaction catalyst by adding sodium borohydride to aqueous solutions of the reactants. Addition of acid was delayed to permit possible reaction between hydride and platinum. With $[PtCl_4^{2-}] = [phen] = 5 \times 10^{-4}$ *M*, 1.2×10^{-4} *M* total available hydride caused an increase of 20% in the second-order rate constant. At 2.0×10^{-4} *M* H^-, the increase was 50%. At 2.1×10^{-3} *M* H^-, all of the $PtCl_4^{2-}$ was reduced to platinum metal before any reaction with phenanthroline could occur. As with ethylene, the rate increases were inadequate to account for the ethanolic reaction.

Because pseudo-zero-order kinetics sometimes occurs in reactions containing limiting amounts of heterogeneous catalysts,[3] platinum metal was examined for catalytic ability. When a small amount of finely divided platinum was generated *in situ*, the reaction was no faster than when no catalyst was present.

Solvolysis.—Since a catalytic mechanism did not seem to be able to account for the increase in the reaction rate caused by alcohol, the role of solvolysis of $PtCl_4^{2-}$ was investigated. Ethanol was not an appropriate solvent, because in the absence of phenanthroline it reduces $PtCl_4^{2-}$ to platinum metal. Other solvents were tested and several were found in which the reactions proceeded at nearly constant rates (Table II). The rates are compared for equal concentrations (11.75

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(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 494 ff.

(3) C. N. Hinshelwood, *J. Chem. Soc.*, 327 (1925); C. N. Hinshelwood and R. E. Burk, *ibid.*, 1105 (1925).

Table II

Zero-Order Rate Constants for Reaction 1 in Various Mixed Solvents[a]

Solvent	Concn,[b] *M*	$10^8 k_0$, *M*/sec
Water	. . .	0.06[c]
Methanol	11.75	0.56 ± 0.01
Ethanol	11.75	2.14 ± 0.03
Acetone	11.75	1.38 ± 0.02
Acetonitrile	11.75	~0.07
Dioxane	5.88	1.31 ± 0.01
Tetrahydrofuran	5.88	3.45 ± 0.14
Dimethyl sulfoxide	5.88	*d*
Diglyme	2.95	2.16 ± 0.05

[a] Conditions: $[PtCl_4^{2-}] = [phen] = 5.0 \times 10^{-4}$ *M;* $[H^+] = 2.0 \times 10^{-3}$ *M;* $[Cl^-] = 6.9 \times 10^{-2}$ *M;* temperature 45°. [b] In aqueous solution. [c] Initial rate of the second-order reaction. [d] Very slow and not zero order.

Table III[a]

Rates of Solvolysis of K_2PtCl_4 to Give the Labile Intermediate and Phenanthroline Substitution of K_2PtCl_4 in 50% Dioxane at 45°

	$10^8 k_0$, *M*/sec	
$[Cl^-]$, *M*	phen absent	phen present
0.0685	0.77 ± 0.09	0.86 ± 0.04
0.0343	0.82 ± 0.03	0.98 ± 0.06
0.0171	1.05 ± 0.03	1.14 ± 0.03
0.0086	1.13 ± 0.03	1.31 ± 0.02

[a] $[PtCl_4^{2-}] = 5 \times 10^{-4}$ *M*, $\mu = 0.082$ *M*, $[H^+] = 1.0 \times 10^{-2}$ *M*, and $[phen] = 5 \times 10^{-4}$ *M* in the substitution reaction.

