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The Acid-Catalyzed Reactions of Transition Metal Complexes. VII. The Acid-Catalyzed Hydrolysis of Some Dinitrodiamineplatinum(II) Compounds

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The acid catalyzed hydrolysis of a series of complexes of the type *cis*-$PtA_2(NO_2)_2$ (where A = pyridine, 4-picoline, 3,5-lutidine, 4-cyanopyridine, 4-isopropylpyridine, 0.5 2,2′-dipyridyl) in aqueous solutions of sulfuric acid at 15.4° have been studied. For all of the substituted pyridine complexes, except the isopropyl compound, the rate of hydrolysis is very insensitive to the substituent in the pyridine ring. The dipyridyl complex is appreciably more reactive than the corresponding dipyridine compound. Analysis of the results by the methods of Bunnett and of Zucker and Hammett favors a unimolecular mechanism involving the protonated substrate.

Introduction

Although several researches on the acid-catalyzed hydrolysis of octahedral cobalt(III) complexes have been published, relatively little work on the corresponding hydrolyses of square-planar platinum(II) complexes has been reported. The dinitrodipyridineplatinum(II) complexes provide a useful series of compounds for such a study especially as various substituents may be used in the pyridine ring.

Experimental Section

Preparations.—Potassium tetranitroplatinate(II) dihydrate[2] was prepared by the action of excess potassium nitrite on potassium tetrachloroplatinate(II). ***cis*-Dinitrodipyridineplatinum(II) and its analogs** were prepared as follows. A solution of the required pyridine (2 mol) in water or acetone was added to an aqueous solution of potassium tetranitroplatinate(II) dihydrate (1 mol). The solution was gently warmed and stirred, and a white precipitate formed after 15 min. The mixture was heated for 2 hr and then cooled and allowed to stand for 12 hr. The precipitate was filtered off, washed with alcohol and then ether, and dried. Analyses are shown in Table I.

Isolation of Reaction Products.—*cis*-Dinitrodipyridineplatinum(II) (0.07 g) was dissolved in 76% sulfuric acid (5 ml). After 4 hr the solution was cooled in an acetone–solid carbon dioxide bath and diluted to *ca.* 15 ml. Solid potassium chloride (0.31 g) was added and the solution became green. After shaking for 1 or 2 min, a fine precipitate appeared. The mixture was allowed to stand for 10 min, and then the pale yellow precipitate was filtered off, washed with water, alcohol, and ether, and dried.

cis-Dinitrodipyridineplatinum(II) factor yielded chloronitrodipyridineplatinum(II). *Anal.* Calcd for $PtC_{10}H_{10}N_3O_2Cl$: C, 27.6; H, 2.30; Pt, 44.81. Found: C, 27.6; H, 2.31; Pt, 45.0. (It is noteworthy that the carbon content is a sensitive pointer to the loss of coordinated pyridine.)

Kinetic Measurements.—The solvent acids contained in Pyrex vessels were placed in a thermostat to attain the required temperature, and the complex (accurately weighed) was added in a porcelain boat. The mixture was shaken rapidly to dissolve the complex and aliquot portions (1 ml) were removed at timed intervals and rapidly pipetted into Pyrex tubes contained in an acetone–solid carbon dioxide bath. After 2 or 3 min the aliquots were carefully diluted while still in the cold bath. (Test experiments showed that this did not lead to a rise in temperature significant enough to affect the results.) The nitrite replaced was estimated colorimetrically by the procedure previously described.[3,4] All of the reaction solvent acids contained sulfanilic acid (*ca.* 0.1 g/20 ml of solvent) which was added about 20 min before the runs were started. The replaced nitrite diazotized an equivalent quantity of sulfanilic acid.

