Rates of Cleavage of Halogen-Bridged Complexes of Platinum(II)

Ralph G. Pearson and Mariel M. Muir[1]

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois. *Received January 24, 1966*

Abstract: The rates of cleavage of some halogen-bridged binuclear complexes of Pt(II) with amines were followed in several nonaqueous solvents. The rate law was the same as that which has been observed for substitution reactions in square-planar complexes, $k_{obsd} = k_1 + k_2[Y]$. The mechanism proposed for the cleavage reactions is very similar to the mechanism for reactions of square-planar complexes. The rate-determining step is the bimolecular attack by either nucleophile or solvent to cleave the first bridge, followed by rapid cleavage of the second bridge. The rates of cleavage reactions are much faster than the rates of substitution reactions in analogous mononuclear complexes. The strength of the Pt–X bond in the bridge must be considerably weaker than in a mononuclear complex.

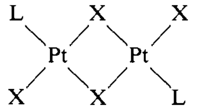
The complexes of Pt(II) which have received the most attention have been mononuclear complexes, in which a single platinum atom is surrounded by its ligands. A considerable amount of work has been done on the mechanisms of reactions of such mononuclear complexes, in particular, on the mechanism of substitution reactions of the square-planar complexes of Pt(II).[2] The kinetics of these reactions obey a two-term rate law

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

where Y is a nucleophile. This has been interpreted as two simultaneous reactions, one reaction with the solvent as the incoming nucleophile and the other with Y as the attacking nucleophile.[3] When the kinetics of these reactions are followed at large excess concentrations of Y, first-order behavior is observed. If the rate constants, k_{obsd}, for these pseudo-first-order reactions are plotted as a function of the concentration of Y, a straight line is obtained. The intercept of this line is k_1, the rate constant for reaction of the complex with solvent, and the slope of the line is k_2, the second-order rate constant for reaction of the complex with Y. The value of k_1 should remain constant for a given solvent as Y is varied, so that if k_{obsd} is plotted against [Y] for several different nucleophiles, a family of lines with a common intercept and different slopes is obtained.[4]

Much less attention has been given to binuclear complexes, although such complexes have been known for some time.[5] It seemed of interest to study the rates of cleavage reactions of some binuclear complexes and to compare the mechanism of cleavage with the mechanism of reaction of the similar mononuclear complexes of Pt(II). For this purpose the halogen-bridged complexes were selected, since they undergo cleavage more readily than thio- or arsenido-bridged complexes.[6]

Halogen-bridged binuclear complexes of the type $Pt_2L_2X_4$ (X = Cl, Br, I, and L = uncharged ligands containing N, S, As, P, Se, and Te) have been prepared by Chatt and Venanzi.[7] These complexes readily undergo symmetrical cleavage with monoamines, a, to yield the complexes $PtaLX_2$.[6a] The complexes $[Pt_2X_6]^{2-}$ (X = Br or I), prepared by Harris, *et al.*,[8] also are cleaved by monoamines to give in most cases $(PtaX_3)^-$.[6b] Molecular weight measurements have shown that the complexes persist in the binuclear form in at least some solvents.[7,8] The complexes are planar,[9] which suggests that the mechanism of cleavage may not be unlike the mechanism of substitution in square-planar complexes. The complexes to be studied were selected to yield information on the effects of changing the bridge atoms and the groups *trans* to the bridge atoms. The complexes were $[Pt_2Br_6]^{2-}$, $[Pt_2I_6]^{2-}$, $Pt_2((CH_3CH_2CH_2CH_2)_3P)_2Cl_4$ $(Pt_2(Bu_3P)_2Cl_4)$, and $Pt_2(pip)_2Cl_4$ where pip = piperidine. The reactions were of the type



$$+ 2a = 2PaLX_2 \qquad (2)$$

Experimental Section

Materials. The bridged complexes, tetraethylammonium tetrabromo-μ,μ'-dibromodiplatinate(II) and tetramethylammonium tetraiodo-μ,μ'-diiodoplatinate(II), $[(CH_3)_4N]_2[Pt_2I_6]$,[8] bis(tri-*n*-butylphosphine)dichloro-μ,μ'-dichlorodiplatinum, $Pt_2(Bu_3P)_2Cl_4$,[7] and dipiperidinedichloro-μ,μ'-dichlorodiplatinum, $Pt_2(pip)_2Cl_4$,[7] the expected products of their reactions with amines,[6] and K_2PtBr_4[10] were prepared following the literature methods indicated. Tetraphenylarsonium trichloropiperidineplatinate(II), $[C_6H_5)_4As[Pt(pip)Cl_3]$, was prepared by suspending $[(C_6H_5)_4As[PtCl_4]$ in acetone containing a stoichiometric amount of piperidine and refluxing in the dark for 18 hr. The light orange product was recrystallized from acetone. In all cases the analyses were satisfactory. The determination of platinum was by ignition. Molar conductances in nitrobenzene checked with those reported in the literature.

