Redox Interchange Reactions of Halogenoplatinum(IV) Complexes. Some Reactions of *trans*-Dihalogenotetramineplatinum(IV) Complexes

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Abstract: The reactions of bromide and iodide with *trans*-Pt(en)(tet)Cl$_2^{2+}$ (en = ethylenediamine, tet = *N,N,N′,N′*-tetramethylethylenediamine) and of iodide with *trans*-Pt(en)(tet)Br$_2^{2+}$ and *trans*-Pt(en)$_2$Cl$_2^{2+}$ have been studied. The last is a substitution reaction that follows the third-order rate law characteristic of formation of the bridged intermediate or transition state $X\cdots Pt^{IV}\cdots X\cdots Pt^{II}\cdots Y$. The reaction of iodide with the sterically hindered *trans*-Pt(en)(tet)X$_2^{2+}$ (X = Cl or Br) is independent of added Pt(en)(tet)$^{2+}$, and most probably proceeds *via* direct reductive attack of iodide on coordinated halide to form Pt(en)(tet)$^{2+}$ as product. The substitution reaction of *trans*-Pt(en)(tet)Cl$_2^{2+}$ with bromide proceeds by a mixture of the two mechanisms. Data obtained here and elsewhere for the direct attack of anions on halides coordinated to platinum(IV) are considered. In all cases they are consistent with a redox mechanism of the type $X\text{–}Pt^{IV}\text{–}X + Y^- \rightarrow X^- + Pt^{II} + XY$ (slow), and linear free energy relationships are observed between free energies of activation and the standard free energies of the proposed reduction reaction. The gradient varies with the nature of the complex from *ca.* 0.5 up to 1, which suggests that the transition state $X\cdots Pt\cdots X\cdots Y$ bears a close resemblance to the products, *i.e.*, there is a considerable degree of bond making and breaking in the transition state.

Halide interchange reactions of *trans*-PtA$_4$X$_2^{2+}$ complexes (A = amine, X = halide) are generally thought to proceed by way of bridged species of the type $Y\cdots Pt^{II}\cdots X\cdots Pt^{IV}\cdots X$, and the kinetics are first order in [Pt(II)], [Pt(IV)], and [Y$^-$].[1] When the amine ligands in the equatorial plane of the platinum(IV) complex are bulky, however, the formation of such bridged species appears to be difficult and the reactions are very much slower.[2] These reactions involve what is effectively the transfer of X$^+$ from the platinum(IV) complex to the platinum(II), the latter acting as a two-electron reducing agent. Reactions of anionic halogenoplatinate(IV) complexes with iodide do not proceed *via* such a bridged intermediate.[3] Instead, we have suggested, a different sort of two-electron redox reaction can occur in which X$^+$ is transferred from the platinum(IV) directly to the iodide ion to form X–I in the rate-determining step.[3] Subsequent rapid reoxidation of the platinum(II) by X–I, with incorporation of the iodine into the complex,[3d] can result in substitution, but this does not necessarily occur if the platinum(II) complex is thermodynamically stable under the conditions obtaining. In some cases anionic complexes can react *via* the bridged intermediate. Thus the reactions of chloride with *trans*-Pt(CN)$_4$Br$_2^{2-}$ and –Pt(NO$_2$)$_4$Br$_2^{2-}$ follow the third-order rate law characteristic of formation of this intermediate.[4] In addition to these two redox mechanisms, the one involving labile platinum(III) intermediates can sometimes operate in these systems.[3e,5] This mechanism is characterized by ready inhibition by hexachloroiridate(IV), etc.

We wish to report studies that show that cationic halogenoplatinum(IV) complexes can also react *via* the two-electron reductive attack by a halide ion when reduction by platinum(II) is inhibited by steric factors. We have studied the kinetics of the reactions of iodide with *trans*-Pt(en)(tet)X$_2^{2+}$ (en = ethylenediamine, tet = *N,N,N′,N′*-tetramethylethylenediamine, X = Cl or Br) and of bromide with *trans*-Pt(en)(tet)Cl$_2^{2+}$. We also report studies of the reaction of iodide with *trans*-Pt(en)$_2$Cl$_2^{2+}$ which proceeds by way of the bridged intermediate.

