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Electrophilic Catalysis in Substitution Reactions of Some Platinum(II) Complexes

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The rate of reaction of *trans*-[Pt(pip)$_2$Cl$_2$] with NO_2^- and $^{36}Cl^-$ in methanol strongly increases in the presence of nitrous acid or boric acid (HA). The reactions *trans*-[Pt(pip)$_2$Cl$_2$] + $Y^- \xrightarrow{(HA)}$ *trans*-[Pt(pip)$_2$YCl] + Cl^- (Y^- = $^{36}Cl^-$ or NO_2^-) take place according to the general rate equation rate = k_1[complex] + k_2[complex][Y^-] + k_3[complex][HA][Y^-]. Nitrous acid exhibits an accelerating effect on the nitrite ion substitution of $PtCl_4^{2-}$, *trans*-[Pt(NH$_3$)$_2$Cl$_2$], and [Pt(dien)Cl]$^+$, but not of [Pt(Et$_4$dien)Cl]$^+$, *trans*-[Pt(pip)$_2$(NO$_2$)Cl], *trans*-[Pt(pip)$_2$Br$_2$], and *trans*-[PtL$_2$Cl$_2$] (L = P(C$_2$H$_5$)$_3$ and As(C$_2$H$_5$)$_3$). For the catalyzed step, a mechanism is proposed involving the formation of a transient intermediate between the complex and HNO_2 or H_3BO_3 followed by a facilitated nucleophilic addition and rearrangement as the rate-determining step.

Introduction

Previous work[1] on *trans*-[Pt(py)$_2$Cl$_2$] has shown that the rate of chloride ion exchange strongly increases in the presence of some acidic compounds such as CH_3COOH, CF_3COOH, and H_3BO_3. This accelerating effect has been attributed to the ability of these compounds to interact with the electrons in the filled d orbitals on platinum by making use of empty π orbitals on the acids. Since acetate and borate ions do not exhibit the same accelerating effect, it has been concluded that these π orbitals are less available in the anionic forms. It was recently observed[2] that nitrous acid in small amounts may have a pronounced accelerating effect on the reactions of some platinum(II) complexes with nitrite ion. For example, it was found that addition of acid greatly accelerated the replacement by NO_2^- of the first Cl^- of *trans*-[Pt(pip)$_2$Cl$_2$], whereas acid had no effect on the rate of substitution of the second chloride ion.[3] It has also been reported that the reaction of *trans*-[Pt(NH$_3$)$_2$(NO$_2$)Cl] with NO_2^- is accelerated in the presence of acetic acid or hydrochloric acid.[4] The reaction appears to proceed *via* the aquo compound *trans*-[Pt(NH$_3$)$_2$(NO$_2$)H$_2$O]$^+$.

Since this catalytic phenomenon had not been further investigated, it was decided to study the kinetics of one such system in some detail. This paper reports the results obtained for the reaction of *trans*-[Pt(pip)$_2$Cl$_2$] with NO_2^- and with Cl^- in the presence of HNO_2 and of H_3BO_3.

Experimental

Materials.—Most of the complexes used in this investigation were known compounds and were prepared by the methods reported previously.[2,5] The preparations of three compounds not mentioned earlier are included.

trans-[Pt(pip)$_2$(NO$_2$)$_2$] was obtained by the reaction between *trans*-[(Pt(pip)$_2$Cl$_2$] and 2 equiv. of $NaNO_2$ in methanol at 30° for 24 hr. The solvent was evaporated under vacuum and the solid residue was washed with water and repeatedly recrystallized from CH_3OH; m.p. 260°.

trans-[Pt(pip)$_2$(NO$_2$)Cl] was prepared by making use of the observation that HNO_2 catalyzes the replacement of Cl^- from *trans*-[Pt(pip)$_2$Cl$_2$] but has no effect on the rate of reaction of *trans*-[Pt(pip)$_2$(NO$_2$)Cl]. This compound was prepared by the reaction of *trans*-[Pt(pip)$_2$Cl$_2$](10^{-2} *M*) with $NaNO_2$ (10^{-2} *M*) in CH_3OH and in the presence of *p*-toluenesulfonic acid (10^{-3} *M*) at 30° for 24 hr. The liquid was evaporated and the solid residue was washed with water and then recrystallized from methanol; m.p. 243°.