Solvents were purified as follows: DMF (N,N-dimethylformamide) was dried over KOH, then distilled from Drierite, bp 153°; acetone was dried over K_2CO_3 and distilled, bp 51°; acetonitrile was dried over Na_2CO_3 and distilled, bp 80–81°; nitrobenzene was was washed with NaOH, dried over $CaCl_2$, passed through a column of alumina, and recrystallized immediately before use.

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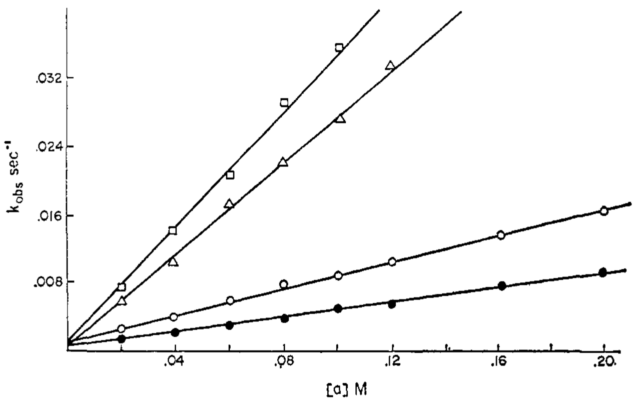

Figure 1. Dependence of k_{obsd} on concentration of amine for reactions of $[Pt_2Br_6]^{2-}$ in DMF at 25°: □, cyclohexylamine; ○, pyridine; △, isopropylamine; ●, N-methylcyclohexylamine.

Pyridine was dried over KOH and redistilled from BaO, bp 113.4–113.8°. Piperidine, α-picoline, cyclohexylamine, N-methylcyclohexylamine, and isopropylamine were redistilled and the middle fraction was collected. Other reagents were used without further purification.

Determination of Rates of Reaction. Standard spectrophotometric techniques were used to follow the reactions. Spectra were obtained with a Cary 14 spectrophotometer. The spectrum of the complex was compared with that of the final reaction mixture, and a wavelength was selected with a large change in absorbance during the course of the reaction and with no appreciable absorption by added reagents such as pyridine.

The cleavage reactions of the halogen-bridged complexes were carried out in 1-cm quartz cells in the thermostated cell compartment of a Cary 14 spectrophotometer. Freshly prepared solutions of complex were used in nearly all cases, since the spectra of the bridged complexes in solution were found to change slowly on standing. The solution of the amine was added with a syringe and the reaction was then followed by recording absorbance at a fixed wavelength against time for the entire reaction. A large excess of amine was used in order to achieve pseudo-first-order conditions. The pseudo-first-order rate constants were obtained by plotting $\log [1/(A - A_\infty)]$ *vs.* t, where A is the absorbance at time t and A_∞ is the absorbance at infinite time.

Water and alcohols were found to be unsuitable as solvents since decomposition of the complex occurred and solubility was very low. $Pt_2(Bu_3P)_2Cl_4$ was found to be too reactive to study with conventional techniques. The other bridged complexes were studied in DMF and in some cases in other nonaqueous solvents. A typical set of values for k_{obsd} are listed in Table I.

Table I. Pseudo-First-Order Rate Constants for the Reaction of $Pt_2Br_6{}^{2-}$ with Pyridine in DMF at 25°

Concn of pyridine, M	k_{obsd}, sec^{-1}
0.0200	0.0027[a]
0.0400	0.0039[b]
0.0600	0.0059[c]
0.0800	0.0076[c]
0.100	0.0094[c]
0.120	0.0105[b]
0.160	0.0139[a]
0.200	0.0166[a]

[a] Average of four runs. [b] Average of three runs. [c] Average of two runs.

The mononuclear complexes analogous to the bridged complexes reacted much more slowly than the binuclear complexes and were followed by measuring the absorbance at suitable time intervals with a Beckman DU spectrophotometer. Determination of the rate of reaction of $[PtBr_4]^{2-}$ with pyridine in DMF was complicated by the fact that the product, $[Pt(py)Br_3]^-$, reacts with pyridine at a comparable rate. The rate constants were obtained by first measuring the rate of reaction of $[Pt(py)Br_3]^-$ with pyridine and then correcting the absorbance data from the over-all reaction to give the rate of the first reaction.