Methods and Results

Materials. Potassium tetrachloroplatinate(II), sodium hexachloroplatinate(IV), and sodium hexachloroiridate(IV) were obtained from Johnson, Matthey and Co., Ltd., and were used as received.

Ethylenediamine (as the dihydrochloride) and *N,N,N′,N′*-tetramethylethylenediamine were both obtained from BDH Ltd., and were also used as received.

Preparation of Compounds. *trans*-[Pt(en)$_2$Cl$_2$]Cl$_2$ was prepared by the published method,[6] the rather yellow product formed initially being recrystallized from alcohol–water solutions and, finally, from hydrochloric acid. The product was almost white and its electronic absorption spectrum agreed with those published previously: λ_{max} 332 and 263 nm, ϵ_{332} 100 and ϵ_{263} 960 cm^{-1} l. mol^{-1} (lit.[6,7] λ_{max} 332 and 263 nm, ϵ_{332} 105 and ϵ_{263} 950 cm^{-1} l. mol^{-1}). *Anal.* Calcd for Pt(en)$_2$Cl$_4$: N, 12.3; C, 10.5; H, 3.5. Found: N, 12.3; C, 10.3; H, 4.3. Analyses for N, C, and H were performed by the departmental microanalytical laboratory.

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Dichloro(N,N,N',N'-tetramethylethylenediamine)platinum(II) was prepared from hexachloroplatinate(IV) by Mann's method.[8] The yellow product was recrystallized from water and converted into (N,N,N',N'-tetramethylethylenediamine)(ethylenediamine)platinum(II) dichloride by addition of a slight excess of ethylenediamine to a hot solution. Insoluble material was filtered off, the filtrate concentrated, and the complex precipitated by addition of ethanol. It was recrystallized from water by addition of alcohol and concentrated hydrochloric acid: λ_{max} 290 and 223 nm, ϵ_{290} 60, ϵ_{223} 450 cm^{-1} l. mol^{-1}. *Anal.* Calcd for Pt(en)(tet)Cl_2: N, 12.7; C, 21.7; H, 5.5. Found: N, 12.8; C, 20.9; H, 6.3.

This platinum(II) complex was converted to the corresponding *trans*-dichloroplatinum(IV) complex by oxidation of a hydrochloric acid solution with chlorine. The orange precipitate that was formed initially was filtered off and yellow crystals of the required product were obtained after concentrating and cooling the filtrate. These were recrystallized twice from dilute hydrochloric acid. The analogous *trans*-dibromoplatinum(IV) complex was obtained in a similar way by oxidation of the platinum(II) complex with bromine in a hydrobromic acid solution and eventual recrystallization from dilute hydrobromic acid. Both the *trans*-dichloro and *trans*-dibromo complexes were indefinitely stable in aqueous solution at room temperature as judged by their unchanging uv–visible spectra. Each was analyzed for platinum by reduction with an excess of iodide and spectrophotometric measurement of the I_3^- produced.

trans-Pt(en)(tet)Cl_2^{2+}: λ_{max} 348 nm, ϵ_{348} 200 cm^{-1} l. mol^{-1}. *trans*-Pt(en)(tet)Br_2^{2+}: λ_{max} 338 nm, ϵ_{338} 830 cm^{-1} l. mol^{-1}. *Anal.* Calcd for Pt(en)(tet)Cl_4: Pt, 38.0; N, 10.9; C, 18.7; H, 4.7. Found: Pt, 37.5; N, 10.4; C, 18.3; H, 4.7. Calcd for Pt(en)(tet)Br_4: Pt, 28.2; N, 8.1; C, 13.9; H, 3.5. Found: Pt, 28.7; N, 7.9; C, 13.6; H, 3.2.

The trans nature of the complexes can be inferred from the similarity of the spectra to analogous *trans*-dihalogenoplatinum(IV) complexes, from the universally observed trans oxidation of tetramineplatinum(II) complexes by halogens, and from the nature of their reactions.

Kinetic Studies. Faster reactions were followed by means of a stopped-flow apparatus that has been described previously,[3b,9] and the slower ones by conventional techniques which involved the use of Perkin-Elmer 137UV and Unicam SP500 spectrophotometers with associated thermostating equipment. Where possible, reacting solutions were contained in foil-wrapped flasks to exclude light.