[Pt(pip)$_2$(NO)(NO$_2$)Cl$_2$] was obtained by the reaction between *trans*-[Pt(pip)$_2$(NO$_2$)Cl] and excess NOCl in anhydrous chloroform at 20°. After 1 hr., the solvent was evaporated under vacuum and the solid was recrystallized from anhydrous chloroform.

All of the complexes prepared were analyzed for platinum by combustion to constant weight of metal in a porcelain crucible.

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

[2] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *ibid.*, **87**, 241 (1965).

[3] U. Belluco, L. Cattalini, and A. Turco, *ibid.*, **86**, 3257 (1964).

[4] A. A. Babaeva and R. I. Rudyi, *Russ. J. Inorg. Chem.*, **6**, 1244 (1961).

[5] The symbols used are pip = piperidine, dien = diethylenetriamine, (Et$_4$dien) = 1,1,7,7-tetraethyldiethylenetriamine.

The results obtained were in good agreement with the values calculated for each compound. The absorption spectra of these complexes are shown in Figure 1.

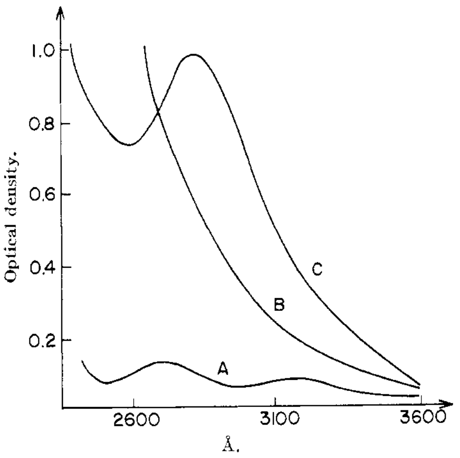

Figure 1.—Spectra in methanol at 30° of: A, *trans*-[Pt(pip)$_2$Cl$_2$]; B, *trans*-[Pt(pip)$_2$(NO$_2$)$_2$]; C, *trans*-[Pt(pip)$_2$(NO$_2$)Cl]. Complex concentration 7 × 10^{-4} *M;* cell length 1 cm.

Kinetics.—The reactions were followed spectrophotometrically by means of a Beckman DU and a Beckman DK-2A recording apparatus with appropriate attachments to maintain the reaction mixture at constant temperature. The spectral changes in the region of 230–320 mμ during the reaction were recorded, and in those cases where the substrate and product have the same absorbancy at some wave length in this region, the spectra showed well-defined isosbestic points. Pseudo-first-order rate constants, k_{obsd}, were obtained graphically by means of the usual first-order plot. Some kinetic runs were made several times under the same conditions and the values of k_{obsd} were generally reproducible to better than 5%. The effect of ionic strength is small judging from a study of the rates of reactions of *trans*-[PtL$_2$Cl$_2$] with various nucleophiles at different ionic strengths.[2] Likewise investigations of the effect of CH$_3$O$^-$ show it is a very poor reagent and its presence does not alter the rates of reaction of these substrates.

The method used to determine the rates of isotopic exchange of the complex with Li^{36}Cl is that described earlier.[6]

Reaction of *trans*-[Pt(pip)$_2$Cl$_2$] with NO$_2^-$ in CH$_3$OH.—These reactions were followed spectrophotometrically using an excess of NO$_2^-$ reagent and maintaining the ionic strength constant at 0.11 *M* with LiNO$_3$. Preliminary spectrophotometric tests showed that NO$_3^-$, CH$_3$O$^-$, *p*-toluenesulfonic acid, CCl$_3$COOH, H$_3$BO$_3$, and HClO$_4$ do not react with the dichloro compound. All three of the complexes involved, dichloro, chloronitro, and dinitro *trans*-[Pt(pip)$_2$X$_2$], obey Beer's law in CH$_3$OH in the 240–320 mμ region, for the range of concentration used. There is no *cis–trans* isomerization at these conditions.

