compounds. However, the residual ratios $(B + C/kT)/D_0$ of the three compounds are of about the same magnitude. The rather large electric dipole strength and large residual $(B + C/kT)$ term of the iodo compound compared to the bromo compound may in part originate from a larger internal heavy-atom effect, I > Br.

7. Preliminary Crystal Structure Parameters of [Ni(py)$_4$I$_2$]. Partly because the $^3T_{1g}(F)$ residual MCD activity of the three halogen compounds is oddly $I^- > Cl^- > Br^-$, the single-crystal X-ray diffraction study of [Ni(py)$_4$I$_2$] was undertaken in this laboratory.[41] Several structural parameters of the dichloro and dibromo analogs had already been obtained a number of years ago.[42] Our crystal of [Ni(py)$_4$I$_2$] was found to be orthorhombic, of space group $D_{2h}{}^{14}$ (No. 60), $d = 1.878$ g/cm^3 (floatation) and $Z = 4$. With $R = 0.064$ the unit cell dimensions were found to be 9.678, 16.076, and 14.004 Å for *a*, *b*, and *c*. The average Ni-N distance is 2.11 Å and Ni-I is 2.88 Å. It is at the moment impossible to determine if the *Dq* parameter of py should vary as reflected in Table III (I > Cl > Br), since from the previously reported study[42] all one knows is that the Ni-N(py) interatomic distance of [Ni(py)$_4$Br$_2$] falls in the range 2.0-2.2 Å, and the Ni-N(py) value of [Ni(py)$_4$Cl$_2$] was not given in the report.[42] There is the additional difficulty that the chloro and bromo crystals lose pyridine rapidly. The full structural report of [Ni(py)$_4$I$_2$] will be the subject of our next article.[41]

Registry No. [Ni(py)$_4$(N$_3$)$_2$], 40354-94-7; Ni(NH$_3$)$_6$Cl$_2$, 10534-88-0; Ni(NH$_3$)$_6$(ClO$_4$)$_2$, 14322-50-0; [Ni(C$_5$H$_5$N)$_4$Cl$_2$], 14077-26-0; [Ni(C$_5$H$_5$N)$_4$Br$_2$], 14129-05-6; [Ni(C$_5$H$_5$N)$_4$I$_2$], 14077-31-7; [Ni(C$_5$H$_5$N)$_4$(NCO)$_2$], 28131-44-4; [Ni(C$_5$H$_5$N)$_4$(NCS)$_2$], 30868-61-2; [Ni(C$_5$H$_5$N)$_4$(NCSe)$_2$], 15277-22-2; [Ni(py)$_6$](ClO$_4$)$_2$, 18346-94-6.

Acknowledgments. Computer calculations were carried out on the IBM 370/165 of the Triangle Universities Computation Center (TUCC). We thank the School of Physical and Mathematical Sciences of this University for funding the liquid helium. We also acknowledge our discussion with Professor R. S. Drago regarding the chemical nature of [Ni(py)$_6$]$^{2+}$.

(41) D. J. Hamm, J. Bordner, and A. F. Schreiner, *Inorg. Chim. Acta*, in press.

(42) M. A. Porai-Kashits, A. S. A. Antzishkina, L. M. Dichareva, and E. K. Jukhnov, *Acta Crystallogr.*, 10, 784 (1957).

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Mercuric Ion Induced Hydrolysis of *trans*-Dibromodinitroethylenediamineplatinum(IV)

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Received January 15, 1973

The hydrolyses of *trans*-Pt(NH$_3$)$_4$Cl$_2$$^{2+}$, *trans*-Pt(NH$_3$)$_4Br_2$$^{2+}$, and *trans*-Pt(en)(NO$_2$)$_2Br_2$ do not occur in acidic aqueous solution. The former two compounds also do not hydrolyze to any extent in an acidic 0.010 *M* mercuric nitrate solution. The latter compound does react completely to form Pt(en)(NO$_2$)$_2$BrOH. The reaction rate is first order with respect to the platinum(IV) complex, mercuric ion, and the catalyst Pt(en)(NO$_2$)$_2$ and at 25.0° has a rate constant of 1.7×10^5 M^{-2} sec^{-1}. The activation parameters are $\Delta H^* = 2.4$ kcal/mol and $\Delta S^* = -26.5$ cal/mol deg. An activated complex in which two single bromide bridges link the three metal ions is proposed.