The Reaction of Iodide with *trans*-Pt(en)$_2$Cl$_2$$^{2+}$. The product of this reaction, *trans*-Pt(en)$_2$I$_2$$^{2+}$, has an absorption maximum at 395 nm, the extinction coefficient of which increases with increasing concentration of free iodide even in the presence of sufficient Pt(en)$_2$$^{2+}$ to suppress reduction completely. No evidence for the formation of significant amounts of an intermediate iodochloro complex was observed, even in the presence of an excess of free chloride, and the latter also had a negligible effect on the kinetics. The kinetics of the reaction in the presence of added Pt(en)$_2$$^{2+}$ were followed by means of the stopped-flow apparatus, the decrease in transmittance at 395 nm being recorded. The ionic strength was maintained at 1.0 *M* with sodium perchlorate. Linear pseudo-first-order rate plots were obtained for over two half-lives. The results are shown in Table I, where each value quoted for a rate constant is the average of three separate determinations. The activation parameters and their standard deviations were obtained by a linear least-squares analysis of the change of log k_3/T with $1/T$. This treatment of the data also yielded a value of ±3.0% for the standard deviation of an individually quoted rate constant.

Table I. Rate Constants for the Reaction of Iodide with *trans*-Pt(en)$_2$Cl$_2$$^{2+}$, μ = 1.0 *M* with NaClO$_4$, [Pt(IV)] = *ca.* 2 × 10^{-4} *M*

Temp, °C	[I$^-$], *M*	10^4[Pt(en)$_2$$^{2+}$], *M*	k_{obsd}, sec^{-1}	10^{-4}k_3,[a] *M*$^{-2}$ sec^{-1}	10^{-4}k_3,[b] *M*$^{-2}$ sec^{-1}
19.3	0.300	3.8	4.01	3.52	3.57
25.0	0.100	5.6	2.20	3.93	3.96
25.0	0.300	5.6	6.29	3.73	3.96
25.0	0.300	5.6	6.71	3.99[c]	3.96
25.0	0.500	5.6	11.4	4.07	3.96
25.0	0.500	2.82	5.69	4.04	3.96
25.0	0.500	8.42	17.1	4.05	3.96
26.3	0.300	3.8	4.66	4.09	4.05
35.8	0.300	3.8	5.32	4.67	4.76
45.5	0.300	3.8	6.37	5.59	5.56

$\Delta H^{\ddagger}$ = 2.5 ± 0.2 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −29.0 ± 0.8 cal mol^{-1} deg^{-1}, k_3 (25°) = 3.96 × 10^4 *M*$^{-2}$ sec^{-1}

[a] $k_3 = k_{obsd}/[I^-][Pt(en)_2^{2+}]$. [b] Values calculated by using the "least-squares" activation parameters. [c] 0.2 *M* added chloride.

The Reaction of Iodide with *trans*-Pt(en)(tet)Cl$_2$$^{2+}$. *trans*-Pt(en)(tet)Cl$_2$$^{2+}$ is completely reduced to Pt(en)(tet)$^{2+}$ by iodide solutions of concentration greater than about 0.01 *M* with quantitative formation of I_3^-. Even at lower concentrations of iodide in the presence of an excess of Pt(en)(tet)$^{2+}$, there is no spectrophotometric evidence for the formation of the diiodoplatinum(IV) complex, and the absorbance of I_3^- is completely unaffected by addition of 0.05–0.1 equiv of Pt(en)(tet)$^{2+}$. The rate of reduction of Pt(en)(tet)Cl$_2$$^{2+}$ by iodide was therefore followed by means of the stopped-flow technique, the decrease in transmittance at 353 nm being recorded. The results are reported in Table II, each quoted rate constant again being the average of three separate determinations. The presence of hexachloroiridate(IV) had no effect on the kinetics. The activation parameters were estimated by the least-squares procedure and the standard deviation of an individually quoted rate constant was ±2.8%.

The Reaction of Iodide with *trans*-Pt(en)(tet)Br$_2$$^{2+}$. The dibromo complex is reduced completely to Pt(en)(tet)$^{2+}$ at concentrations of iodide in excess of 0.5 *M*. At such concentrations the rate was too fast to follow even with the stopped-flow apparatus, but at lower concentrations at which the rate was just observable, the reaction did not appear to go to completion. However, measurements of initial rates of decreasing transmittance at 353 nm showed that the rate at 25° and ionic strength of 1.0 *M* was approximately first order in iodide and unaffected by added Pt(en)(tet)$^{2+}$.