In some runs carried out in the presence of NaNO$_2$ (10^{-2}–10^{-1} *M*) and CH$_3$O$^-$ ([CH$_3$O$^-$] = 0.05[NO$_2^-$]),[7] the final product was *trans*-[Pt(pip)$_2$(NO$_2$)$_2$] and it was not possible to detect the presence of the intermediate *trans*-[Pt(pip)$_2$(NO$_2$)Cl], because the replacement of both Cl$^-$ groups takes place with comparable rates. The spectral changes for the reaction examined at these conditions are shown in Figure 2.

With the addition of a small amount of acid to this reaction mixture, the results observed are dramatically different from those of the reaction without added acid, as is shown in Figure 3. Under these conditions, *trans*-[Pt(pip)$_2$(NO$_2$)Cl] can be detected and the isosbestic point at 265 mμ is due to this compound and to the dinitro compound.

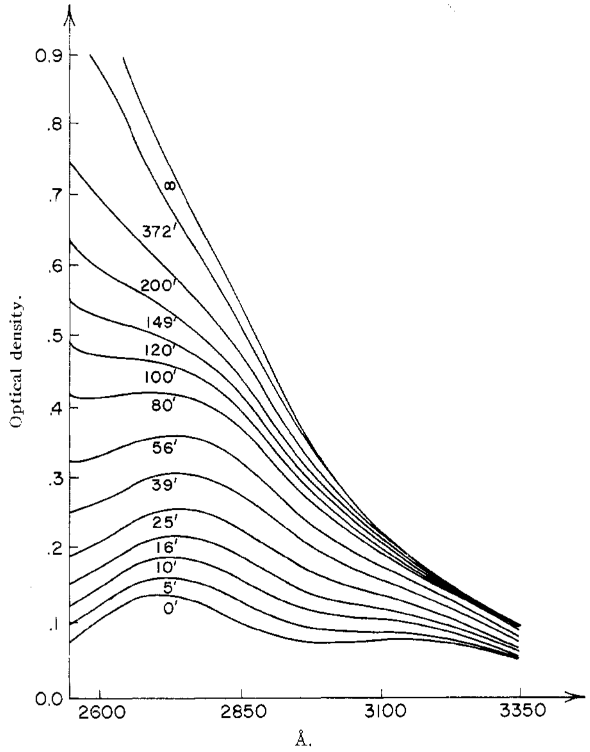

Figure 2.—Spectral changes during the reaction in methanol at 30° of *trans*-[Pt(pip)$_2$Cl$_2$] (0 time) with NO$_2^-$ to yield *trans*-[Pt(pip)$_2$(NO$_2$)$_2$] (infinite time). Complex concentration 7 × 10^{-4} *M;* cell length 1 cm.