Products of all kinetic runs were confirmed by comparing the spectrum of the final reaction mixture with the spectrum of the expected product.

Results and Discussion

The pseudo-first-order rate constants, k_{obsd}, for the reactions of the bridged complexes were plotted as shown in Figure 1, k_{obsd} *vs.* the concentration of the amine, [a]. Straight lines with nonzero intercepts were obtained, which indicates a rate law of the form

$$\text{rate} = (k_1 + k_2[\text{a}])[\text{complex}] = k_{obsd}\,[\text{complex}] \quad (3)$$

where k_2 is the slope of the line and k_1 is the intercept. Values for the intercepts and slopes, calculated from the data by a least-squares fit, are listed in Table II. The deviations in the intercepts are large, but it is evident that k_1 is a constant for a given complex and solvent. This is the same rate law as that which square-planar complexes obey. As expected, the mononuclear complexes $[PtBr_4]^{2-}$ and $[Pt(pip)Cl_3]^-$ followed the rate law 3. The values of k_1 and k_2 for these complexes are given in Table III. These rate constants are much smaller than the rate constants for the cleavage reactions of the analogous bridged complexes.

Table II. First-Order and Second-Order Rate Constants for Reactions of Halogen-Bridged Complexes with Amines at 25.0°

Solvent	Amine	$k_1 \times 10^4$, sec^{-1}[a]	k_2, M^{-1} sec^{-1}[b]
	$[Pt_2Br_6]^{2-} + 2a \rightarrow 2\,[Pt(a)Br_3]^-$		
DMF	Cyclohexylamine	2	0.360
	Isopropylamine	7	0.254
	Pyridine	8	0.080
	α-Picoline	3	0.089
	N-Methylcyclohexylamine	3	0.045
Acetone	Pyridine	4	0.088
	Piperidine	3	0.48
Acetonitrile	Pyridine	30	0.33
Nitrobenzene	Pyridine	10	0.176
	$[Pt_2I_6]^{2-} + 2a \rightarrow 2[Pt(a)I_3]^-$		
DMF	Pyridine	1	0.0223
	$Pt_2(pip)_2Cl_4 + 2a \rightarrow 2Pt(pip)\,(a)Cl_2$		
DMF	Pyridine	7	0.0182
	Piperidine	5	0.064

[a] The standard deviation in k_1 is large. In most cases it is of the same order of magnitude as k_1, which is not surprising since k_1 is the intercept of a line with a relatively large slope. [b] The standard deviation in k_2 is about 5% of the value of k_2 in nearly all cases, although for a few values it is smaller than 5%.

Table III. First-Order and Second-Order Rate Constants for Reactions of Square-Planar Complexes with Amines in DMF at 25°

Complex	Amine	$k_1 \times 10^6$, sec^{-1}	$k_2 \times 10^5$, M^{-1} sec^{-1}
$[Pt(pip)Cl_3]^-$	pip	3.7	3.0
	py	2.0	1.86
$[PtBr_4]^{2-}$	py	2.3	3.0
$[Pt(py\ Br_3]^-$	py	3.5	6.4

Measurements of freezing-point lowering in nitrobenzene were in agreement with the results of Harris, *et al.*,[8] and show that the binuclear structure persists in nitrobenzene solution. Since the rate of reaction in

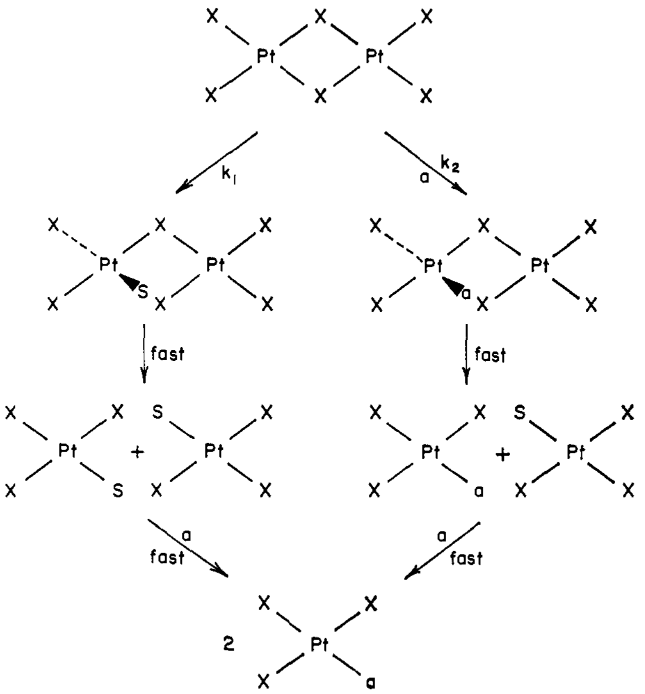

Figure 2. Mechanism of cleavage in halogen-bridged complexes.