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(8) F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 2772 (1958).
(9) D. J. Hewkin, Ph.D. Thesis, London University, 1967.

Table II. Rate Parameters for Reaction of Iodide with *trans*-Pt(en)(tet)Cl_2^{2+}, $\mu = 1.0\ M$ with $NaClO_4$, [Pt(IV)] = *ca.* $7.5 \times 10^{-5}\ M$

Temp, °C	[I^-], M	10^4[Pt(en)-(tet)$^{2+}$], M	k_{obsd}, sec^{-1}	k_2,[a] M^{-1} sec^{-1}	k_2,[b] M^{-1} sec^{-1}
17.3	0.100	1.02	1.00	10.0	10.05
17.3	0.100	1.02	0.99	9.9[c]	10.05
23.2	0.050	0.94	0.79	15.8	16.5
23.2	0.100	0.00	1.65	16.5	16.5
23.2	0.100	0.94	1.67	16.7	16.5
23.2	0.100	1.78	1.66	16.6	16.5
23.2	0.100	2.95	1.64	16.4	16.5
23.2	0.300	0.00	5.15	17.2	16.5
23.2	0.500	0.00	8.21	16.4	16.5
25.4	0.100	0.00	2.00	20.0	19.7
34.9	0.100	0.00	4.23	42.3	41.7
43.5	0.100	0.00	7.75	77.5	78.8

$\Delta H^{\ddagger} = 13.8 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6.5 \pm 0.6$ cal mol^{-1} deg^{-1}, k_2 (25°) = 19.1 M^{-1} sec^{-1}

[a] $k_2 = k_{obsd}/[I^-]$. [b] Calculated by using the "least-squares" activation parameters. [c] [$IrCl_6^{2-}$] = $9 \times 10^{-6}\ M$.

Table III. Rate Parameters for the Reaction of Bromide with *trans*-Pt(en)(tet)Cl_2^{2+}, $\mu = 1.0\ M$ with $NaClO_4$, [Pt(IV)] = *ca.* $5 \times 10^{-4}\ M$

Temp, °C	[Br^-], M	10^4[Pt(en)-(tet)$^{2+}$], M	$10^4 k_{obsd}$, sec^{-1}	$10^4 k_{obsd}$/[Br^-], M^{-1} sec^{-1}
54.0	1.0	2.10	3.47	3.47
54.0	1.0	4.32	5.13	5.13
54.0	1.0	7.44	7.23	7.23
54.0	1.0	5.91	6.18	6.18
54.0	0.5	5.91	3.08	6.16
65.0	1.0	2.10	5.63	5.63
65.0	1.0	4.32	8.49	8.49
65.0	1.0	7.44	11.77	11.77
65.0	1.0	7.44	11.28	11.28
75.0	1.0	2.10	8.28	8.28
75.0	1.0	4.32	12.0	12.0
75.0	1.0	5.91	15.6	15.6
75.0	1.0	5.91	14.9	14.9
75.0	1.0	7.44	17.5	17.5
75.0	0.50	7.44	8.73	17.5
75.0	0.25	8.50	4.82	19.3
75.0	0.50	8.50	9.70	19.4
75.0	0.75	8.50	14.2	18.9
75.0	1.0	8.50	19.3	19.3

	$10^4 k_a$,[a] M^{-1} sec^{-1}	$10 k_b$,[a] M^{-2} sec^{-1}
54.0	2.00 ± 0.06	7.08 ± 0.12
65.0	3.38 ± 0.44	11.1 ± 0.8
75.0	4.72 ± 0.33	17.2 ± 0.5

$\Delta H_a^{\ddagger} = 8.6 \pm 0.8$ kcal mol^{-1}, $\Delta H_b^{\ddagger} = 8.9 \pm 0.4$ kcal mol^{-1}
$\Delta S_a^{\ddagger} = -49.3 \pm 2.3$ cal mol^{-1} deg^{-1}, $\Delta S_b^{\ddagger} = -32.3 \pm 1.1$ cal mol^{-1} deg^{-1}
k_a (25°) = $5.1 \times 10^{-5}\ M^{-1}$ sec^{-1}, k_b (25°) = 0.17 M^{-2} sec^{-1}

[a] $k_{obsd} = k_a[Br^-] + k_b[Br^-][Pt(en)(tet)^{2+}]$.