Results

When complexes of the type *cis*-dinitrodipyridineplatinum(II) are dissolved in solutions of moderately concentrated sulfuric acid, *i.e.*, 75% and lower, one of the nitro groups is replaced and the overall reaction may be written

$$Pt(py)_2(NO_2)_2 + H_3O^+ \longrightarrow Pt(py)_2NO_2(H_2O)^+ + HNO_2$$

At higher concentrations of sulfuric acid the situation is more complicated. The main features of the dependence of the rate of hydrolysis on (i) the acid concentration and (ii) the substituent in the pyridine ring are illustrated in Figure 1 and may be summarized as follows. (1) At the lower acid concentrations studied, log k (k = first-order rate constant) *vs.* acidity function H_0 is a straight line of unit slope (region A in Figure 1). (2) As the acid concentration increases, a region (region B) is reached in which the rate of hydrolysis is nearly independent of the acid concentration. (3) However, at the highest acid concentration (region C), the rate of hydrolysis is again acidity function dependent. There are at least two possible explanations for this second increase in rate with acid concentration, *viz.*, (a) a nitro group is being replaced from a doubly, as opposed to a singly, protonated complex ion and /or (b) the second nitro group is being replaced extremely rapidly. Typical results are given in Table II.

Another notable feature of the results is that, except at the highest acid concentrations used (region C), the rate of hydrolysis is virtually independent of the substituent in the pyridine ring. There appears to be some dependence of hydrolysis rate on ring substituent in region C. The fact that all of these complex substrates are hydrolyzed at similar rates in a given acid concentration gave rise to the suspicion that the pyridine ligands were replaced very rapidly before the loss of the nitro groups. (*I.e.*, in each case were we

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(1) To whom requests for reprints should be sent.

(2) J. R. Kuebler, Jr., and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **74**, 3535 (1952).

(3) P. J. Staples, *J. Chem. Soc., A*, 45 (1967).

(4) K. Anne Pilkington and P. J. Staples, *J. Inorg. Nucl. Chem.*, **29**, 1029 (1967).

Table I

Analyses

Compound	% found C	% found H	% found N	% calcd C	% calcd H	% calcd N
cis-Pt(py)$_2$(NO$_2$)$_2$	26.9	2.41	12.65	27.0	2.25	12.6
cis-Pt(4-pic)$_2$(NO$_2$)$_2$	30.0	2.94	12.15	30.4	2.96	11.8
cis-Pt(4-*i*-C$_3$H$_7$-py)$_2$(NO$_2$)$_2$	35.9	4.4	10.7	36.3	4.2	10.5
cis-Pt(3,5-lutidine)$_2$(NO$_2$)$_2$	33.6	3.63	11.2	33.6	3.60	11.2
cis-Pt(4-cyanopy)$_2$(NO$_2$)$_2$	29.25	1.58	16.6	29.1	1.61	16.9
Pt-2,2′-dipy(NO$_2$)$_2$[a]	27.3	2.0	...	27.1	1.8	...
trans-Pt(py)$_2$(NO$_2$)$_2$	26.95	2.5	12.7	27.0	2.25	12.6

[a] Pt: found, 44.3; calcd, 44.0.

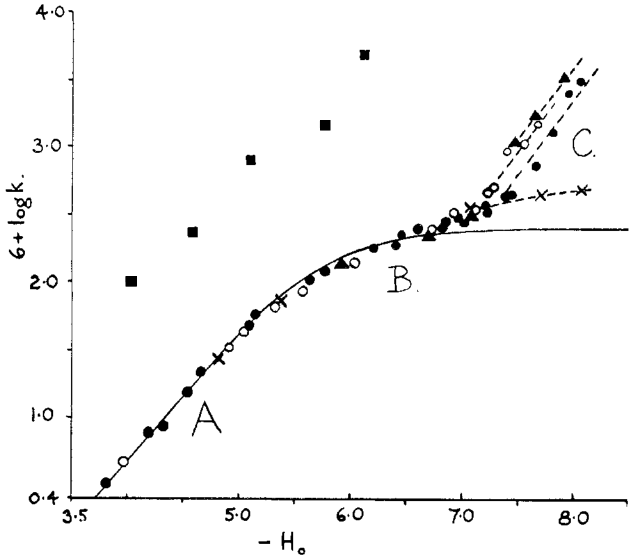

Figure 1.—Variation of rate of hydrolysis of some *cis*-dinitrobis(pyridine–X)platinum(II) complexes with sulfuric acid concentration at 15.4°. X = hydrogen, ●; 4-methyl, ○; 3,5-dimethyl, ▲; 4-cyano, ×; 2,2′-dipyridyl, ■. The continuous line was calculated using eq 1 with K_a = 5.29 × 10^5 and 10^4k_2 = 2.5 sec^{-1}.