M) of coordination groups (except for tetrahydrofuran and dimethyl sulfoxide, which are at half this concentration, because 11.75 *M* solutions are almost entirely nonaqueous). Dioxane was chosen for a more detailed study of the solvolysis reaction. All of the ingredients of the substitution reaction mixture except phenanthroline were mixed. Aliquots were removed at intervals and pipetted into phenanthroline solutions. Then almost immediately the reaction was quenched with iron(II). The results were almost the same as if phenanthroline had been added at the beginning of the reaction. In other words, a pseudo-zero-order reaction was occurring between $PtCl_4^{2-}$ and the solvent that produced an intermediate with which phenanthroline reacted very rapidly. Table III compares rates of some solvolysis and substitution reactions. The slightly faster rate (by about 12%) of the solvolysis reaction is the result of two differences between the reactions. The substitution reaction was somewhat speeded up by the direct reaction between $PtCl_4^{2-}$ and phenanthroline, and some of the labile intermediate in the solvolysis reaction was being inactivated by another reaction (see below). The change of the solvolysis rate constants with chloride concentration was the result of the reversibility of the solvolysis reactions. It did not fit any simple functional pattern, and, as will be shown later, some complicated dependence of rate upon $[Cl^-]$ is to be expected. The dependence of the substitution rate upon $[Cl^-]$ has been explained.[1] Figure 3 shows a typical solvolysis reaction where phenanthroline was added to each aliquot as it was withdrawn from the reaction mixture. The labile intermediate built up to a maximum concentration and then slowly disappeared, indicating that it further reacted to give a nonlabile species. Points from a corresponding substitution reaction in which phenanthroline was present in the original reaction mixture are shown for comparison. When the same experiment was tried with pure water as the solvent, a marginal effect was detected. The most phenanthroline that disappeared quickly was 2%, and this occurred about 10^5 sec after the beginning of the reaction. Observing the solvolysis led to another conclusion that was not apparent in the substitution reaction. Even when the phenanthroline was added to the reaction in which the labile intermediate had reached its maximum concentration (so that three-fourths or more of the phenanthroline reacted immediately), Pt(phen)Cl_2 did not appear at once. Instead, it precipitated slowly over a period of about 0.5 hr. Because Pt(phen)Cl_2 is very insoluble and shows no tendency to form supersaturated solutions, it must not have been the initial product of the fast phenanthroline reaction.

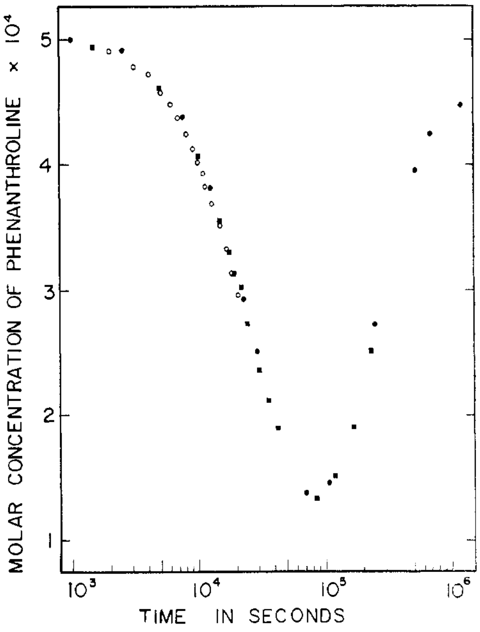

Figure 3.—Solvolysis of $PtCl_4^{2-}$ to give a labile intermediate as measured by the immediate disappearance of added phenanthroline. Filled points (●, ■) represent two independent reactions. Empty circles represent the reaction under the same conditions except that phenanthroline has been added at the beginning. Conditions are the same as the second entry in Table III.

The kinetics problem has now been simplified to explaining how a series of presumably pseudo-first-order solvolysis reactions can produce the labile species at a constant rate. This problem, applied to radioactive decay series, was solved by Rutherford.[4] He showed that the product of the third of three consecutive first-order reactions could be generated at a constant rate. Successive rate constants must decrease moderately and

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[4] E. Rutherford, "Radioactive Substances and Their Radiations," Cambridge University Press, London, 1913, p 420.

by about the same amount with each step. We simulated this kind of behavior on an analog computer and found that the curve shape could be made quite similar to that in Figure 1. Two consecutive reactions would not produce this result, but more than three reactions would, if some of the steps were very fast.

