sequence of total dipole moments should be $R_3N < R_3As \simeq R_3P$. In terms of this model π-bonding would play a less significant role in understanding the relative donor abilities of these ligands toward transition metals.

This approach is continued in a description[24] of the relative donor tendencies of the primary, secondary, and tertiary ethylphosphines toward Co(II).

Acknowledgments.—We are indebted to Mr. M. Nichols and Dr. M. L. Corrin for their assistance with the X-ray diffraction work. W. E. H. thanks the Continental Oil Co. for a fellowship and grant, the Woodrow Wilson Foundation, the Koppers Co., and the National Science Foundation for fellowship support during the course of this research. The authors acknowledge their great debt to Professor Robert W. Parry for his association with certain preliminary portions of the work.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y., AND THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS

Kinetics of the Reactions of Diethylenetriamineaquoplatinum(II) Ion with Different Ligands

BY HARRY B. GRAY AND RICHARD J. OLCOTT

Received November 1, 1961

The rates of the reactions of $Pt(dien)H_2O^{2+}$ (dien = diethylenetriamine) with different ligands are reported and compared with the rates obtained for the reactions of the $Pt(dien)Br^{+}$ complex. A reagent independent rate, as well as a totally second order rate, is observed for the reaction of the aquo complex with Cl^- and NO_2^-. The mechanistic significance of this first-order rate is discussed. It is concluded that an aquo complex, formed by an S_N2 reaction with water, is the principal intermediate in the totally first-order reactions of platinum(II) complexes.

Introduction

Ligand substitution reactions of square-planar metal complexes in solution have been found in general to exhibit a combination of first- and second-order rate behavior.[1-11]

The mechanism which leads to second-order kinetics can be visualized as a direct bimolecular reaction between the incoming ligand and the complex. However, although there is now considerable evidence that the first-order process involves the solvent to some degree, the extent of this solvent participation is unknown. In water solution the acid hydrolysis reaction completely accounts for the first-order rates found for $^{36}Cl^-$ exchange with different chloroplatinum(II) complexes, where sufficient kinetic data are available.[3-6] Thus an aquo complex must be involved as the first-order reaction intermediate in these cases.

Since the mechanism leading to the aquo complex intermediate is still a matter of speculation, it seemed desirable to study in detail the reaction rates of one particular aquo complex, $Pt(dien)H_2O^{2+}$, with a variety of different ligands. This complex was chosen since the reaction kinetics of the "parent" $Pt(dien)X^+$ (X = Cl, Br, I) complexes have been studied extensively.[8-10]

Experimental

A. Materials.—The $[Pt(dien)NO_3]NO_3$ complex used was prepared and analyzed as described earlier.[8] All other materials used were reagent grade.

B. Determination of Reaction Rates.—The $Pt(dien)H_2O^{2+}$ solutions were prepared by dissolving [Pt(dien)-

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[1] R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954).

[2] A. A. Grinberg, *Russ. J. Inorg. Chem.*, **4**, 139 (1959).

[3] L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **77**, 2965 (1955).

[4] T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *ibid.*, **80**, 536 (1958).

[5] T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *ibid.*, **81**, 10 (1959).

[6] D. S. Martin, Jr., private communication.

[7] D. Banerjea, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **79**, 4055 (1957).

[8] F. Basolo, H. B. Gray, and R. G. Pearson, *ibid.*, **82**, 4200 (1960).

[9] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).

[10] H. B. Gray, *J. Am. Chem. Soc.*, in press.

[11] R. G. Pearson, H. B. Gray, and F. Basolo, *ibid.*, **82**, 787 (1960).

$NO_3]NO_3$ in water, which liberates the coördinated nitrate instantaneously[8]

$$Pt(dien)NO_3^+ + H_2O \xrightarrow{\text{very fast}} Pt(dien)H_2O^{2+} + NO_3^- \quad (1)$$

Thus the conductances of these solutions correspond to completely dissociated nitrate ions and doubly charged cations (molar conductance of $Pt(dien)H_2O^{2+}$ is 113 in 0.0004 M solution, 120 in 0.0002 M solution at 25°). Furthermore, the reactions reported in this work go to completion as judged by the total conductance changes

$$Pt(dien)H_2O^{2+} + X^- \longrightarrow Pt(dien)X^+ + H_2O \quad (2)$$

observed. This gives an additional check that the reacting solution initially contained $Pt(dien)H_2O^{2+}$.

