and therefore small variations in this small contribution have a very minor effect upon the total field strength. Conversely, the increase from one to two benzimidazole ligands in going from the $[CoX_3(C_7H_6N_2)]^-$ to $[CoX_2(C_7H_6N_2)_2]$ complexes has a very marked effect on both the spectra and the magnetic moments.

Acknowledgment.—We gratefully acknowledge the generous financial support of the National Institutes of Health.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

Rates of Some Substitution Reactions of Platinum(II) Complexes

BY HARRY B. GRAY[1]

RECEIVED SEPTEMBER 22, 1961

Rates of replacement of halide by different ligands in platinum(II) complexes of the type $[Pt(dien)(halide)]^+$ are reported.[2] The results show that both first order and second order reactions occur. The mechanisms which may lead to the first and second order rate laws are discussed. The bimolecular reactivities of different incoming ligands in reactions of platinum complexes decrease in the order

$$SC(NH_2)_2 \approx CNS^- \approx I^- > N_3^- \approx NO_2^- > py \approx NH_3 \approx Br^- > Cl^- > H_2O > OH^- \approx NH_2CH_2COOH$$

which is also approximately the order of decreasing *trans*-effect of these ligands. The relative reactivities of Cl^- and NO_2^- in reactions of different platinum(II) complexes vary strikingly with the charge on the complex, and this is interpreted in terms of the electronic features of a possible reaction mechanism.

Introduction

In previous papers[3,4] it has been suggested that a general rate law for ligand substitutions in square planar metal complexes is

$$\text{Rate} = \{k_1 + k_2\,[Y]\}\,[\text{complex}] \qquad (1)$$

where k_1 and k_2 are first and second order rate constants, respectively, and Y is the entering group. This form of rate law was first "discovered" in square planar reactions by Rich and Taube[5] for the exchange of $^{36}Cl^-$ with $AuCl_4^-$ and more recently by Martin[6] for *trans*-$Pt(NH_3)_2Cl_2$-$^{36}Cl^-$ exchange, and Basolo, *et al.*,[3,4] for reactions of platinum(II), palladium(II) and nickel(II) complexes with pyridine in water or ethanol solution. Also, although not specifically mentioned at the time, all previous work on square planar kinetics is consistent with this form of rate law.[7]

This present study will show that eq. 1 is valid for reactions of platinum(II) complexes in water solution with a number of different reagents. The reaction studied is the replacement of a halide ligand in complexes of the type $Pt(dien)X^+$, *viz.*

$$Pt(dien)X^+ + Y^- \longrightarrow Pt(dien)Y^+ + X^- \qquad (2)$$

The mechanisms which can account for k_1 and k_2 will also be discussed.

Experimental

A. Preparation and Purification of Materials.—The [Pt(dien)X] X and [Pt(dien)X] NO_3 complexes used in this study had been prepared previously following methods described in the literature. Other minor preparatory details and the analyses have been given.[3]

Reagent grade pyridine was dried with KOH and distilled, b.p. 114°: other materials used were reagent grade.

Sodium hydroxide solutions were prepared using distilled water which had previously been boiled and flushed with nitrogen to remove CO_2. The NaOH concentrations were checked by conductivity measurements.

B. Determination of Reaction Rates. (1) Conductance Method.—Reactions studied by this method were the following

$$Pt(dien)Br^+ + SC(NH_2)_2 \longrightarrow Pt(dien)\{SC(NH_2)_2\}^{2+} + Br^- \qquad (3)$$

$$Pt(dien)X^+ + OH^- \longrightarrow Pt(dien)OH^+ + X^- \qquad (4)$$

The conductivity of aqueous solutions of the complexes corresponded to 1:1 electrolytes and did not change with time. Thus no net hydrolysis occurred, *e.g.*

$$Pt(dien)X^+ + H_2O \not\longrightarrow Pt(dien)H_2O^{2+} + X^- \qquad (5)$$

Standard aqueous solutions of complex and reactant were thermostated in a Y-shaped conductance cell and, after the desired temperature was reached, were mixed by tipping the cell. Complete concentration data for these reactions are given in Table I. At the concentrations used both reactions 3 and 4 went to completion as judged by the total conductance changes observed.[8] The completeness of reaction 4 as well as the rate constants were checked spectroscopically as discussed in the next section. Pseudo first order rate constants were evaluated as described earlier[9] and are given in Table I.