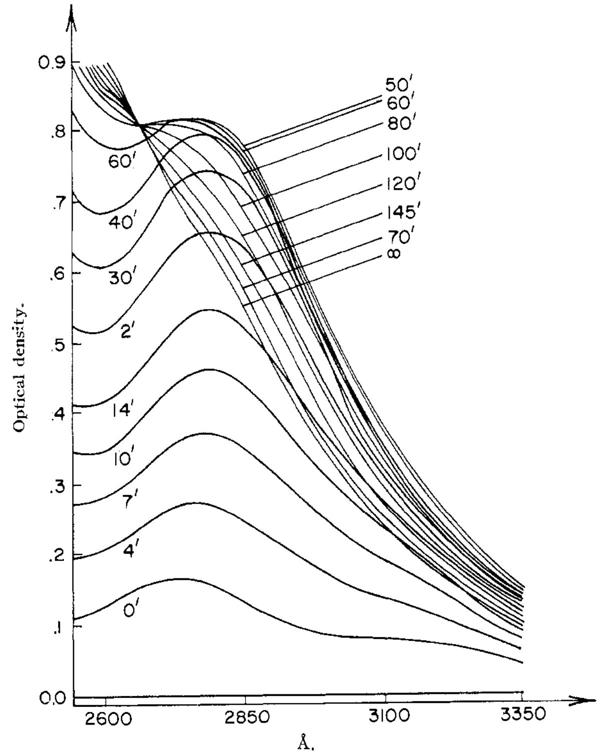

Figure 3.—Spectral changes during the reaction in methanol at 30° of *trans*-[Pt(pip)$_2$Cl$_2$] with NO$_2^-$ in the presence of HNO$_2$ to yield *trans*-[Pt(pip)$_2$(NO$_2$)$_2$]. Complex concentration 7 × 10^{-4} *M;* cell length 1 cm.

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(6) U. Belluco, L. Cattalini, and A. Turco, *J. Am. Chem. Soc.*, **86**, 226 (1964).

(7) Methoxide ion was added in order to repress the formation of HNO$_2$ resulting from the methanolysis of NO$_2^-$.

The rate of reaction 1 was followed by measuring the changes

$$trans\text{-}[Pt(pip)_2Cl_2] + NO_2^- \xrightarrow{HNO_2} trans\text{-}[Pt(pip)_2(NO_2)Cl] + Cl^- \quad (1)$$

in optical density at 265 mμ of a reaction mixture over a period of time and estimating the decrease in concentration of the starting material. This was done using the equation $D_\lambda = \epsilon_1(a - x) + \epsilon_2 x$ to calculate the concentration of the unreacted *trans*-$[Pt(pip)_2Cl_2]$ at various times during the course of reaction. In this equation D_λ is the optical density at 265 mμ, a is the initial concentration of the dichloro compound, ϵ_1 is its molar extinction coefficient at 265 mμ, ϵ_2 is the molar extinction coefficient of the chloronitro and the dinitro complexes at 265 mμ, and x is the concentration of the reacted *trans*-$[Pt(pip)_2Cl_2]$ at time t.

The rate of displacement of the second Cl^- (2) was followed

$$trans\text{-}[Pt(pip)_2(NO_2)Cl] + NO_2^- \rightarrow trans\text{-}[Pt(pip)_2(NO_2)_2] + Cl^- \quad (2)$$

at 280 mμ, where the difference of the absorbances of starting material and final product is largest. In these experiments solutions of *trans*-$[Pt(pip)_2(NO_2)Cl]$ were used.

Results and Discussion

Extensive kinetic studies[8] of substitution reactions of platinum(II) complexes show that these reactions proceed by a two-term rate law (3), where k_1 is a first-

$$\text{rate} = k_1[\text{complex}] + k_2[\text{complex}][Y] \quad (3)$$

order rate constant and k_2 is a second-order rate constant for the direct reagent displacement path.

The data in Tables I, II, and III show that the rates of reaction of *trans*-$[Pt(pip)_2Cl_2]$ witn NO_2^- or $^{36}Cl^-$ are markedly increased upon the addition of HNO_2 or H_3BO_3. Furthermore the results obtained are in good agreement with the three-term rate expression (4), where k_{obsd} is the experimental first-order rate constant and k_3 is the rate constant for the reaction path in which the complex, the reagent Y, and the acid HA are all present in the activated complex. Consistent with (4), the linear plot of Figure 4 was obtained by plotting k_{obsd} (Table I) *vs.* $[HNO_2]$ at constant $[NO_2^-]$. The slope of this line gives k_3 (M^{-2} sec.$^{-1}$); the intercept at $[HNO_2] = 0$ is equal to $k_1 + k_2[NO_2^-]$. The intercept value obtained is in good agreement with the values of $k_1 = 1.2 \times 10^{-5}$ sec.$^{-1}$ and $k_2 = 2.04 \times 10^{-3}$ M^{-1} sec.$^{-1}$ that were determined independently[2] in the absence of HNO_2.