A stoichiometric mechanism can now be written that is consistent with all of the kinetic data

$$\mathrm{PtCl_4^{2-} + S \longrightarrow PtSCl_3^- + Cl^-} \qquad (2)$$

$$\mathrm{PtSCl_3^- + S \longrightarrow PtS_2Cl_2 + Cl^-} \qquad (3)$$

$$\mathrm{PtS_2Cl_2 + S \longrightarrow PtS_3Cl^+ + Cl^-} \qquad (4)$$

$$\mathrm{PtS_3Cl^+ + phen \longrightarrow Pt(phen)SCl^+ + 2S} \qquad (5)$$

$$\mathrm{Pt(phen)SCl^+ + Cl^- \longrightarrow Pt(phen)Cl_2 + S} \qquad (6)$$

The comparative order of reaction rates is: $2 > 3 > 4 \ll 5 \gg 6$. S is a molecule of solvent, and although it is not possible to distinguish between water and the other solvent, it seems reasonable that at least one of the S's is not water. On the other hand, it will be shown that the product of reaction 4 does contain a water molecule or a hydroxide ion. The first three reactions are reversible, which accounts for the complex rate decrease with increasing chloride concentration. This is not the only consistent mechanism that might be written for the reaction. In particular, the possibility of one kind of solvent molecule substituting the other has been ignored. The authors feel that the proposed mechanism has the advantage of being the simplest and most straightforward of the possible mechanisms. A slight elaboration of step 4 is indicated below.

In an effort to make the identification of the labile intermediate species more substantial, the solvolysis reaction in 50% dioxane was followed conductometrically (Figure 4). These data were compared with those for the substitution reaction under the same conditions (except that phenanthroline was present), followed in the usual way. It was anticipated that the onset of solvolysis reaction 4 could be located, because reactions 2 and 3 do not produce any additional ionic charges, but (4) does. Thus in Figure 4, the region A–B may have been associated with reactions 2 and 3, and (4) became predominent after B. The time for A–B in the solvolysis reaction was about the same as the induction period of the substitution reaction. In other words, phenanthroline began to disappear from the substitution at about the same time as $\mathrm{PtS_3Cl^+}$ began to appear in the solvolysis reaction. The rise in conductivity in region B–C seems to be too great to be associated with reaction 3. However, this rise was accompanied by an increase in acidity of the solution and was therefore partly due to deprotonation of an aquo ligand. After the acidity became approximately constant, the rate of the reaction as judged by the conductivity rise (region C–D) was in good agreement with the rate of substitution, both being about 2×10^{-8} *M*/sec. Furthermore, when the times in which the two reactions would be completed were estimated, good agreement was found (24,000 sec for solvolysis by conductivity and 26,000 sec for substitution by spectrophotometry). Although quantitative interpretation of the pH results must be done with some caution because of the nonaqueous solvent, the rate constant for the reaction calculated from the acidity increase (corresponding to region B–C of the conductivity measurements) was also about 2×10^{-8} *M*/sec. A consistent picture of the solvolysis must therefore involve the product of reaction 4 having been in equilibrium with its conjugate base. The degree of deprotonation was extensive at first, but leveled off as higher acidities were reached.

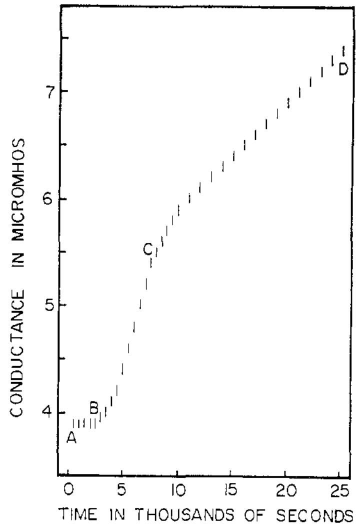

Figure 4.—Solvolysis of $\mathrm{PtCl_4^{2-}}$ in 50% dioxane followed by conductivity. $[\mathrm{PtCl_4^{2-}}] = 5 \times 10^{-4}$ *M*.

Conclusion

Solvolytic promotion of substitution rates is common in reactions of platinum(II) compounds (see ref 2, p 375 ff). Previously reported reactions (except see ref 1) have had a pseudo-first-order solvolysis step followed by a fast substitution step, leading to first-order kinetics for the solvent route to the product. The reaction reported here is unique in that apparently three consecutive solvolysis steps take place before a fast substitution occurs, resulting in a nearly constant rate for the over-all reaction. The formation of the substitution-labile species coincides with the appearance of hydroxide in the platinum(II) coordination sphere. Water as a ligand does not produce fast substitution by phenanthroline, and it would appear that molecules of the other solvents do not do so either. It seems to the authors that the hydroxide is the real contributor to the lability, rather than merely being coincidental with it. It cannot be the ability of the hydroxide to labilize a ligand *cis* or *trans* to itself that causes the fast reaction, but rather its ability as a leaving group.