The reactions given by eq. 2 were followed by both spectrophotometric and conductivity methods. The details of the experimental procedures and the treatment of the data have been given in previous publications.[7-10] Complete concentration data are given in the tables for the separate reactions. The $Pt(dien)X^+$ product complexes of eq. 2 have been isolated as $[Pt(dien)X]X$ salts,[8] and their spectra and conductivities in water are known.[10,12] This offers proof that the reaction rates being followed in solution actually correspond to eq. 2, since the product solutions were identical physically with independently prepared $Pt(dien)X^+$ solutions.

Good first-order plots were obtained from the data in all cases. These reactions must be regarded as pseudo first-order when the concentration of reacting ligand is much greater than the $Pt(dien)H_2O^{2+}$ concentration. However, even at comparable concentrations of ligand and complex, good first-order behavior existed. The possible significance of this is given in the next section.

Results and Discussion

Pseudo first-order rate constants (k_{obs}) are reported in Table I for the reaction of $Pt(dien)H_2O^{2+}$ with different ligands. The reaction rates are approximately, but not exactly, second order. This departure from total second-order behavior will be discussed later.

By looking at the ratio of rates of the $Pt(dien)Br^+$ and $Pt(dien)H_2O^{2+}$ complexes with different ligands it is clear that the aquo complex is reactive enough to be an intermediate in the reactions of the bromo complex. The reactivities of different ligands toward $Pt(dien)H_2O^{2+}$ are seen to decrease in the order

$$OH^- \gg I^- \sim CNS^- > Br^- > Cl^- > NO_2^- > py$$

The reaction of $Pt(dien)H_2O^{2+}$ with OH^- is immeasurably fast, as expected, since conversion to $Pt(dien)OH^+$ in this case requires only a proton transfer. This contrasts with the inert behavior found for hydroxide ion in *substitution* reactions of platinum(II) complexes.[2,7,10] The reactivity order for the other ligands, which must displace H_2O from the complex, is approximately the same as is observed for substitutions in $Pt(dien)X^+$ complexes.[10]

TABLE I

RATES OF REACTION OF $Pt(dien)H_2O^{2+}$ WITH VARIOUS LIGANDS IN WATER SOLUTION AT 25°

Ligand	Ligand concn., M	$Pt(dien)-H_2O^{2+}$ concn., M	$k_{obs}\ 10^2$, sec.$^{-1}$	Reactivity relative to $Pt(dien)-Br^+$ [a]
Cl^-	0.005	0.0002	0.53	*ca.* 50
	.003	.0002	.30	
	.001	.0002	.13	
	.0004	.0002	.067	
	.0002	.0002	.046[b]	
Br^-	.005	.0002	3.5	
	.003	.0002	1.8	
	.001	.0002	0.73	
I^-	.001	.0002	3.9	*ca.* 50
NO_2^-	.00451	.0002	0.30	
	.00266	.0002	.17	
	.00092	.0002	.090	*ca.* 30
	.000245	.0002	.027	
CNS^-	.001	.0002	1.45	*ca.* 20
OH^-	.005	.0002	Too fast to	Very
	.0005	.0002	measure	large
Pyridine	.005	.00125	0.19	*ca.* 100
	.0004	.0004	.031	

[a] Expressed as the ratio of k_{obs} for the aquo complex to k_{obs} for the bromo complex, for the same initial concentrations of reactants. Data for the $Pt(dien)Br^+$ reactions are taken from ref. 8 and ref. 10. [b] Reaction is 80% complete at equilibrium. All other reactions go to completion.

Competition experiments, summarized in Table II, provide additional evidence that an aquo complex is the intermediate in the first-order reactions of the $Pt(dien)X^+$ complexes. The rates and products of the reactions of $Pt(dien)X^+$ and $Pt(dien)H_2O^{2+}$ with the reactant pairs X^-, OH^- and X^-, py are reported, with X^- as Br^- or I^-. Notice that the first-order reaction rates of OH^- with $Pt(dien)X^+$ complexes are not affected by adding a considerable amount of X^- to the solution. This must mean that the principal first-order intermediate always selects OH^- over I^- or Br^-. As expected, $Pt(dien)H_2O^{2+}$ reacts with the same OH^-, X^- combinations to give *ca.* 100% $Pt(dien)OH^+$ complex. Furthermore, the principal first-order rate for the reaction between $Pt(dien)X^+$ and pyridine is strongly inhibited by the addition of X^-. Consistent with this, $Pt(dien)H_2O^{2+}$ is completely converted to $Pt(dien)X^+$ in the presence of the same X^-, py combinations.

There are two fundamentally different paths

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(12) H. B. Gray, unpublished results.