$$k_{obsd} = k_1 + k_2[Y] + k_3[HA][Y] \quad (4)$$

TABLE I

RATES OF THE REACTION

trans-$Pt(pip)_2Cl_2 + NO_2^- \rightarrow$ *trans*-$[Pt(pip)_2(NO_2)Cl] + Cl^-$ IN THE PRESENCE OF HNO_2[a]

Experiment no.	HNO_2,[b] 10^3M	NO_2^-, 10^3 M	10^4k_{obsd}, sec.$^{-1}$	k_3[c]
1	0.0	20.0	0.5	. . .
2	0.5	20.0	1.8	13
3	1.0	20.0	3.3	14
4[d]	1.0	20.0	4.5	14
5	1.6	20.0	4.6	13
6	3.4	20.0	10	14
7	5.2	20.0	15	14
8	6.4	20.0	18	14
9[e]	6.4	20.0	18	14
10	8.0	20.0	22	13
11	12.8	20.0	36	14
12	1.32	0.0	0.01	. . .
13	1.32	5.0	1.1	13
14	1.32	11.6	2.6	14
15	1.32	16.6	3.7	14

[a] Solvent CH_3OH; temperature 30°; [complex] $= 7 \times 10^{-4}$ M; $\mu = 0.1$ M with $LiNO_3$. [b] The HNO_2 in solution was formed by the addition of either CCl_3COOH or *p*-toluenesulfonic acid to the solution of $NaNO_2$. [c] k_3 in M^{-2} sec.$^{-1}$; $k_3 = (k_{obsd} - (k_1 + k_2[NO_2^-]))/[HNO_2][NO_2^-]$; $k_1 = 1.2 \times 10^{-5}$ sec.$^{-1}$; $k_2 = 2.04 \times 10^{-3}$ M^{-1} sec.$^{-1}$.[2] [d] Temperature 45°; $k_1 = 5 \times 10^{-5}$ sec.$^{-1}$; $k_2 = 62.5 \times 10^{-4}$ M^{-1} sec.$^{-1}$. [e] Added acid $= HClO_4$.

TABLE II

RATES OF ISOTOPIC EXCHANGE OF *trans*-$[Pt(pip)_2Cl_2]$ WITH $Li^{36}Cl$ IN THE PRESENCE OF HNO_2[a]

Experiment no.	HNO_2, 10^3M	$^{36}Cl^-$, 10^3M	10^4k_{obsd}, sec.$^{-1}$	k_3[b]
16	0.0	44	0.7	. . .
17	1.1	44	1.1	1.2
18	4.4	44	3.2	1.4
19	4.4	11	0.78	1.2

[a] Solvent CH_3OH; temperature 30°; [complex] $= 5 \times 10^{-3}$ M; $\mu = 0.1$ M with $LiNO_3$. [b] $k_3 = (k_{obsd} - (k_1 + k_2[Cl^-]))/[HNO_2][Cl^-]$; $k_1 = 1.2 \times 10^{-5}$ sec.$^{-1}$; $k_2 = 0.925 \times 10^{-3}$ M^{-1} sec.$^{-1}$.[2]

A reaction mechanism to explain the third term in the rate law is shown in Figure 5. The catalyzed path is shown as involving the rate-determining reaction of a six-coordinated platinum(II) complex with HNO_2 (H_3BO_3) and NO_2^- (Cl^-) occupying the fifth and sixth coordination sites. There are several conceivable paths whereby this intermediate could decompose to the final product. In the absence of any real evidence, the mechanism has been kept as much like that of the uncatalyzed reactions of platinum(II) complexes as possible. Thus the formation of a trigonal bipyramidal, five-coordinated intermediate is shown as rate-determining.