This conclusion is difficult to rationalize. In the previous paper we conclude that reactions between platinum(II) compounds and phenanthroline are characterized by a transition state in which the leaving group is extensively dissociated. Such a mechanism does not explain why hydroxide is a good leaving group, for it is strongly held by platinum.[5] Instead, it appears that there must be little breaking of the strong platinum–hydroxide bond in the transition state. This would probably lead to an intermediate of octahedral platinum coordination. The unusual lability of hydroxide would then result from the ease with which it moved from the equatorial position in the square-planar reactant to the axial position in the octahedral intermediate. This in turn might result from the nonstereospecific σ bonding between hydroxide and platinum suggested by Basolo and Pearson (see ref 2, p 384).

Acknowledgment.—The authors wish to thank Professor Fred Basolo for the gift of the platinum(0) compound.

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(5) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 33, 34.

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Coordination of Palladium by Azo and Related Functional Groups

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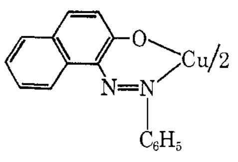
The preparation and physical properties of the simple azo complexes *trans*-$(RN{=}NR)_2PdX_2$ ($R = CH_3, C_6H_5$; $X = Cl, Br$) are reported. Infrared and nmr spectral observations indicate that each azo group is coordinated to palladium through a single nitrogen lone pair. Similar complexes of azoxybenzene could not be prepared, but it is possible to deprotonate azoxybenzene to form dichlorobis[2-(phenylazoxy)phenyl]dipalladium(II), 6. The dimer is readily cleaved by organic bases to give monomeric species. The preparation and properties of $(C_6H_5NO)_2PdCl_2$ are reported.

Introduction

Despite the fact that bonding between azo groups and transition metal ions is implicated in a large number of complexes, especially complexes of azo dyes, these are relatively few examples of compounds which involve ligands that are coordinated to a metal solely by means of an azo function. The largest group of simple azo complexes involves Cu(I); these generally have the constitution $(RN{=}NR)Cu_2Cl_2$.[1–3] In fact formation of a red cuprous chloride complex appears to be a qualitative test for the presence of the azo function. Platinum complexes of an azo compound which is constrained into the *cis* configuration[4] and of phenyldiimide (C_6H_5NNH)[5] have recently been reported. In the latter case it is interesting to note that coordination has stabilized a species whose existence otherwise is quite transitory.[6] Palladium and silver complexes of benzocinnoline[7] and a titanium complex of azobenzene[8] have also been described.

Although it has been suggested[9,10] that the metal–azo bond may involve an electronic structure analogous to that encountered in metal–olefin complexes, the few physical studies that have been conducted on azo complexes have indicated that a nitrogen lone pair rather than the π bond is the σ-donor site.[4,11–13] An X-ray crystallographic study[11] of $(CH_3N{=}NCH_3)Cu_2Cl_2$ has demonstrated that the azo function binds two copper ions through the two nitrogen lone pairs; the azomethane molecule maintains a *trans* configuration with little change in geometry from the free molecule. Similarily, X-ray studies of the two copper chelates **1**[12] and **2**[13] show that the metal is coordinated to a single nitrogen.



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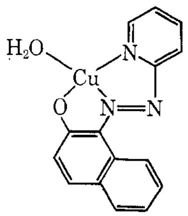

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Although olefinic coordination had been suggested for the product obtained from treating platinum tetrachloride with azobenzene in acetic acid, the compound has been recently shown to be a hexachloroplatinate(IV) salt of protonated azobenzene.[14]

Since the simplest azo molecule, diimide (HN=NH), is, especially in the complexed state, a likely intermediate in the biological fixation of molecular nitrogen, we have undertaken studies to elucidate the nature of

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