Reaction 3 is shown to depend on the concentration of thiourea, and at low thiourea concentrations first order behavior was not observed for the complete reaction. This is expected since there is an appreciable thiourea concentration change during the course of the reaction. The values of the pseudo first order rate constants in these cases were obtained by graphing only the data for the first 25% of reaction.

(2) Spectrophotometric Method.—Reactions studied by this method were

$$Pt(dien)Cl^+ + Y^- \rightleftharpoons Pt(dien)Y^+ + Cl^- \qquad (6)$$
$$(Y^- = Br^- \text{ or } I^-)$$

$$Pt(dien)Br^+ + Y^- \rightleftharpoons Pt(dien)Y^+ + Br^- \qquad (7)$$
$$(Y^- = Cl^-, I^-, NO_2^-, CNS^- \text{ or } N_3^-)$$

---

[1] Department of Chemistry, Columbia University, New York 27, New York.

[2] Abbreviations used in this paper: dien = diethylenetriamine, py = pyridine, X^- = halide.

[3] F. Basolo, H. B. Gray and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

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

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

[6] D. S. Martin, Jr., and R. J. Adams, "Advances in the Chemistry of the Coordination Compounds," Macmillan Co., New York, N. Y., 1961, pp. 579–589.

[7] (a) F. Basolo and R. G. Pearson. "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 172–212; (b) A. A. Grinberg. *Russian J. Inorg. Chem.*, **4**, 139 (1959); (c) More recent articles are cited in ref. 3.

[8] In reaction 3 the molar conductance of $Pt(dien)\{SC(NH_2)_2\}^{2+}$ is assumed to be two times that of $Pt(dien)X^+$.

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

TABLE I

RATES OF REACTION OF SOME PLATINUM(II) COMPLEXES WITH VARIOUS REAGENTS IN WATER AT 25°

Complex, concn. (*M*)		Reactant, concn. (*M*)		Added substance	$k_{obsd}\ 10^4$, sec.$^{-1}$
[Pt(dien)Cl] Cl	0.005	$^{36}Cl^-(HCl)$	0.007	0.2 *M* KNO_3	1.12
	.005		.01	.2 *M* KNO_3	1.27
	.005		.02	.2 *M* KNO_3	1.77
	.005		.03	.2 *M* KNO_3	2.23
	.0018	$Br^-(KBr)$	.005	....	1.04
	.0018		.015	....	1.60
	.0018		.02	....	1.87
	.0018		.025	....	2.12
	.0018	$I^-(KI)$	.01	....	25.7
	.0018		.025	....	55.0
	.0073	$OH^-(NaOH)$	.0073	....	1.0
	.0073		.017	....	1.0
[Pt(dien)Br] Br	.0018	$Cl^-(KCl)$	.10	0.15 *M* KNO_3	1.72
	.0018		.25	....	3.03
	.0018	$I^-(KI)$	.01	....	35.5
	.0018		.025	....	70
	.0018		.04	....	105
	.001	$NO_2^-(NaNO_2)$	.001	....	0.27
	.0018		.01	....	0.61
	.0018		.02	....	1.0
	.0018		.025	....	1.15
	.0018		.04	....	1.65
	.0018	$CNS^-(KCNS)$	.01	....	53.3
	.0018		.017	....	76.7
	.0018		.04	....	175
	.0018		.05	....	230
[Pt(dien)Br] Br	.0002	$SC(NH_2)_2$	.0005	....	5.33
	.0004		.001	....	7.67
	.0004		.002	....	16.2
	.0004		.005	....	40
	.0018	$N_3^-(NaN_3)$	.01	....	1.33
	.0018		.0125	....	1.58
	.0018		.0135	0.001 *M* $HClO_4$, .0125 *M* $LiNO_3$	1.58
	.0018		.025	....	2.67
	.0018		.0275	.0025 *M* $HClO_4$	2.67
	.0018		.05	....	4.33
	.001	$OH^-(NaOH)$	.001	....	1.32
	.001		.0011	....	1.32
	.001		.00143	....	1.32
	.001		.00287	....	1.32
	.001		.00574	....	1.32
	.0073		.0073	....	1.32
	.0073		.017	....	1.32
[Pt(dien)I] I	.0018	$Cl^-(KCl)$	.10	....	0.55
	.0018		.25	....	0.92
	.0018	$Br^-(KBr)$	.025	....	1.07
	.0018		.05	....	1.80
	.0073	$OH^-(NaOH)$	.0073	....	0.417
	.0073		.017	....	0.417