nitrobenzene is similar to the rates of cleavage in the other solvents used, the bridged species presumably also remain intact in the other solvents. The spectrum of a given complex did not change appreciably from one solvent to another. If the bridged complex were immediately cleaved by solvent to give complexes of the type $[Pt(solvent)Br_3]^-$, for example, the spectrum should change with changes in solvent. If solutions of the complexes in the various solvents are allowed to stand, significant changes in the spectrum do occur. These presumably correspond to cleavage by solvent.

From the kinetic data and the evidence for existence of the bridged complexes in solution for reasonable periods of time, a mechanism for the cleavage reactions with monoamines can be proposed, as shown in Figure 2. The original bridged complex can undergo one of two initial reactions. It can undergo attack at one platinum atom by the amine to give the intermediate shown, which would presumably be rather unstable. No evidence for complexes of Pt(II) containing a single halogen bridge were found in the literature. The next step, the breaking of the second bridge, looks just like the first, except that it occurs much more rapidly than the first step. The alternate reaction path begins with attack on one platinum by the solvent to give the unstable single bridged intermediate, which then reacts rapidly to give the products. Such a mechanism fits the observed rate expression 3, where k_2 is a bimolecular rate constant and k_1 the rate constant for reaction with the solvent.

The mechanism outlined above bears many similarities to the mechanism of subtitution in square-planar complexes. In particular the transition states are probably very much alike. Figure 3 shows in more detail the mechanism for cleavage of the first bridge, with the proposed transition state in which one platinum atom is in a trigonal-bipyramidal configuration, like the transition state which has been proposed for the reactions of square-planar complexes. It seems quite reasonable that the mechanisms would be similar since the arrangement of ligands around a given platinum atom in the bridged complex is quite similar to the arrangement in a square-planar complex. Both types of complex are probably solvated above and below the plane of the molecule. The solvent molecules were omitted from Figure 2 in order to avoid crowding in the drawing.

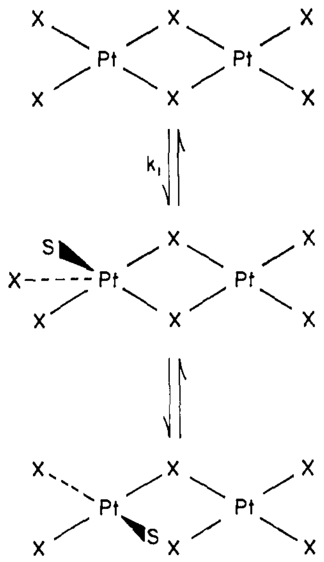

Figure 3. Mechanism of the initial step in cleavage by solvent showing the transition state and intermediate.

In the case of the bridged complexes, the ease with which the Pt–X bond breaks must be greater than for the square-planar complexes. The rate constants in Tables II and III show that the bridged complexes are cleaved at a rate about 10^3 as large as the rate of substitution in the analogous square-planar complexes. A comparison of rate of reaction as the halogen atom in the complex is varied is of interest. The rate of cleavage of the iodo bridge is less than the rate of cleavage of the bromo bridge. This is opposite in order to the rates of substitution for X in the complexes $[PtX_4]^{2-}$ and $[PtLX_3]^-$, in which the order of reactivity is I > Br > Cl.[2,11] In this latter case the order is explained on the basis of the *trans* effect;[12] that is, in these complexes there is an X atom *trans* to the X which leaves, and the X with the largest *trans* effect will have the greatest labilizing ability and will cause the greatest rate of substitution. The order of the *trans* effect is I > Br > Cl. In complexes in which the group *trans* to X remains unchanged, such as $[Pt(dien)X]^+$, the order of reactivity is Cl > Br > I, which is also the order of increasing bond strength.[3]

The results obtained for the reactivities of the bridged complexes, then, seem to show that the effect of the Pt–X bond strength is more important than the labilizing ability of the group *trans* to the bridge. The *trans* effect cannot be completely ignored for these bridged systems, however. The very great reactivity of the complex $Pt_2(Bu_3P)_2Cl_4$ compared to the much less reactive $Pt_2(pip)_2Cl_4$ is rather clear evidence that the *trans* effect is operating in these systems. The labilizing

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ability of the tributylphosphine ligand is very large compared to that of Cl which is greater than that of piperidine. The configurations of the products of the cleavage reactions also follow the predictions of the *trans* effect.[6a] For the amine complex, a mixture of isomers of Pt(pip)aCl_2 was obtained, but the spectral data indicated the first product was probably *cis*, the expected isomer on the basis of the *trans* effect.