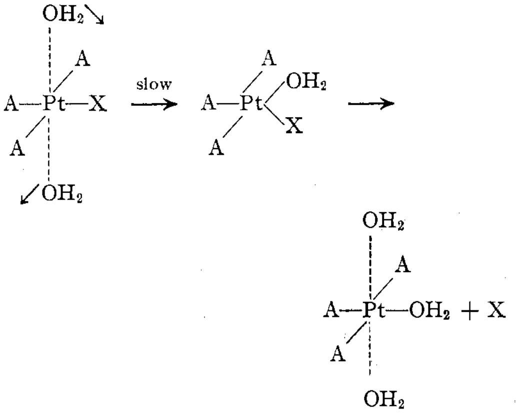
TABLE II

COMPARISON OF THE RATES AND PRODUCTS OF THE REACTIONS OF $Pt(dien)X^+$ AND $Pt(dien)H_2O^{2+}$ WITH VARIOUS LIGANDS IN WATER SOLUTION AT 25°

Complex concn., M	Potential reactants and ions initially present in solution, M		Reaction products	First-order reaction rates, k_1 (10^4) sec.$^{-1}$
$Pt(dien)Br^+$				
0.001	0.001 Br^-	0.001 OH^-	100% $Pt(dien)OH^+$	1.32
.001	.005 Br^-	.001 OH^-	100% $Pt(dien)OH^+$	1.32
.0012	.0024 NO_3^-	.00124 py	100% $Pt(dien)py^{2+}$	0.83
.001	.001 Br^-	.00124 py	100% $Pt(dien)py^{2+}$	.03
$Pt(dien)I^+$				
0.007	.007 I^-	.007 OH^-	100% $Pt(dien)OH^+$	.42
.007	.009 I^-	.007 OH^-	100% $Pt(dien)OH^+$	.42
.007	.015 I^-	.007 OH^-	100% $Pt(dien)OH^+$	.42
.007	.03 I^-	.007 OH^-	100% $Pt(dien)OH^+$	.42
$Pt(dien)H_2O^{2+}$				
0.0005	.001 NO_3^- .001 Br^-	.001 py	100% $Pt(dien)Br^+$	[a]
.0005	.001 NO_3^- .0025 Br^-	.0025 py	100% $Pt(dien)Br^+$	[a]
.0005	.001 NO_3^- .0025 I^-	.0025 py	100% $Pt(dien)I^+$	[a]
.0005	.001 NO_3^-	.001 OH^- .001 Br^-	100% $Pt(dien)OH^+$	Too fast to measure
.0005	.001 NO_3^- .03 I^-	.007 OH^-	100% $Pt(dien)OH^+$	Too fast to measure

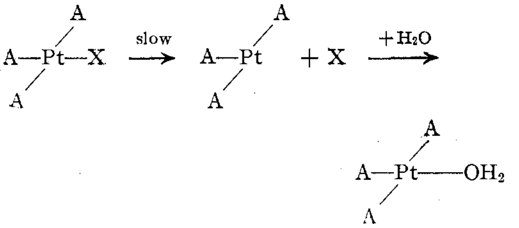
[a] These reactions are rapid and almost completely second order. The halide complexes are the sole initial reaction products, but they subsequently react slowly and completely with the pyridine in solution.

which can lead to an intermediate aquo complex, which in water solution undoubtedly has a tetragonal structure[13]: (a) an SN2 reaction with water, *via* a trigonal bypyramid transition state



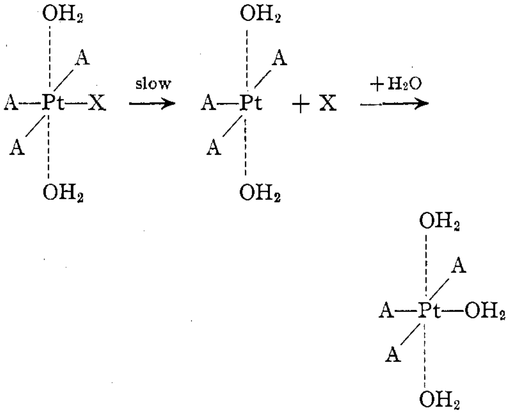
(3)

and (b) a dissociative type mechanism, which can be either an SN1, with no solvent interaction in the transition state



(4)

or a mechanism which allows the two axial solvent molecules to stabilize an unstable square pyramid intermediate



(5)

The evidence against the pure SN1 mechanism (eq. 4) can be summarized by three observations: (a) the first-order rate constants for reactions of platinum(II) complexes in water solution are *invariant* to changes in the net charge on the complex,[3-7,10] (b) sterically hindered platinum(II) complexes, which block the solvent from the metal ion, react much slower (1/20 to 1/100,000) than analogous unhindered complexes,[9,11] and

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[13] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 186.