$$\mathrm{Pt(dien)I^+ + Y^- \rightleftarrows Pt(dien)Y^+ + I^-} \qquad (8)$$

$$(\mathrm{Y^- = Cl^-\ or\ Br^-})$$

The ultraviolet spectra of the $Pt(dien)X^+$ complexes were plotted with a Beckman DK-2 recording spectrophotometer. Principal maxima occur at 270 mμ($X^- = Cl^-$), 275 mμ ($X^- = Br^-$) and 300 mμ ($X^- = I^-$). The reactions of these complexes with other halides were followed by measuring changes in optical density at the wave length of the suitable maximum for the solution under investigation. The reactions of $Pt(dien)Br^+$ with NO_2^-, N_3^- and CNS^- were followed at 270, 300 and 325 mμ, respectively, where the absorbancies of the product complexes are considerably larger than the starting complex. All the experiments were carried out using both the Beckman DK-2 and a Beckman DU, with a cell compartment thermostated at the desired temperature. The concentration of reagent Y in most cases greatly exceeds the complex concentration as shown in Table I. Pseudo first order rate constants (k_{obs}) were obtained graphically by the standard methods.[10] The optical densities were always measured against a blank of reagent Y solution of the same concentration as in the reacting solution.

The reactions are reversible in aqueous solution but were made to go essentially to completion in most cases by having a large excess of reagent Y. Thus the final constant value of the optical density is used as $O.D._\infty$ in the calculations. The completeness of the reactions was checked by comparing the ultraviolet spectrum of a solution of product com-

---

[10] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, Chap. 3.

TABLE II

SUMMARY OF BIMOLECULAR RATE CONSTANTS FOR REACTIONS OF PLATINUM(II) COMPLEXES WITH VARIOUS REAGENTS IN WATER AT 25°

Complex	$k_2 \times 10^4$, M^{-1} sec.$^{-1}$ for reaction with OH$^-$	Cl$^-$	Br$^-$	I$^-$	NH$_3$	py	NO$_2^-$	N$_3^-$	CNS$^-$	SC(NH$_2$)$_2$	gly
[Pt(NH$_3$)$_3$Cl] Cl	0[a]	0.6[h]	..	..	37[e]	0[b]	87[b]	..	..	733[b]	..
[Pt(dien)Cl] Cl	0	50	53	2000	....	53[c]	...	..	..	...	..
[Pt(dien)Br] Br	0	8.8	..	2300	....	33[c]	37	77	4300	8300	..
[Pt(dien)I] I	0	2.3	2.9	..	....	15[c]	...	..	..	...	..
trans-[Pt(NH$_3$)$_2$Cl$_2$]	0[b]	7.8[b]	..	..	190[b]	...	>9000[b]	..	..	>9000[b]	0[b]
K[Pt(NH$_3$)Cl$_3$]	0[a]	0[e]	..	..	11.4[a]	32.8[a]	...	..	..	...	..
K$_2$[PtCl$_4$]	0[b]	0[f]	..	..	4.2[a]	17.2[a]	[g]	..	..	...	.

[a] From ref. 7b. [b] From ref. 9. [c] From ref. 3. [d] From ref. 6. [e] From ref. 13. [f] From ref. 15a. [g] Sodium nitrite (0.005 *M*) shows an initially rapid reaction with this complex. However, this initial reaction product was not identified. [h] F. Aprile and D. S. Martin, Jr., Abstracts of Papers, 140th Meeting of the American Chemical Society, Chicago, Sept., 1961.

plex, at the desired concentration, with the final spectrum obtained for the reacting solution. The reactions of Pt(dien)I$^+$(eq.8) with chloride and bromide did not go to completion under any conditions since the equilibrium greatly favors the iodo complex. In these cases plots were made with only the first few points calculated using a value of O.D.$_\infty$ estimated for complete reaction to get the $k_{obsd.}$ for the forward process. The values of $k_{obsd.}$ obtained for all the reactions studied by the spectrophotometric method are given in Table I.