TABLE III

RATES OF THE REACTION *trans*-$[Pt(pip)_2Cl_2] + NO_2^- \rightarrow$ *trans*-$[Pt(pip)_2(NO_2)Cl] + Cl^-$ IN THE PRESENCE OF H_3BO_3[a]

Experiment no.	H_3BO_3, 10^3M	NO_2^-, 10^3M	10^4k_{obsd}, sec.$^{-1}$	k_3[b]
20	. . .	80	1.6	. . .
21	8	40	4.2	1.0
22	8	80	8.7	1.1

[a] Solvent CH_3OH; temperature 30°; [complex] $= 7 \times 10^{-4}$ M; $\mu = 0.1$ M with $LiNO_3$. [b] $k_3 = (k_{obsd} - (k_1 + k_2[NO_2^-]))/[H_3BO_3][NO_2^-]$.

The mechanism is identical with what has previously been proposed[8] except that HNO_2 takes the place of one solvent molecule. The catalysis occurs either because there is a higher concentration of the six-coordinated

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[8] (a) H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962); H. B. Gray and R. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962); (b) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 388 (1962).

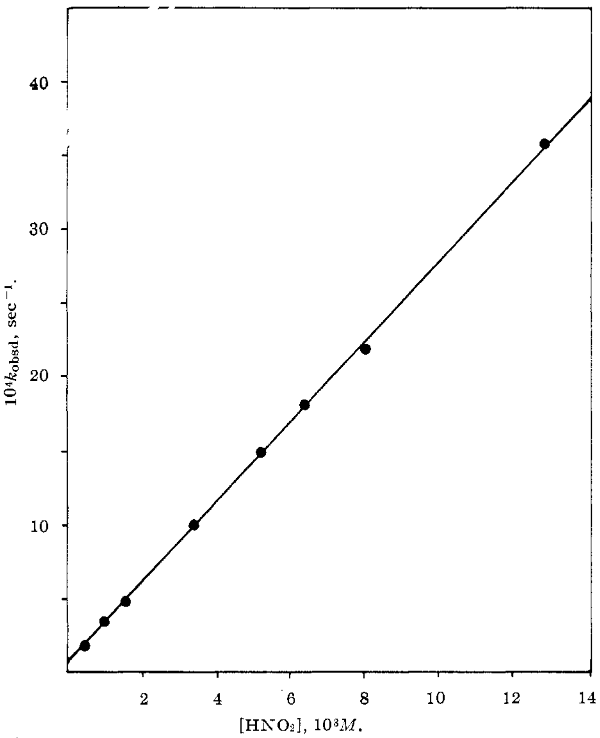

Figure 4.—Rates of reaction, k_{obsd}, of *trans*-[$Pt(pip)_2Cl_2$] in methanol at 30° to yield *trans*-[$Pt(pip)_2(NO_2)Cl$] as a function of the concentration of HNO_2 at constant NO_2^- concentration (20×10^{-3} *M*).

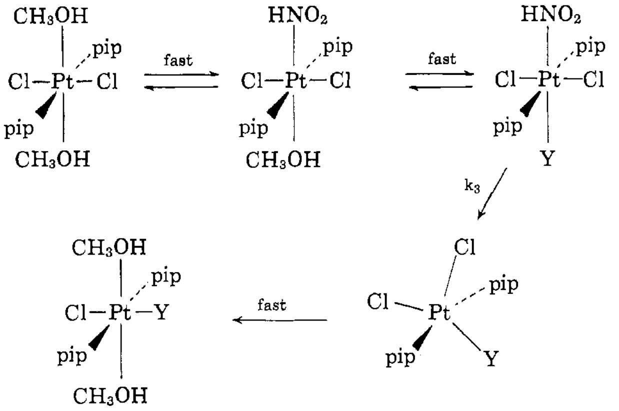

Figure 5.—Mechanism of Cl^- displacement from *trans*-[$Pt(pip)_2Cl_2$] by NO_2^- and $^{36}Cl^-$ catalyzed by HNO_2 in methanol solution.

intermediate containing the reagent Y or because it reacts more rapidly. The first explanation seems more plausible since the assumed role of nitrous or boric acid is to remove π electrons from platinum. This in turn would make it easier for the metal to accept σ electrons from a nucleophile such as NO_2^- or Cl^-.