The second-order rate constant was *ca.* $3 \times 10^3\ M^{-1}$ sec^{-1}.

The Reaction of Bromide with *trans*-Pt(en)(tet)Cl_2^{2+}. The rate of this reaction is sufficiently slow that it can be followed by conventional spectrophotometric techniques, *trans*-Pt(en)(tet)Br_2^{2+} being formed quantitatively. The growth in absorbance at 338 nm was followed. In the presence of added Pt(en)(tet)$^{2+}$ good linear pseudo-first-order rate plots were obtained for one to two half-lives, and the observed rate constants were given by $k_{obsd} = (k_a + k_b[Pt(II)])[Br^-]$. In the absence of Pt(en)(tet)$^{2+}$, however, the rate plots were curved and the initial slopes were less than half those expected from the value obtained for k_a. No evidence for the formation of significant amounts of an intermediate bromochloro complex was observed. The results of measurements in the presence of added Pt(en)(tet)$^{2+}$ are given in Table III. Values of k_a and k_b were obtained according to the rate law $k_{obsd}/[Br^-] = k_a + k_b[Pt(II)]$ by a weighted least-squares analysis. Each value of $k_{obsd}/[Br^-]$ was assigned the same percentage standard deviation which was shown by the analysis to be ±2.4%.

Spectroscopic Interaction between *trans*-Pt(en)(tet)Br_2^{2+} and Free Bromide. The spectrum of *trans*-Pt(en)(tet)Br_2^{2+} was found to change on addition of free bromide ions. No new peaks were observed, but there was a general enhancement of the absorbance. The changes were complete by the time measurements could be made and the solutions were stable indefinitely. At 338 nm, an ionic strength of 1.0 *M*, and 25°, the extinction coefficient increased linearly with concentration of added bromide from 830 to 1325 cm^{-1} l. mol^{-1} at [Br^-] = 1.0 *M*, *i.e.*, with a gradient of 4.95×10^2 cm^{-1} l.^{2} mol^{-2}. This increase was unaffected by the presence of Pt(en)(tet)$^{2+}$.

Discussion

The activation parameters for the reactions that involve $X \cdots Pt^{IV} \cdots Y \cdots Pt^{II} \cdots Z$ bridged intermediates or transition states are compared in Table IV with relevant data from the literature. The species $PtA_4 \cdots Z^+$ evidently becomes a much more effective reducing agent as Z changes along the series Cl, Br, I, since the affinity of PtA_4^{2+} for Z^- is unlikely to depend greatly on Z. A similar, but (as far as Z = I is concerned) less pronounced effect is shown by the enthalpies of activation for the reactions of $Pt(NH_3)_5I^{3+}$ with $Pt(NH_3)_4^{2+}$ and Z^-.[10] This trend shows that the reducing power of the PtA_4Z^+ moiety increases along this series, as expected for a mechanism which can be regarded as a nucleophilic attack by the five-coordinate PtA_4Z^+ on the chloride coordinated to the platinum(IV) or, alternatively, as transfer of Cl^+ to the PtA_4Z^+.

Comparison of the parameters when X = Y = Cl, Z = Br, and $A_4 = (NH_3)_4$[11] or (en)(tet) shows that the slowness of the redox reaction of the hindered complex is due less to a relatively unfavorable enthalpy of activation than to a relatively unfavorable entropy of activation. This probably implies that the steric effect of the bulky ligand, tet, slightly increases the enthalpy required for the formation of the bridge, but that the unfavorable entropy caused by the stereochemically more limited way in which an effective bridge can be formed is even more important.

Relationships between kinetic and thermodynamic parameters for these redox reactions have been observed.[11b,12] They suggest a growing similarity between the transition states and the products as the reactions become thermodynamically more favorable, and the importance of the nature of the bridging group has also been emphasized.[11]

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(10) W. R. Mason and R. C. Johnson, *Inorg. Chem.*, 4, 1258 (1965).

(11) (a) R. R. Rettew and R. C. Johnson, *ibid.*, 4, 1565 (1965); (b) S. G. Bailey and R. C. Johnson, *ibid.*, 8, 2596 (1969).