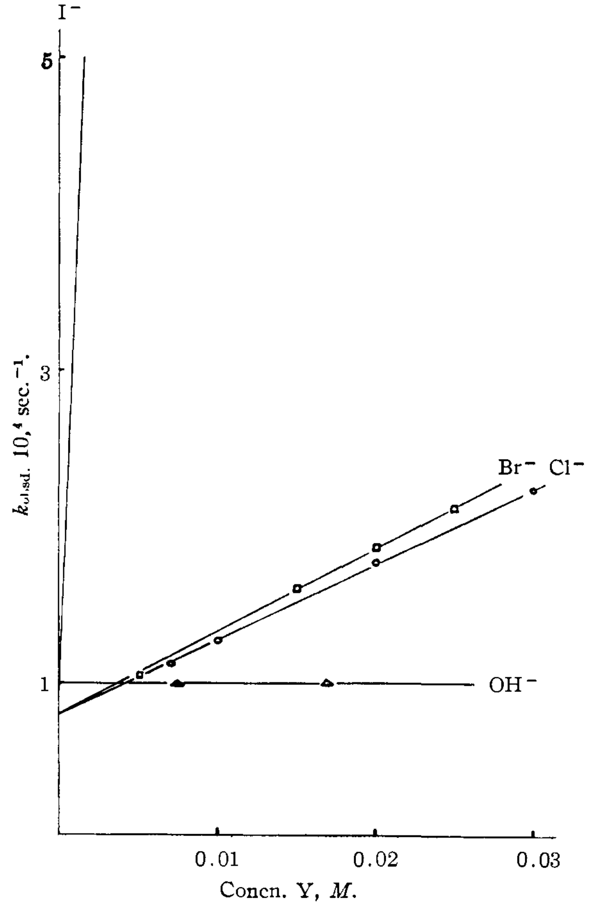


Fig. 1.—Dependence of $k_{obsd.}$ on concentration of Y at 25°.

Both the completeness and the rates of reactions of Pt(dien)X$^+$ complexes with NaOH(eq. 4) were checked spectrophotometrically. A solution of known concentration of Pt(dien)OH$^+$ was prepared by dissolving [Pt(dien)NO$_3$]NO$_3$ in water, which immediately gives Pt(dien)H$_2$O^{2+},[3,11] and allowing it to react with one equivalent of NaOH. The ultraviolet spectrum of this solution was identical with the final spectra obtained for the reacting solutions. Rate constants, evaluated at respective maxima of the Pt(dien)X$^+$ complexes as described above, agreed well (not over 5% deviation) with the ones determined by conductivity.

(3) **Radioisotope Method.**—This was applied in studying the exchange reaction

$$\text{Pt(dien)Cl}^+ + {}^{36}\text{Cl}^- \rightleftharpoons \text{Pt(dien)}^{36}\text{Cl}^+ + \text{Cl}^- \quad (9)$$

in aqueous solution using H^{36}Cl as the source of radiochloride. The experimental procedure followed has been given previously.[9,12] Pseudo first order rate constants are given in Table I.

Results

The kinetic results given in Table I can best be described by the equation

$$k_{obsd.} = k_1 + k_2[Y] \quad (10)$$

This equation is of course equivalent to eq. 1, in which $k_{obsd.}$ is a pseudo first order rate constant. In order to clearly illustrate the validity of eq. 10, plots of $k_{obsd.}$ *vs.* [Y] are shown in Fig. 1 for the reactions of Pt(dien)Cl$^+$ with several different reagents. These plots are straight lines with slopes equal to k_2 and intercepts equal to k_1.

The reactions of [Pt(dien)Br]Br have been studied more extensively, and the rates all appear to conform to eq. 10. It should be mentioned that the plot of $k_{obsd.}$ *vs.* [NO$_2^-$] for [Pt(dien)Br]Br shows some departure from linearity, giving slightly lower $k_{obsd.}$ values than expected at low initial concentrations of NO$_2^-$. This is very likely the result of effective competition for the reaction intermediate by the Br$^-$ present in solution. This point will be discussed later.