There is evidence to support the idea that increasing positive charge on the central atom accelerates the rate of reaction of planar complexes. For example, gold(III) complexes react about 10^4 times faster than the analogous isoelectronic Pt(II) complexes.[9] It is also noteworthy that the reactions of cationic Au(III) complexes proceed almost exclusively by the reagent path, with the solvent making only a negligible contribution to the over-all rate of reaction. Here also the experimental results for the reaction of *trans*-[$Pt(pip)_2Cl_2$] show no catalysis of the solvent path.

It is significant that the mechanism proposed in Figure 5 for the acid-catalyzed reaction requires that the five-coordinated species shown be an active intermediate and not an activated complex. This is necessary because the rate data show that the acid is present in the transition state, but it is not present in the five-coordinated species which therefore cannot be the activated complex. Stable five-coordinated complexes of Pt(II) have been isolated and shown to have a trigonal bipyramidal structure.[10]

Several other observations were made which can be adequately explained on the basis of this mechanism for acid catalysis. There is no direct evidence for the formation of a species of the type *trans*-[$Pt(pip)_2Cl_2$]···HNO_2 in this system, but Haake[11] reports that the addition of NO_2^- to a water solution of *cis*-[$Pt(NH_3)_2(NO_2)Cl$] causes an immediate change in the ultraviolet spectrum of the complex, followed by slow chloride ion displacement. The spectral changes were attributed to association of NO_2^- to the complex. We have repeated this experiment and obtained the same results but also find that at pH >7 in aqueous solution there is no immediate change in the spectrum of the complex upon addition of NO_2^-. This change appears only at pH <7, becoming more intense with increasing acidity, and presumably is due to the presence of HNO_2 resulting from the hydrolysis of NO_2^-. If the interaction is largely with the filled d orbital electrons on Pt(II), then it is to be expected that an associated species would form more readily with HNO_2, which is more electrophilic than NO_2^-.

Under the conditions of Tables I and II it was found that the reactions of *trans*-[$Pt(P(C_2H_5)_3)_2Cl_2$], *trans*-[$Pt(As(C_2H_5)_3)_2Cl_2$], *trans*-[$Pt(pip)_2(NO_2)Cl$], [$Pt(Et_4dien)Cl]^+$, and *trans*-[$Pt(pip)_2Br_2$] were not catalyzed by HNO_2. This can be explained on the basis of the proposed mechanism for all of the compounds, except perhaps the last one. Thus, the first three compounds contain the π-electron-withdrawing ligands $P(C_2H_5)_3$, $As(C_2H_5)_3$, and NO_2^-, respectively. While π bonding in the ground state may be small,[12] the addition of a nucleophile will produce a stress which these ligands can alleviate by increased π bonding. Thus, these ligands take the place of the nitrous acid, which is then not required or, at least, is not as helpful. It is also possible that bromide ion can be a sufficiently good π acceptor, under conditions of stress due to a high electron density on the platinum. This would explain the lack of catalysis in [$Pt(pip)_2Br_2$].

For the complex [$Pt(Et_4dien)Cl]^+$, the Pt(II) is

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[9] W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964).

[10] G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 170 (1961); R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).

[11] P. Haake, *Proc. Chem. Soc.*, 278 (1962).

[12] L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956); D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964); C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, Chapter 9, p. 7.

shielded by the four ethyl groups preventing it from interacting with HNO_2 along the z axis.[13] Reactions of the analogous complex $[Pt(dien)Cl]^+$, where Pt(II) is accessible, are catalyzed by HNO_2. This observation is important because it supports the view that interaction with Pt(II) is involved rather than an electrophilic attack on the departing Cl^-.