(c) for reactions in different solvents, first-order rates seem to bear no relation to the dielectric constant of the medium, but, however, do roughly parallel the coördinating ability of the solvent toward platinum(II).[11] On the basis of this evidence the SN1 mechanism will be eliminated, and only paths 3 and 5 will be considered as possible principal reaction mechanisms.

If the dissociative mechanism (eq. 5) leads to the aquo complex intermediate, the square pyramid transition state is required to react only with water, and never with any other potential ligand. Otherwise, the observed first-order radiochloride exchange rates found by Martin, *et al.*,[3-6] would not be directly related to the acid hydrolysis rates of the corresponding chloro complexes. That is, if any other major first-order exchange path exists, such as direct capture of the dissociative transition state by $^{36}Cl^-$, the observed chloride exchange rate would have been faster than the acid hydrolysis rate. For path 5 to be consistent then, the reaction between an aquo complex and an incoming chloride ligand is required to follow a rate law completely first order in chloride. With this restriction, it now is necessary to examine the experimental rates more closely.

Figure 1 shows that plots of k_{obs} *vs.* $[X^-]$ for the reactions of $Pt(dien)H_2O^{2+}$ with Cl^- and NO_2^- give straight lines, but with appreciable and equal intercepts.[14] This intercept is certainly an indication that the aquo complex itself undergoes a reaction which is independent of Cl^- and NO_2^- concentration. As additional evidence, almost perfect first-order kinetic plots were obtained for very low (0.0002–0.0004 *M*) and comparable initial concentrations of $Pt(dien)H_2O^{2+}$ and Cl^- or NO_2^-, the concentration region in which the totally first-order process predominates. The only reasonable totally first-order reaction path available for the aquo complex involves the dissociation of water, thus forming a transition state which should resemble the postulated square pyramid. Since this path is apparently observed and leads to a net chemical reaction, Cl^- and NO_2^- must be able to compete very efficiently with water for this transition state. *Thus, by showing that a dissociative path exists for* $Pt(dien)H_2O^{2+}$, *it is necessary to conclude that the principal mechanism responsible for the observed first-order rates for* $Pt(dien)X^+$ *complexes does not involve this unstable dissociative intermediate. This leaves path 3, involving a trigonal bipyramid intermediate, as the only mechanism consistent with all of the experimental facts.*

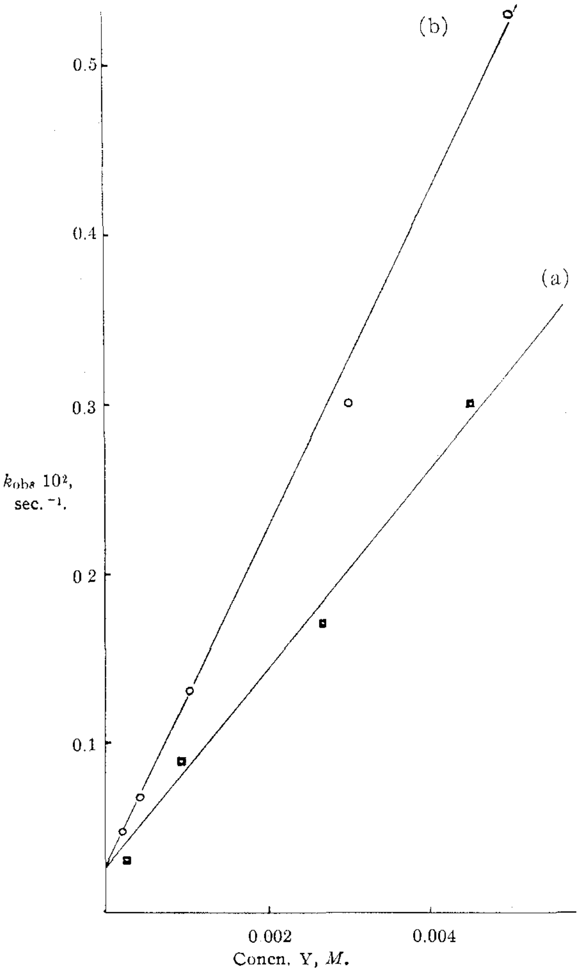

Fig. 1.—Dependence of k_{obs} on concentration of X^- at 25° for $Pt(dien)H_2O^{2+}$ reactions: (a) $X^- = NO_2^-$; (b) $X^- = Cl^-$.