The *trans* effect can also be invoked to explain the symmetrical cleavage of the complexes $Pt_2L_2X_4$, since in the intermediate it will always be a bond to the platinum which remained the same during the first step which will be labilized most strongly. For the complexes $[Pt_2X_6]^{2-}$ the situation is less clear. The same group is *trans* to both of the bonds in the intermediate which might be broken, and one might expect a mixture of symmetrical and unsymmetrical cleavage. One explanation of the observed preference for symmetrical cleavage is that a choice of bonds to be cleaved does not exist because the intermediate does not exist. Perhaps the cleavage of the second bridge begins on the other platinum before the ligands on the first platinum atom have finished rearranging from the five-coordinated transition state to their final square-planar or tetragonal configuration.

Another explanation may be found, if one compares the activation energies for symmetrical and unsymmetrical cleavage by considering the equilibrium between the products of symmetrical and unsymmetrical cleavage. The formation constants for the series of complexes $[Pt(NH_3)_xCl_{4-x}]^{(x-2)+}$ are known[13] and the equilibrium constant for

$$[PtCl_4]^{2+} + cis\text{-}[Pt(NH_3)_2Cl_2] \overset{K}{\rightleftharpoons} 2[Pt(NH_3)Cl_3]^- \qquad (4)$$

is found to be equal to 5 × 10^2. Since the products of symmetrical cleavage are the more stable products, it may be that the energy barrier for symmetrical cleavage is lower than for unsymmetrical cleavage, in which case the thermodynamically stable products would also be the kinetically observed products.

In summary, although the difference in reactivity is great, the square-planar complexes and the binuclear halogen-bridged complexes of Pt(II) undergo reactions which follow essentially the same mechanism.

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Phosphorus Trioxide as a Tetradentate Ligand.
I. Transition Metal Complexes

Jean G. Riess[1] and John R. Van Wazer

Contribution from the Monsanto Company, Central Research Department, St. Louis, Missouri.

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Abstract: Phosphorus trioxide, P_4O_6, replaces carbon monoxide in metal carbonyl complexes to give a new class of coordination compounds in which P_4O_6 behaves as a polydentate, nonchelating ligand. When treated with an excess of nickel carbonyl, the symmetrical bird-cage structure of P_4O_6 successively coordinates from one to four tricarbonyl nickel groups. The symmetrical compound, $P_4O_6[Ni(CO)_3]_4$, has been isolated as a crystalline species. When P_4O_6 is in excess, from one to three of the carbonyls of $Ni(CO)_4$ may be substituted by different P_4O_6 groups. When neither reagent is present in large excess, nickel atoms are bridged by P_4O_6 molecules which, in turn, are bridged by nickel atoms so as to give network structures. As expected from the polyfunctionality of P_4O_6 and Ni, there are two gel points in the system at Ni/P_4O_6 mole ratios of *ca.* 0.25 and 4.

As part of a study of the chemistry of phosphorus trioxide,[2] the P_4O_6 bird-cage molecule was tested as a complexing ligand in coordination chemistry. We were pleased to find that nickel carbonyl and phosphorus trioxide reacted readily, with evolution of carbon monoxide. The results of this study are described below along with some exploratory experiments designed to show the general applicability of the P_4O_6 molecule as a polydentate ligand which, because of its large tetrahedral structure, is unable to form a chelate with a single atom of a metal.

Experimental Section

The nickel carbonyl (hereafter called nickel tetracarbonyl) employed in this work was produced by the Mathieson Co.; the phosphorus trioxide, P_4O_6, was obtained several years ago from G. Mikulaschek of the University of Munich. The phosphorus trioxide was made according to the standard method[3] and was freed[4] from dissolved white phosphorus by four successive ultraviolet irradiations, each followed by high-vacuum distillation. It was a clear, colorless liquid (sharp mp at 22.6°; lit.[4] 23.8°) exhibiting a single narrow peak at −113 ppm in its P^{31} nuclear magnetic resonance (nmr) spectrum. Unless otherwise noted, the reactions reported here were carried out by freezing the P_4O_6 into a

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