Table II

First-Order Rate Constants for the Hydrolysis of *cis*-Dinitrodipyridineplatinum(II) in Aqueous Sulfuric Acid at 15.4°

[H$_2$SO$_4$], *M*	10^4k, sec^{-1}	[H$_2$SO$_4$], *M*	10^4k, sec^{-1}	[H$_2$SO$_4$], *M*	10^4k, sec^{-1}
7.90	0.032	12.48	1.86	13.82	3.36
8.60	0.076	12.57	2.29	14.13	4.33
9.30	0.154	12.79	2.50	14.17	4.81
9.50	0.214	13.12	2.51	14.51	7.2
10.32	0.473	13.18	2.76	14.78	12.8
10.44	0.577	13.43	2.98	15.02	25
11.25	1.02	13.47	2.89	15.17	31
12.13	1.79	13.78	3.66		

studying the rate of loss of a nitro group from an equilibrium mixture of *cis*- and *trans*-diaquodinitroplatinum(II) complexes?) Proof that the pyridine ligands were not being replaced came from experiments in which the reaction solution was quenched by cooling and dilution after 7 half-lives. The solution was treated with potassium chloride and a precipitate of a chloronitrodipyridine complex was obtained (see Experimental Section). Further evidence that the pyridine ligands were not replaced came from (a) a comparative study of the ultraviolet spectra of product solutions and of pyridine and pyridine plus complex solutions and (b) a colorimetric test for pyridine on the diluted solution.

The so-called "*trans* effect" which has been widely applied in the preparative chemistry of platinum(II) compounds is apparent in these acid-catalyzed systems. In the cases of dinitrodipyridineplatinum(II) and the dinitrodiamine[5] analogs, the *trans* isomer is more reactive than the *cis* complex; *i.e.*, in acid of a given concentration the *trans* isomer reacts faster than the *cis* complex. However, in the case of the dinitrobis(diethyl sulfide)platinum(II) complexes[5] the reverse appears to be true. This is in agreement with a *trans*-effect order: S(C$_2$H$_5$)$_2$ > NO$_2$ > py or NH$_3$.

Discussion

The three regions of Figure 1 may be interpreted as follows. Region A corresponds to the replacement of one nitro group from a substrate which is appreciably monoprotonated. Region B corresponds to the rate of replacement of a nitro group from a complex substrate which is fully monoprotonated. Region C is less easy to interpret unambiguously. The rate constants which were measured in this region referred to the replacement of the first nitro group (*i.e.*, the "infinity reading" for the reaction was equivalent to one nitro group, not two). It was found, however, that the second nitro group was replaced at a measurable rate. The increase in rate observed in region C may be considered as arising from one or more of the following conditions. The simplest of these is that the aquonitro complex product is itself protonated and then loses nitrous acid to yield the diaquo complex. This mechanism cannot, however, be the sole explanation of the observed effect since this implies that the second limiting rate constant would be not more than twice as great as the first limiting rate constant (*i.e.*, corresponding to a measurable reaction followed by an immeasurably fast reaction giving an over-all rate constant equal to twice that for the rate-determining step). The experimental results are consistent with the alternative explanation that two protons are added to the dinitro substrate and that the nitro groups are lost from a double protonated intermediate. This reaction would be simultaneous with the reaction of regions A and B and thus there is no calculable upper limit for its rate constant. However, although it is possible to rule out a purely consecutive mechanism, it is not pos-

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[5] D. Colenutt, P. J. Staples, and A. Thompson, unpublished results.

sible to show whether region C is due purely to the simultaneous reaction or to a mixture of the consecutive and simultaneous paths.

The lack of change in rate of hydrolysis as the substituent in the pyridine ring changes calls for comment. Although this lack of change of rate of reaction as substituent changes has been encountered before[6] in the aquation of platinum(II) complexes, the similarity in behavior is even more marked in our results. The complexes which actually exist in solution will be very similar indeed because the two axial positions will almost certainly be occupied, *i.e.*, most probably by water molecules or possibly, but less likely, by bisulfato groups. The effect of these water molecules on the energy levels of the 5d orbitals would be quite marked and could easily override the effect of the pyridine ligands. The relatively small electrostatic differences caused by substitution in the pyridine rings would then be too small to affect the reactivity of the complex.