(12) A. Peloso, *Gazz. Chim. Ital.*, 99, 1025 (1969).

Table IV. Activation Parameters for Reactions Involving Bridged Intermediate Species $X\cdots Pt^{IV}(A)_4\cdots Y\cdots Pt^{II}(A)_4\cdots Z$ (A = Amine Ligand, X^-, Y^-, and Z^- Are Halide Ions)

X	Y	Z	A_4	μ, *M*	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$k_{25°}$, M^{-2} sec^{-1}	*K*
Cl[a]	Cl	Cl	$(en)_2$	0.01	11	−16	15	1
Cl[b]	Cl	Br	$(NH_3)_4$	0.2	7.5	−24	108	17
Cl	Cl	I	$(en)_2$	1.0	2.5 ± 0.2	−29 ± 1	4.0×10^4	
Cl	Cl	Br	(en)(tet)	1.0	8.9 ± 0.4	−32 ± 1	0.168	

[a] Reference 2a. [b] Reference 11.

Although the sterically unhindered halogenoamine complexes of platinum(IV) generally require the presence of platinum(II) before reactions can occur at all readily, there is some evidence that reactions can still occur in its absence.[10,11] When the amine ligands are bulky (and the bridging mechanism involving platinum(II) is less favored), then the reactions not involving platinum(II) become relatively more significant. We consider that the [Pt(II)]-independent reactions of these cationic halogenoplatinum(IV) complexes occur by way of the same redox mechanism already proposed for substitution of iodide into anionic halogenoplatinate(IV) complexes.[3] In this mechanism the iodide attacks the coordinated halide ligand, X^-, and X^+ is formally transferred to the iodide with concomitant two-electron reduction of the platinum(IV). Subsequent rapid reoxidation of the platinum(II) by I–X, together with incorporation of another iodide into the complex, leads to the formation of the *trans*-diiodo product. Correlations of kinetic parameters for substitution with related thermodynamic parameters for reduction have suggested that the extent of reduction in the transition state is quite large.[3a,b]

Peloso and his coworkers[13] have proposed a related mechanism for reduction of the neutral complexes PtL_2X_4 (L = tertiary phosphine or arsine, etc.; X = Cl or Br). These are reduced in methanolic solution by SCN^-, I^-, $SeCN^-$, and $S_2O_3^{2-}$ at rates that are first order in [anion]. The rates increase along this series of anions to exactly the same extent regardless of the complex, and this is believed to indicate that the degree of bond making and breaking in the transition state is small. This behavior is, however, merely consistent with the free energies of activation being proportional to the standard free energies of reduction, *i.e.*, $\Delta G^{\ddagger} = c\Delta G°$, and the extent of bond making and breaking in the transition state is indicated by the value of *c*. If the rate-determining step is $PtL_2X_4 + Y^{n-} \rightarrow PtL_2X_2 + X^- + XY^{(n-1)-}$, then $\Delta G^{\ddagger} = c\Delta G_1° + c\Delta G_2°$, where $\Delta G_1°$ is the standard free energy for the reduction $PtL_2X_4 + 2e \rightarrow PtL_2X_2 + 2X^-$, and $\Delta G_2°$ is that for the oxidation $X^- + Y^{n-} \rightarrow XY^{(n-1)-} + 2e$. Hence, for a given complex and various reducing anions, $\Delta G^{\ddagger}$ will be proportional to $\Delta G_2°$; *i.e.* the dependence of the rate of reduction on the nature of Y^{n-} will be the same whatever the substrate. For a given anion, $\Delta G^{\ddagger}$ will be proportional to $\Delta G_1°$; *i.e.*, the dependence of the rate on the nature of the complex will be the same whatever the anion. This is exactly the behavior observed by Peloso, *et al.*