Introduction

Little research has been published dealing with the mechanisms of hydrolysis reactions of platinum(IV) complexes in neutral or acidic solution. The available results deal with the anionic complexes PtCl$_6$$^{2-}$,[1] PtBr$_6$$^{2-}$,[2] PtI$_6$$^{2-}$,[3] and Pt(CN)$_4Br_2$$^{2-}$.[4] The hydrolyses of the hexahalides lead ultimately to the loss of several halide ions. The rates of the reactions of the chloro and bromo complexes are quite sensitive to light. Dissociative processes and mechanisms involving redox have been proposed for both thermal and photochemical processes.

We are not aware of hydrolysis studies of neutral or acidic solutions of uncharged or cationic haloammineplatinum(IV) complexes. Aqueous solutions of complexes of this type can generally be kept for long periods without hydrolysis. This fact would account for the absence of hydrolysis studies. Data presented in this article indicate that two of these complexes are stable with respect to hydrolysis even in the presence of mercuric ion. Haloammineplatinum(IV) complexes do hydrolyze in basic solution and kinetic studies have been published.[5]

Mercuric ion has been used to accelerate the rate of hydrolysis of halo complexes of metal ions such as cobalt(III) and chromium(III).[6] The presence of mercuric ions can also shift an otherwise unfavorable hydrolysis equilibrium by complexing the halide ion as it is released.

Results and Discussion

The reactions of mercuric ion with several haloammineplatinum(IV) complexes were studied. Large changes were observed in the ultraviolet spectra of *trans*-Pt(en)(NO$_2$)$_2$Br$_2$ solutions when mercuric ions were added in the presence of Pt(en)(NO$_2$)$_2$.

Several types of evidence were collected to verify the identity of the platinum(IV) product. The suspected product, Pt(en)(NO$_2$)$_2$BrOH, was synthesized by the reaction of solutions of silver nitrate and Pt(en)(NO$_2$)$_2$Br$_2$. The fol-

(1) L. E. Cox, D. G. Peters, and E. L. Wehry, *J. Inorg. Nucl. Chem.*, 34, 297 (1972).

(2) L. I. Elding and L. Gustafson, *Inorg. Chim. Acta*, 5, 643 (1971).

(3) B. Corain and A. J. Poe, *J. Chem. Soc.*, 1633 (1967).

(4) C. E. Skinner and M. M. Jones, *J. Amer. Chem. Soc.*, 91, 1984 (1969).

(5) R. C. Johnson, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, 24, 59 (1962); A. A. Grinberg and A. A. Korableva, *Russ. J. Inorg. Chem.*, 11, 409 (1966).

(6) J. N. Bronsted and R. Livingston, *J. Amer. Chem. Soc.*, 49, 435 (1927); J. H. Espenson and J. P. Birk, *Inorg. Chem.*, 4, 527 (1965).