Discussion

The two term rate law found is consistent with the two step mechanisms which have been proposed for ligand substitutions in square planar metal complexes.[7a,13] Thus the first order rate probably represents a relatively slow reaction with the solvent (H$_2$O in this case), which is followed by rapid pickup of the incoming Y ligand. The second order rate is simply due to a direct bimolecular (S$_N$2) reaction between the incoming ligand and the complex.

It is interesting to quantitatively compare the reactivities of different reagents with platinum(II) complexes. Bimolecular rate constants, calcu-

---

(11) H. B. Gray and R. J. Olcott, to be published.

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

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

lated from the data in Table I and from selected data of other workers, are given in Table II for a variety of complexes and reagents. The order of decreasing reactivity of different reagents is approximately

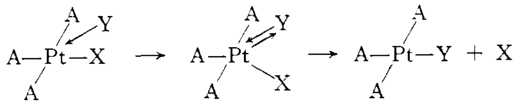
$$SC(NH_2)_2 \approx CNS^- \approx I^- > N_3^- \approx NO_2^- > py \approx NH_3 \approx Br^- > Cl^- > H_2O$$
$$OH^- \approx NH_2CH_2COOH$$

As was originally suggested by Banerjea, *et al.*,[9] this is very nearly the order of decreasing *trans*-effect for these ligands, which is[7a]

$$SC(NH_2)_2 \approx NO_2^- \approx I^- \approx CNS^- > Br^- > Cl^- > py > NH_3 > OH^-$$

From the results in Table II it is clear that the relative bimolecular reactivities of different reagents vary, sometimes quite strikingly, depending on the charge type of the reactant platinum(II) complex in question. This effect is perhaps shown best by Cl^- and NO_2^- as will be discussed below.

The ligands which are effective reagents for platinum(II) substitution reactions clearly have the capacity to form metal to ligand π-bonds. That is, in these cases it is possible to stabilize the transition state by the formation of π-bonds, using electrons in the 5*d* Pt orbitals and empty or partially empty ligand orbitals. Thus the reagent attack by the more effective ligands can be pictured as both nucleophilic and electrophilic, or *biphilic*[12]


(11)

For these reactions the configuration of the transition state is most likely a trigonal bipyramid, since this allows more metal orbitals to π-bond.[14]

It is remarkable, but expected from the previous π-bonding considerations, that hydroxide ion is so ineffective. For every platinum(II) complex studied the hydroxide ion reaction is completely first order ($k_2 = 0$). A first order plot is shown in Fig. 2 for the reaction between 0.001 *M*[Pt(dien)Br] Br and 0.001 *M* NaOH. Data in Table I also show that the rate of this reaction is completely independent of hydroxide ion concentration over a considerable range. This must mean that ordinary organic nucleophilic power is unimportant in reactions of platinum(II). Since hydroxide ion has no empty orbitals energetically suited for bonding purposes, there can be no contribution of an electrophilic nature to the initial attack on platinum. There is instead a considerable repulsion between the filled orbitals of OH^- and Pt. Even when the platinum complexes have a net charge of +1, the reaction is entirely first order.

The nucleophilic nature of the reagent is more important, and the electrophilic nature correspondingly less important, as the positive charge on the complex increases. For example, NO_2^- reacts rapidly with negatively charged and neutral complexes but very slowly with positively charged complexes. Thus its effectiveness must be mainly due to its electrophilic ability, which is markedly reduced when the platinum orbitals are contracted due to increased positive charge. On the other hand, chloride ion exhibits no direct bimolecular reaction whatsoever with negatively charged complexes but does react bimolecularly with some neutral and cationic platinum(II) complexes. Chloride has little, if any, ability to π-bond with the platinum in the manner described above, so its attack must be almost entirely nucleophilic, which is enhanced by the *d* orbital contraction as a result of increased positive charge on the complex.