The difference in behavior of the dipyridyl complex as compared with the dipyridine complexes can be explained in two ways which are really the same in principle. The dipyridyl ligand forms π bonds of the ligand to metal type better than does the single pyridine ring. The formation of such π bonds is equivalent to a net transfer of charge from the ligand to metal and thus a reduction in the ligand-field effect of the dipyridyl. Alternatively, the greater rigidity of the dipyridyl ligand (*i.e.*, its planarity) in comparison with the monodentate pyridine ligands allows easier access to the axial positions for water molecules thus increasing the electrostatic effects of the water molecules as compared with the dipyridyl ligand. This is similar to the explanation given by Haake[7] for the relative rates of reaction of the corresponding dichloro complexes with dithiooxamide.

The results for the isopropyl complex are more complicated. In region A there is an induction period before a first-order plot is obtained, and in region C the removal of the second nitro group appears to be much faster than the removal of the first. This is shown by the calculated first-order rate constants assuming (a) the "infinity reading" corresponds to one nitro group which gives a curved plot and (b) the "infinity reading" corresponds to both nitro groups which gives good straight lines. The complicated behavior could be due to steric hindrance to the entering groups by the isopropyl residues.

Another noteworthy feature of the results is that, once the limiting rate is attained, it is not maintained for any appreciable acidity range before the rate again increases. This may be explained on the grounds that when the substrate is fully protonated, it is effectively a platinum(III) complex which would be relatively unstable, and the preferred oxidation state, platinum(IV), is quickly attained by further protonation.

As a narrow range of acid concentrations over which the rate of hydrolysis was hardly dependent on the acid concentration was observed, it was possible to analyze the results further. Systems showing a limiting maximum rate have been analyzed using the equation[8]

$$\log k_f = \log k_2 - H_0 - \log (h_0 + K_a) \qquad (1)$$

where k_f is the first-order rate constant, k_2 is the maximum limiting rate (region B, Figure 1), H_0 is the Hammett acidity function, K_a is the dissociation constant of the conjugate acid of the substrate, and h_0 is $-$antilog H_0. All quantities in eq 1 are known except K_a which was evaluated by the method previously described.[8] The agreement between this analysis and the experimental results is shown in Figure 1. The parameters used to calculate the theoretical line were $K_a = 5.29 \times 10^5$ and $10^4 k_2 = 2.5 \text{ sec}^{-1}$.

The Zucker–Hammett[9] and Bunnett[10] treatments both favor a unimolecular breakdown of the protonated complex. A plot of log k *vs* acidity function has a slope of 0.97 (see Figure 1). Plots of $\log k + H_0$ *vs.* $\log a_{H_2O}$ have slopes between 0.0 and -0.1. However, most of the evidence in the literature favors a bimolecular mechanism for the reactions of platinum(II) complexes. Further work is in progress to investigate a series of complexes in which the pyridine-type ligand has substituents, especially in the 2 position, which could sterically hinder the incoming water molecule in a bimolecular mechanism.

In a recent paper Jolly, *et al.*,[11] cite evidence for a type of cobalt–oxygen bond fission during the acid-catalyzed hydrolysis of nitropentaamminecobalt(III) salts. The type of experiments performed in this investigation do not distinguish between cobalt–nitrogen bond breaking and the mechanism proposed by Jolly (*cf.* alkyl and acyl fission in ester hydrolysis).

It is interesting to note that although these complexes are nonionic, the apparent pK_a values are at least as high (if not higher) than those of singly charged cations, *e.g.*, *cis*- and *trans*-dinitrobis(ethylenediamine)-cobalt(III) salts.[8] It would appear that the leaving ligand, *e.g.*, azido or nitro, has a significant effect on the ease of protonation.

Another possible reason for the differences between platinum(II) and cobalt(III) complexes is that the proton may be situated in different positions, *i.e.*, on the nitro group in the cobalt(III) complex but on the lone pairs in the axial positions in the platinum(II) complex. This point is receiving further experimental investigation.

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