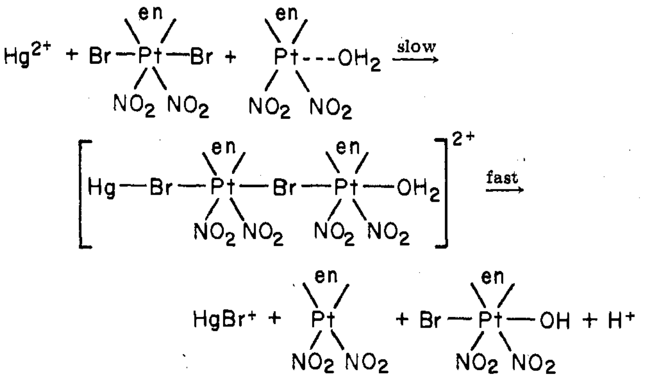
lowing observations indicate that the reaction studied involved the hydrolysis of a single bromide and the formation of $Pt(en)(NO_2)_2BrOH$ (presumably the trans isomer) (eq 1).

$$Pt(en)(NO_2)_2Br_2 + Hg^{2+} \rightarrow Pt(en)(NO_2)_2BrOH + HgBr^+ + H^+ \quad (1)$$

(a) The spectrum of the product of the reaction of Hg^{2+} with $Pt(en)(NO_2)_2Br_2$ (ϵ(at 205 nm) 2.84×10^4) agrees well with the spectrum of the independently synthesized $Pt(en)(NO_2)_2BrOH$ (ϵ(at 205 nm) 2.77×10^4). Both have a maximum at 205 nm and similar absorptivities at this wavelength. (The kinetic reaction mixture was cation exchanged to remove Hg^{2+} and $HgBr^+$ before the spectrum was run.) (b) There were no absorbance changes in a solution of $Pt(en)(NO_2)_2BrOH$ and Hg^{2+} in the presence of $Pt(en)(NO_2)_2$ in a 6-hr period. (c) Only 1 equiv of bromide per molecule of $Pt(en)(NO_2)_2Br_2$ is precipitated on reaction with excess silver ion. (d) The presence of an isosbestic point at 223 nm during the kinetic runs suggests that no long-lived intermediates are present. This is most simply explained in terms of a simple hydrolysis of one bromide. (e) Both the product of the reaction studied and the independently prepared $Pt(en)(NO_2)_2BrOH$ react readily with bromide ion to regenerate the spectrum of $Pt(en)(NO_2)_2Br_2$. This suggests that they are the same.

Reaction 1 has a first-order rate dependence on platinum(IV), $Pt(en)(NO_2)_2Br_2$, and mercuric ion. The concentration of perchloric acid was varied from 0.001 to 0.5 *M* with little effect on the reaction rate. It was not possible to investigate neutral and basic solutions since mercuric ion is precipitated under these conditions. The reaction rate increased as the ionic strength was increased from 0.004 to 0.54 *M*. The temperature dependence of the rate constant was determined by studies at 15.0, 25.0, and 35.0°. The activation parameters are $\Delta H^* = 2.4$ kcal/mol and $\Delta S^* = -26.5$ cal/mol deg. Rate data are presented in Table I.

A mechanism which is consistent with the kinetic data is



The formation of an inner-sphere bridge between a platinum(II) and a platinum(IV) compound has been reported in the activated complex of a variety of substitution reactions of platinum(IV) complexes.[7] Similarly good evidence for halide bridges between mercuric ion and the metal in a variety of metal halide complexes has been presented.[8] The mechanism for this reaction is unusual in the formulation of an activated complex linking three metal centers through two bromide bridges. The formation of the activated complex most probably occurs in at least two steps: the association of the platinum(IV) complex with mercuric ion and the association of the platinum(IV) complex with platinum(II). There is no evidence to suggest which of these two reactions occurs first. Both are probably fast; but since there is no evidence for the adducts, they are presumably unstable. The spectrum of a solution of mercuric ion and $Pt(en)(NO_2)_2Br_2$ corresponds to the sum of the individual spectra. In some other systems, mercuric ion adducts have been detected in solution.[8]

Table I. Rate Data[a]