There are some data available that enable an estimation of *c* to be made. Ahrland and Chatt[14] measured reduction potentials for the reactions $PtL_2Cl_4 + 2e \rightarrow PtL_2Cl_2 + 2Cl^-$ in aqueous phenol at 25°, where L = *cis*- or *trans*-P-*n*-Pr_3 or *trans*-S-*n*-Pr_2. Corresponding values of $\Delta G_1°$ are found to be 16.9, 16.1, and 20.4 kcal mol^{-1}, respectively, as compared with corresponding values of $\Delta G^{\ddagger}$ at 25° of 10.46, 8.81, and 13.52 kcal mol^{-1}, from the data of Peloso, *et al.*, for reduction by iodide in methanol.[13] The difference in solvents used in the kinetic and thermodynamic measurements will probably not have an important effect on the relative values of the parameters. A plot of $\Delta G^{\ddagger}$ against $\Delta G_1°$ gives quite a good straight line with a gradient, *c*, of *ca.* 1.0 ± 0.1. Thermodynamic data are not, unfortunately, available to check whether a similar value of *c* is obtained when Y^{n-} is varied and the complex kept the same. The fact that a similar dependence of log *k* on the nature of Y^{n-} is found for both chloro and bromo complexes must imply that $\Delta G_2°$ also varies in the same way for both complexes.

These reduction reactions therefore show very much the same behavior as the substitution reactions in the close parallel between the kinetic and thermodynamic parameters[3a,b]; *i.e.*, the transition state resembles the products of the redox reaction and a considerable degree of bond making and breaking occurs in all cases.

Skinner and Jones[15] have shown that the replacement of one bromide in *trans*-$Pt(CN)_4Br_2^{2-}$ by OH^- proceeds by two kinetically independent paths, one that is first order in [OH^-] and the other first order in [Br^-]. They have proposed yet another mechanism for reactions of the already very versatile platinum(IV) complexes. This involves formation of an associated species $X\cdots Br{-}Pt(CN)_4Br^{3-}$ (X = OH or Br), in which X^- enhances the dissociative interchange of a bromide ligand (trans to the site of the association) and a water molecule. Skinner and Jones do not consider that a redox mechanism is possible when X = OH, although several cases of reduction of platinum(IV) complexes by hydroxide are known. *trans*-$Pt(CN)_4I_2^{2-}$ is reduced to $Pt(CN)_4^{2-}$ approximately according to the rate law $k_{obsd} = k_a[OH^-] + k_b[I^-]$,[3b] which is analogous to that for base hydrolysis of the dibromo complex, and several halogenoamine-platinum(IV) complexes are reduced by hydroxide.[16] Skinner and Jones also argue that the redox mechanism is not capable of explaining the term which is first order in [Br^-]. It is said that the HOBr, which would be formed extensively from the intermediate Br_2 under the conditions obtaining, is incapable of oxidizing the $Pt(CN)_4^{2-}$ to *trans*-$Pt(CN)_4Br_2^{2-}$ on both thermodynamic and kinetic grounds. Thus, a value of 0.75 V is quoted for the oxidation potential of HOBr as compared

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(13) A. Peloso, G. Dolcetti, and R. Ettore, *Inorg. Chim. Acta*, 1, 307, 403 (1967); *Gazz. Chim. Ital.*, 97, 955, 1507 (1967).

(14) S. Ahrland and J. Chatt, *J. Chem. Soc.*, 1379 (1957).

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

(16) R. C. Johnson, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, 24, 59 (1962); A. A. Grinberg, *Sv. Kem. Tidskr.*, 73, 199 (1961).

to a value of *ca.* 0.7 V which they obtained for the oxidation potential of *trans*-$Pt(CN)_4Br_2^{2-}$. Since the oxidation potential of the $Pt(CN)_4^{2-} + 2Cl^- | Pt(CN)_4Cl_2^{2-}$ couple is −0.89 V,[17] a value of *ca.* −0.7 V seems reasonable for the corresponding bromide system. However, the value of 0.76 V said to be the oxidation potential of HOBr seems to be a quote of the value −0.76 V listed by Latimer[18] for the oxidation potential of the couple $2OH^- + Br^- | BrO^- + H_2O$. A knowledge of the acidity constant of HOBr[18] enables a value of $E_{ox}^0 = -0.92$ V for $HO^- + Br^- \rightarrow HOBr + 2e$ to be calculated, and this is quite negative enough for HOBr to oxidize $Pt(CN)_4^{2-} + 2Br^-$ to *trans*-$Pt(CN)_4Br_2^{2-}$. Skinner and Jones' argument is, in any case, quite irrelevant since it is not required that the $Pt(CN)_4^{2-}$ be oxidized to $Pt(CN)_4Br_2^{2-}$ but only to the more stable $Pt(CN)_4Br(OH)^{2-}$. The available thermodynamic data[15,19] show that, under the conditions of pH and [Br^-] obtaining in these experiments, less than 0.01% of the platinum would be present as unoxidized $Pt(CN)_4^{2-}$ at equilibrium. They also argue that coordination of "HBrO" to $Pt(CN)_4^{2-}$ during an oxidation reaction is unlikely, although the reason for this is hard to see, especially if the hypobromous acid is written more correctly as HOBr.[20] The final point raised by Skinner and Jones has, however, some validity. It has to do with the bromine scavengers phenol and aniline which effect the reduction of *trans*-$Pt(CN)_4Br_2^{2-}$ at rates that are significantly different from each other. Even in the presence of substantial amounts of added $Pt(CN)_4^{2-}$ reduction is still effected by these scavengers. This raises the question of the susceptibility of the intermediates, Br_2 or BrOH, to competitive reactions. If there is some affinity between $Pt(CN)_4^{2-}$ and Br_2 or BrOH, then reoxidation of the same platinum to which they had originally been attached may be more probable than their reactions with phenol or aniline or with added $Pt(CN)_4^{2-}$. This point requires further study.