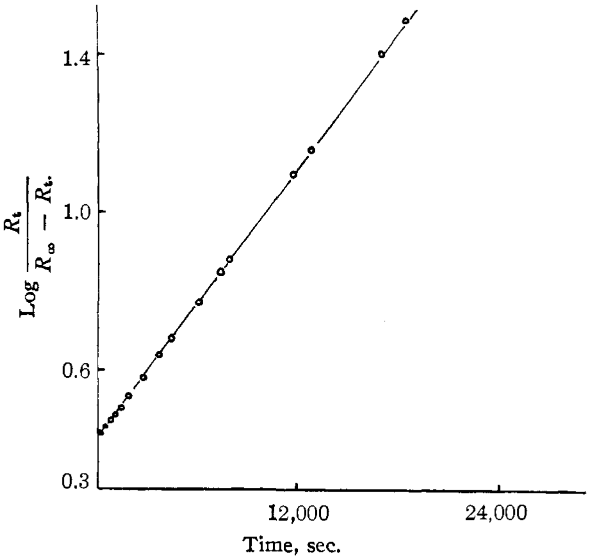


Fig. 2.—First order plot for the reaction of [Pt(dien)Br]Br with OH^- at 25°. Concn. of complex, 0.001 *M;* of NaOH, 0.001 *M*.

A list of first order rate constants is given in Table III for a number of platinum(II) complexes. This list also includes some important earlier work of other investigators. For any mechanism in which the leaving group is lost in the slow step, k_1 values are expected to be equal and reagent independent for the same complex. This is seen to be the case in most of the examples given. The reaction between pyridine and [Pt(dien)Br]Br is an exception, however, since a much smaller k_1 value is obtained than in the reactions of other reagents with this same complex. Since the equilibrium in the [Pt(dien)Br]Br–pyridine system is not affected by varying free [Br^-] or [pyridine] over a considerable range (the reactions went to completion in all the cases reported in ref. 3.), this rate retardation must be due to the fact that the more important first order reaction intermediate reacts much more rapidly with bromide ion than with pyridine. This is demonstrated by reacting the complex $[Pt(dien)Br]NO_3$, which in solution furnishes no free bromide ion initially, with pyridine. This complex reacts rapidly at first, but as bromide is liberated the reaction rate is drastically retarded until only a very slow first order rate remains. This residual first order rate is equal to the small k_1 value reported for the [Pt(dien)Br]Br-pyridine reaction, and it is not affected by further liberation of bromide ion. A first order plot is shown in Fig. 3 of the rate data from this experiment at a low initial concentration of pyridine, the concentration

---

[14] G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

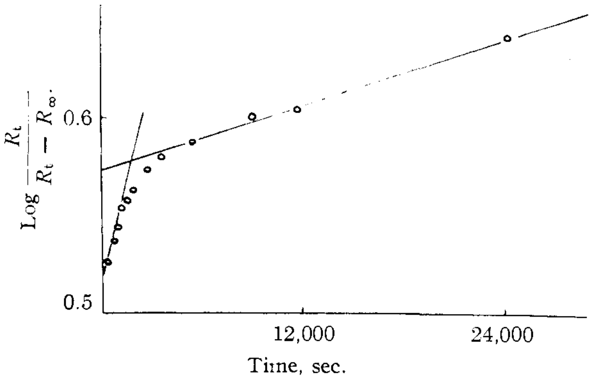


Fig. 3.—First order plot of the reaction of [Pt(dien)Br]NO_3 with pyridine at 25°. Concn. of complex, 0.0012 *M;* of pyridine, 0.00124 *M;* KNO_3, 0.0012 *M.* (a) $k = 7.3 \times 10^{-5}$ sec.$^{-1}$; (b) $k = 6.1 \times 10^{-6}$ sec.$^{-1}$

region in which totally first order processes should predominate. This plot shows that the initial rapid reaction rate is nearly equal to the first order rate observed for reactions of this complex with other ligands. Therefore, the other ligands must compete with bromide much more effectively than pyridine does for the principal intermediate.

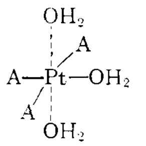
TABLE III

SUMMARY OF FIRST ORDER RATE CONSTANTS FOR REACTIONS OF PLATINUM(II) COMPLEXES WITH VARIOUS REAGENTS IN WATER AT 25°

Complex	$k_1 \times 10^6$, sec.$^{-1}$ for reaction with Cl^-	 Pyridine	 OH^-	 Br^-
[Pt(NH_3)$_3$Cl]Cl	15^a	16.7^a	21.7^b	..
[Pt(dien)Cl]Cl	78	....	100	80
[Pt(dien)Br]Br	83	2.9^c	132	..
[Pt(dien)Br]NO_3	..	83	..	..
[Pt(dien)I]I	33	....	42	48
trans-[Pt(NH_3)$_2$$Cl_2$]	100^d	108^a	102^a	..
K[Pt(NH_3)Cl_3]	37^e	....	60^b	..
K_2[$PtCl_4$]	38^f	....	37^b	..