$10^5 \times$ [Pt(II)], *M*	$10^3 \times$ k_{obsd}, sec^{-1}	$10^{-5} \times$ k_3, M^{-2} sec^{-1}	$10^4 \times$ $[Hg^{2+}]$, *M*	$10^3 \times$ k_{obsd}, sec^{-1}	$10^{-5} \times$ k_3, M^{-2} sec^{-1}
	25.0°[b]			25.0°[h]	
0.50	0.85	1.7	1.0	0.83	1.7
1.0	1.8	1.8	2.0	1.7	1.7
2.0	3.5	1.8	4.0	3.3	1.7
2.5	4.1	1.6	5.0	4.3	1.7
4.0	7.1	1.8	6.0	4.6	1.5
5.0	10.2[c]	2.0	8.0	6.2	1.5
5.0	9.0[d]	1.8		15.0°[h]	
5.0	7.2[e]	1.4			
5.0	6.2[f]	1.2	5.0	3.5	1.4
5.0	5.1[g]	1.0		35.0°[h]	
			5.0	5.0	2.0

[a] $[Pt(II)] = [Pt(en)(NO_2)_2]$; $[Pt(en)(NO_2)_2Br_2] = 2.5 \times 10^{-5}$ *M*, $[H^+] = 0.54$ *M*, ionic strength 0.54. [b] $[Hg^{2+}] = 1.00 \times 10^{-3}$ *M*. [c] $[H^+] = 0.11$ *M*. [d] $[H^+] = 3.0 \times 10^{-3}$ *M*. [e] $[H^+] = 1.0 \times 10^{-3}$ *M*. [f] $[H^+] = 1.0 \times 10^{-3}$ *M*, ionic strength 8.0×10^{-2}. [g] $[H^+] = 1.0 \times 10^{-3}$ *M*, ionic strength 4.0×10^{-3}. [h] $[Pt(en)(NO_2)_2] = 5.0 \times 10^{-5}$ *M*.

Plots of appropriate observed rate constants against the concentration of mercuric ion or $Pt(en)(NO_2)_2$ go through the origin within experimental error. This indicates that both are required if the reaction is to proceed at a reasonable rate. The rate dependence on Hg^{2+} indicates that even when the hydrolysis equilibrium is favorable, the rate of unassisted hydrolysis is small. A conservative upper limit would be 10^{-4} sec^{-1} at 25.0° at $[Pt(en)(NO_2)_2] = 5.0 \times 10^{-5}$ *M*.

On the basis of the proposed mechanism the formation of $Pt(en)(NO_2)_2BrOH$ as the product of the reaction is not surprising. Bromide ion functions as a bridging group in the proposed mechanism. In a similar mechanism for the loss of a second bromide ion, hydroxide ion would have to be the bridging group. Previous studies on platinum(II)-catalyzed reactions have indicated that hydroxide ion provides much slower reactions than bromide ion when it is in the bridging position and may be completely ineffective.[7]

The activation parameters obtained are consistent with the postulated mechanism. At −26.5 cal/mol deg the entropy of activation is very unfavorable. This is reasonable considering the need to aggregate four independent units into the activated complex. The 2.4-kcal/mol enthalpy of activation is quite low. Related reactions which do not involve mercuric ion have values in the 5-8-kcal range. This suggests that the reaction between Hg^{2+} and $Pt(en)(NO_2)_2Br_2$ is exothermic.

Early in the studies it was observed that the absorbance of aqueous solutions of $Pt(en)(NO_2)_2Br_2$ at 235 nm decreased as the solution aged. Samples exposed to sunlight showed rapid and large changes in absorbance. A slow change in absorbance was observed for solutions protected from light. The change in absorbance had been previously reported and was attributed to hydrolysis.[9] We have not found references to light sensitivity. In order to check this earlier work aqueous solutions of $Pt(en)(NO_2)_2Br_2$ were stoppered tightly and exposed to room light. After several days a bromide-selective electrode was introduced into the solutions, and it indicated a bromide concentration of less than 5×10^{-6} *M*,

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(7) W. R. Mason, *Coord. Chem. Rev.*, **7**, 241 (1972).