We have also observed qualitatively that there is a nitrous acid catalysis of the reactions of nitrite ion with *trans*-$[Pt(NH_3)_2Cl_2]$ and with $PtCl_4^{2-}$. In aqueous solution at pH >7 these reactions are much slower than previously reported.[8] This suggests that the more rapid rates are due to catalysis by small amounts of HNO_2 resulting from the solvolysis of NO_2^-.

That boric acid and acetic acid, which can behave as electrophiles, are also catalysts for these reactions affords support to the proposed mechanism. However, alternative mechanisms for the catalysis by HNO_2 have been considered and some experiments were done that show these to be unlikely. The possibility exists of an oxidation–reduction catalysis involving labile Pt(III) species[14] formed as a result of the reaction of Pt(II) with HNO_2. In order to test this possibility, duplicate experiments were carried out in the presence of added Ce(IV) or Pt(IV) and in every case the values of k_{obsd} were the same as was found in the absence of these substances.

Nitrosyl–platinum complexes of the types PtA_4NOX and PtA_2Y_2NOX can be prepared by the reaction of NOX with platinum(II) complexes.[15] Here NOX is a species such as N_2O_3 or NOCl. The form of rate law 1 argues against a rate-determining step with either of these possible reactants. When only nitrous acid is present, for example, there is no reaction whatever (see Table I). A reaction with N_2O_3 would give a rate dependent on the square of the HNO_2 concentration, *e.g.*

$$2HNO_2 \overset{\text{fast}}{\rightleftharpoons} N_2O_3 + H_2O$$

Furthermore, the complex $[Pt(pip)_2NONO_2Cl]_2$, which might be an intermediate in the nitrous acid catalyzed reaction, was prepared according to the directions in the literature[15] and it was found to be unreactive under our reaction conditions. Hydrazoic acid was found not to be a catalyst in spite of potential π bonding capability. This suggests that hydrogen bonding of H in HA to the leaving halide ion at the same time that A is π bonded to Pt(II) may be important. This same suggestion was made earlier[1] to explain why methyl acetate and methyl borate were not catalysts.

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[13] W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

[14] R. L. Rich and H. Taube, *ibid.*, **76**, 2608 (1954).

[15] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 775 (1961); I. I. Chernyaev and L. A. Nazarova, *Russ. J. Inorg. Chem.*, **8**, 1049 (1963); L. L. Flores, I. Raskovan, and R. Levitus, *J. Inorg. Nucl. Chem.*, **26**, 1126 (1964).

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The Kinetics of Replacement Reactions of Complexes of the Transition Metals with 1,10-Phenanthroline and 2,2′-Bipyridine

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The kinetics of formation and dissociation of metal complexes of 1,10-phenanthroline, 2,2′-bipyridine, and some related ligands have been measured by the stopped-flow method. The second-order formation rate constant for the mono complex increases in the sequence $Ni^{2+} < Co^{2+} < Fe^{2+} \sim Mn^{2+} < Zn^{2+} < Cu^{2+} \sim Cd^{2+} < Ag^+ < Hg^{2+}$. Although most attention was directed to the 1:1 complexes, some of the reactions of the higher species were examined also. Agreement between thermodynamic data obtained from kinetic and equilibrium studies was good. The results are discussed in terms of current ideas on the mechanism of complex ion reactions.

Introduction

When this work was commenced it was becoming apparent that the rate constants for the formation of nickel complexes with a variety of ligands were similar and that dissociation of the complex controlled its stability.[2] At the same time, it was clearly emerging that the formation of complexes of the bivalent transition metals, at least with simple ligands, was controlled by the water exchange rate of the aquated metal ion, and that once again the ligand had a minimal influence.[3]

It seemed worthwhile then to investigate the general

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[2] A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 2901 (1960).

[3] M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960); M. Eigen, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 371.