The above interpretation must be viewed with some caution, due to the extreme difficulty of proving the existence of a totally first-order reaction rate for $Pt(dien)H_2O^{2+}$ (or any aquo complex). To appreciate this difficulty, it is sufficient to recall the observed "first-order" reaction between $Rh(NH_3)_5H_2O^{3+}$ and Br^-, which is instead probably second order.[15] The fact that first-order plots of the kinetic data were obtained at low, comparable concentrations of complex and Br^- was attributed to an acceleration of the second-order rate, due to decreasing ionic strength, as the reaction progressed. However, in the present case, since the same "first-order" intercept was obtained for Cl^- and for

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(14) These reactions are singled out because they are slow enough to permit accurate measurements.

(15) A. B. Lamb, *J. Am. Chem. Soc.*, **61**, 699 (1939).

NO_2^- (also for py with the data available), and furthermore since ionic strength effects usually are negligible in all platinum(II) reactions, the totally first-order rate interpretation seems reasonable.

It is interesting to compare the second-order rate constants for Cl^- and NO_2^-, obtained from the slopes of the lines shown in Fig. 1. Nitrite ion actually reacts slower than chloride with this doubly charged platinum(II) complex cation, in sharp contrast to the relative reactivities of these ions with neutral and negatively charged platinum(II) complexes. These data are given in Table III. There is a dramatic decrease in the NO_2^- to Cl^- reactivity ratio in going from $PtCl_4^{2-}$ to $Pt(dien)H_2O^{2+}$, which is consistent with the proposal that the NO_2^- attack on platinum(II) is mainly electrophilic, while the Cl^- attack is mainly nucleophilic.[10]

TABLE III

BIMOLECULAR RATE CONSTANTS IN WATER SOLUTION AT 25° FOR Cl^- AND NO_2^- AS REACTANTS FOR SEVERAL PLATINUM(II) COMPLEXES[a]

Complex	k_2 10^4 M^{-1} sec.$^{-1}$ Cl^-	NO_2^-
$Pt(dien)H_2O^{2+}$	1×10^4	0.56×10^4
$Pt(dien)Br^+$	8.8	37
$Pt(NH_3)_3Cl^+$	0.7	87
trans-$Pt(NH_3)_2Cl_2$	7.8	$>10^4$
$PtCl_4^{2-}$	~ 0	$>10^4$

[a] Data not reported in this work taken from ref. 10.

Acknowledgments.—The authors are indebted to Professor Ralph G. Pearson for several suggestions during the course of this work. This work was supported by the National Science Foundation.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

The Solid Rare Earth Chelates of Ethylenediaminetetraacetic Acid[1]

BY R. S. KOLAT AND J. E. POWELL

Received June 23, 1961

The solid acidic chelates formed by the reaction of the tripositive rare earth ions with the protonated ethylene, diamine-N,N,N′,N′-tetraacetate ligand have been studied by means of thermobalance, infrared, and X-ray diffraction measurements. The oven-dried (110° for 24 hr.) chelates of cerium through samarium were found to be monohydrated, while the remaining members were anhydrous. Infrared studies suggested that the change in hydration number was accompanied by a change in the amino acid ligand from a pentadentate to a hexadentate configuration. Measurements of the acid dissociation constants of these chelates indicated that a corresponding change does not take place in solution.

Introduction

The ability of ethylenediaminetetraacetic acid (abbreviated $H_4(EDTA)$) to form exceptionally stable chelates with the trivalent rare earth ions (abbreviated Ln) is well known. The study of these chelates was initially of a practical nature since differences in the stability constants of chelates of adjacent rare earth ions afford a means of separating rare earth mixtures in ion-exchange systems.[2] However, since the rare earths constitute a series of trivalent ions with gradually decreasing radii, they offer an excellent opportunity to study the theoretical aspects of chelation. Conversely, the study of chelation has afforded a means of comparing the individual properties of rare earth ions. It has been shown that the stabilities of rare earth chelates generally increase as the atomic number increases due to the so-called lanthanide contraction.

Most of the published information on the rare earth chelates has been concerned with their properties in aqueous solutions. Studies of the solid compounds have been limited to several preliminary investigations of rare earth–EDTA chelates. Brintzinger and his co-workers have reported the preparation of the compounds

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[1] Contribution No. 1030. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] F. H. Spedding and J. E. Powell, *Chem. Eng. Progr., Symp. Ser.*, **50**, No. 14 (1954).