(8) L. C. Falk and R. G. Linck, *Inorg. Chem.*, **10**, 215 (1971).

(9) I. I. Chernyaev, N. N. Zheligovskaya, and N. P. Vasileva, *Russ. J. Inorg. Chem.*, **13**, 547 (1968).

the lower limit of the electrode. This indicates that bromide ion is not a product of this reaction. The solutions were evaporated at room temperature and green crystals were collected. Elemental analysis did not suggest a simple formula, but the ratio of nitrogen to platinum was less than 3. This suggests that the decomposition is a redox process that leads to the loss of nitrite ion. In any case the decomposition is sufficiently slow that it does not interfere with the mercuric ion assisted hydrolysis, if fresh platinum solutions are used and they are protected from bright light sources.

Before the successful studies with *trans*-$Pt(en)(NO_2)_2Br_2$ were begun, attempts were made to induce the hydrolysis of *trans*-$Pt(NH_3)_4Cl_2^{2+}$ and *trans*-$Pt(NH_3)_4Br_2^{2+}$ using acidic solutions of mercuric ion. In the former case no changes in ultraviolet absorbance occurred even in the presence of $Pt(NH_3)_4^{2+}$, a probable catalyst. Since the hydrolysis products are known to absorb differently than the reactants, this demonstrates that no reaction occurs. Since the $Pt(en)(NO_2)_2Br_2$ reacts so rapidly in the presence of mercuric ion, it seems probable that failure to observe a reaction with $Pt(NH_3)_4Cl_2^{2+}$ reflects stability with respect to hydrolysis rather than a kinetic effect.

This conclusion is supported by the fact that rapid but small absorbance changes occurred in solutions containing mercuric ion and *trans*-$Pt(NH_3)_4Br_2^{2+}$. Hydrolysis of one bromide under the same conditions would lead to much larger absorbance changes. The absorbance changes became greater as the mercuric ion concentration was increased. This would suggest that an equilibrium is set up but that little hydrolysis occurs. In all cases the change in absorbance was too small to allow convenient kinetic studies.

Several anionic platinum(IV) complexes hydrolyze spontaneously in acidic solution. The neutral complex, *trans*-$Pt(en)(NO_2)_2Br_2$, decomposes slowly in acidic solution, but hydrolysis which yields bromide ion does not occur. Mercuric ion does induce rather rapid hydrolysis to yield $HgBr^+$. The hydrolysis of the cationic complexes *trans*-$Pt(NH_3)_4Cl_2^{2+}$ and *trans*-$Pt(NH_3)_4Br_2^{2+}$ does not occur to any extent even in the presence of mercuric ion. It therefore appears that the stability of a platinum(IV)-halide bond with respect to hydrolysis is appreciably dependent on the charge on the metal complex.

The dependence of the rate of the mercuric ion assisted hydrolysis of *trans*-$Pt(en)(NO_2)_2Br_2$ on the concentration of $Pt(en)(NO_2)_2$ provides an additional example of the importance of platinum(II) catalysis in platinum(IV) chemistry. The uncharged bromoplatinum complex and the mercuric ion should provide particularly suitable conditions for a mechanism which involves a rate-determining cleavage of the platinum-bromide bond. The observed rate data indicate that a dissociative mechanism does not provide a significant reaction rate even under these favorable conditions.

Experimental Section

Preparation of Compounds. Potassium tetrachloroplatinate(II),[10] $Pt(NH_3)_4(ClO_4)_2$,[11,12] *trans*-$Pt(NH_3)_4Cl_2(NO_3)_2$,[12] *trans*-$Pt(NH_3)_4Br_2(NO_3)_2$,[12] $Pt(en)Cl_2$,[13] $Pt(en)(NO_2)_2$,[14] and $Pt(en)(NO_2)_2Br_2$[14] were all prepared by published procedures. The analysis on the last compound follows. *Anal.* Calcd for $Pt(C_2N_2H_8)(NO_2)_2Br_2$: Pt, 38.46; Br, 31.56. Found: Pt, 38.48; Br, 31.10. Solutions of $Pt(en)(NO_2)_2Br_2$ are light sensitive and were carefully shielded from light as much as possible.