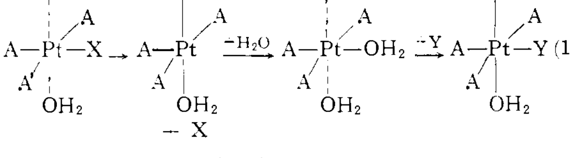
[a] From ref. 9. [b] From ref. 7b. [c] From ref. 3. [d] From ref. 6. [e] From ref. 13. [f] From ref. 15a.

The principal intermediate in the first order reactions is most likely a tetragonal aquo complex



(12)

which can be formed either by direct bimolecular reaction of water and complex (see eq. 11) or by a more subtle dissociation of the leaving group, with help from two water molecules at axial positions, *i.e.*



(13)

Both of these mechanisms are consistent with the observed invariance of k_1 with changes in the net charge on the complex. An S_N1 mechanism, in which there is no solvent participation, is highly unlikely in these cases.

Qualitative and quantitative observations confirm that platinum(II) aquo complexes react rapidly enough with ligands to be possible intermediates in reactions with over-all first order rate behavior.[9,11,15] It is also interesting to note that platinum(II) complexes which hydrolyze in solution do so at a rate equal to the k_1 value for reactions of the complex with other reagents.[6,9,15] It is possible to obtain this proposed intermediate aquo complex in the Pt(dien)X^+ series by dissolving [Pt(dien)-NO_3]NO_3 in water.[3] The resulting Pt(dien)H_2O^{2+} reacts much more rapidly with bromide than with pyridine, and in fact, a small amount (0.002 *M*) of bromide ion is sufficient to convert this complex completely into Pt(dien)Br^+ in the presence of 0.005 *M* pyridine.[11] These facts are consistent with the earlier observations of bromide inhibition of the first order part of the Pt(dien)Br^+-pyridine reaction, and therefore suggest that the aquo complex is the principal intermediate in the first order reactions. The slow residual first order rate for the [Pt(dien)Br]Br–pyridine reaction must be due to some mechanistic path which does not involve an aquo complex.

Since NO_2^- also reacts more slowly than Br^- with Pt(dien)H_2O^{2+},[11] it is easy to understand the non-linearity of the k_{obs} *vs.* [NO_2^-] plot at low NO_2^- concentrations, which was mentioned earlier.

Data in Tables II and III afford some other comparisons. For example, the rate of halide replacement decreases in the order $Cl^- \approx Br^- > I^-$, in analogous complexes, while the reagent reactivity and *trans*-effect order is the opposite $I^- > Br^- > Cl^-$. This explains the puzzling phenomena observed by Grinberg and Nikol'skaya,[16] that in the exchange reactions

$$PtX_4^{2-} + {}^*X^- \rightleftarrows Pt\,{}^*X_4^{2-} + X^- \qquad (14)$$

$$(X^- = CN^-, I^-, Br^- \text{ or } Cl^-)$$

the order of decreasing exchange rate is $CN^- > I^- > Br^- > Cl^-$, which is also the order of decreasing stability of these compounds. Thus the lability of the more stable PtI_4^{2-} is not due to any inherent tendency of the Pt-I bond to rupture but can be blamed either on the large *trans*-effect or the high reactivity of iodide ion or a combination of the two.

Acknowledgments.—The author is grateful to Professors Ralph G. Pearson and Fred Basolo for his introduction into inorganic mechanistic studies and for many helpful discussions concerning this work. I am also indebted to Professor D. S. Martin, Jr., for communicating results to me prior to publication. This research was supported in part by the National Science Foundation and in part by the Atomic Energy Commission, under contract AT(11-1)-89-project No. 2.

---

(15) (a) L. F. Grantham, T. S. Elleman and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **77**, 2865 (1955); (b) T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., *ibid.*, **80**, 536 (1958).

(16) A. A. Grinberg and L. E. Nikol'skaya, *Zhur. Priklad. Khim.*, **2**, 542 (1949); *ibid.*, **24**, 893 (1951).