trans-Bromohydroxoethylenediamineplatinum(IV) was prepared by adding to 0.5 g of $Pt(en)(NO_2)_2Br_2$ dissolved in 100 ml of distilled water a small amount of $Pt(en)(NO_2)_2$. The solution was protected from light and gently warmed. One equivalent of silver nitrate was added slowly to the warm solution with stirring. After 10 min the silver bromide was filtered off. The clear yellow solution was evaporated at room temperature on a rotary evaporator to approximately 20 ml. A pale yellow precipitate formed. The solution was cooled for 0.5 hr at 0° and the product was collected on a glass filter. It was dried at room temperature under vacuum. The yield was 42.6%. *Anal.* Calcd for $PtC_2H_8N_2(NO_2)_2BrOH$: Pt, 43.92; Br, 18.00. Found: Pt, 44.08; Br, 18.88.

Mercuric nitrate solutions were prepared from reagent grade mercuric nitrate dissolved in dilute perchloric acid. Solutions were analyzed for Hg(II) gravimetrically by precipitation of the periodate.[15]

Duplicate kinetic runs were made with mercuric perchlorate in place of the nitrate. Mercuric perchlorate solutions were prepared from reagent grade mercuric nitrate. The mercuric ion was precipitated as the oxide with sodium carbonate. The white oxide was washed with demineralized water and redissolved in perchloric acid. This procedure was repeated three times.

Platinum analyses were done by ignition of the compounds. Halide analyses were done gravimetrically. Microanalyses were by Atlantic Microlab.

Kinetic Measurements. Kinetics were followed spectrophotometrically on a Beckman DU spectrophotometer modified with a Gilford 220 absorbance indicator. The cell compartment was thermostated to better than ±0.02°. The reactions were studied under pseudo-first-order conditions. The ionic strength of the solutions was maintained with $NaClO_4$. Perchloric acid was used to adjust solution acidity. Fresh platinum(II) and -(IV) solutions were prepared each day kinetics were run. Duplicate kinetic runs were carried out and average values are reported in Table I. Duplicate runs reproduced reasonably well with deviations less than 10%. Infinite-time absorbances on kinetic solutions were consistent with those expected from the spectra of the reaction products.

The hydrolysis of *trans*-$Pt(en)(NO_2)_2Br_2$ was studied at 240 nm where this reactant absorbs appreciably more than its hydrolysis product. Rate data were analyzed by a Gauss-Newton nonlinear least-squares fit to the equation $A = A_\infty + (A_0 - A_\infty)\exp(-kt)$. Absorbance *vs.* time data covering 4 half-lives were in general used and the fit to the equation was in general within the uncertainty of the absorbance measurements.

Registry No. *trans*-$Pt(en)(NO_2)_2Br_2$, 27647-78-5; *trans*-$Pt(en)(NO_2)_2BrOH$, 40685-54-9; $[Pt(en)(NO_2)_2]$, 15413-16-8; mercury, 7439-97-6.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(10) W. E. Cooley and D. H. Busch, *Inorg. Syn.*, **5**, 208 (1957).

(11) R. N. Keller, *Inorg. Syn.*, **2**, 251 (1953).

(12) R. R. Rettew and R. C. Johnson, *Inorg. Chem.*, **4**, 1565 (1965).

(13) F. Basolo, J. C. Bailar, Jr., and A. R. Tarr, *J. Amer. Chem. Soc.*, **72**, 2433 (1950).

(14) A. Syamal and R. C. Johnson, *Inorg. Chem.*, **9**, 265 (1970).

(15) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, Wiley, New York, N. Y., 1961, p 488.