The activation enthalpy for the reaction with bromide is only 14 kcal mol^{-1},[15] compared with a value of over 30 kcal mol^{-1} that might reasonably be expected for the unassisted dissociation of bromide from a platinum(IV) complex. It seems most unlikely that the weakly associated species $Br\cdots Br\text{–}Pt(CN)_4Br^{3-}$ would be that much more reactive. On the other hand, the redox mechanism is quite satisfactory in explaining Skinner and Jones' data and no new mechanism needs to be postulated. A close parallel between the kinetic parameters and the thermodynamics for reduction can be demonstrated. Thus the reduction potentials for the reactions *trans*-$PtL_4Br_2^{2-} + 2e \rightarrow PtL_4^{2-} + 2Br^-$ are 0.59[17] and *ca.* 0.7 V[15] when L = Br and CN, respectively. $\Delta(\Delta G_1°)$ (see above) is therefore *ca.* 5 kcal mol^{-1}, which is approximately equal to the value of $\Delta(\Delta G^{\ddagger})$ for reduction by iodide.[3b,e] In view of the uncertainty in the reduction potentials, *c* is not distinguishably different from unity. A more precise value of *c* can be obtained, however, by comparing data for the reactions of *trans*-$Pt(CN)_4Br_2^{2-}$ with bromide, hydroxide, and iodide. Values of $\Delta G^{\ddagger}$ are 20.7, 14.7, and 10.6 kcal mol^{-1}, respectively, while data in ref 21 for the reactions $2Br^- \rightarrow Br_2 + 2e$, $Br^- + OH^- \rightarrow BrOH + 2e$, and $Br^- + I^- \rightarrow BrI + 2e$ provide corresponding values for $\Delta G_2°$ of 50.8, 42.7, and 36.3 kcal mol^{-1}. A good linear plot of $\Delta G^{\ddagger}$ against $\Delta G_2°$ is obtained with a gradient, *c*, of 0.7.

The reaction of $Pt(CN)_4Br_2^{2-}$ with chloride proceeds relatively slowly in the absence of added $Pt(CN)_4^{2-}$,[4] and it was suggested that this slow reaction might be due to $Pt(CN)_4^{2-}$ present as impurity in the sample of $Pt(CN)_4Br_2^{2-}$. It is, however, possible to predict an approximate value for the direct reductive attack of chloride on coordinated bromide in $Pt(CN)_4Br_2^{2-}$ by comparison with the kinetic and thermodynamic data for the corresponding attack by bromide. $\Delta G_2°$ for attack by chloride will be larger than that for attack by bromide by an amount equal to the standard free energy change for the reaction $Br_2 + Cl^- \rightarrow BrCl + Br^-$ in aqueous solution. A value for the standard free energy of formation of BrCl is known only for the gaseous molecule, but inspection of available data[21] for the halogens and interhalogens suggests that the value for BrCl in aqueous solution will be about 2 ± 1 kcal mol^{-1} lower. The value of $\Delta G_2°$ for reaction with chloride then becomes 5.3 ± 1 kcal mol^{-1} greater than that for reaction with bromide. Since *c* is known to be *ca.* 0.7 for this system, $\Delta G^{\ddagger}$ will be *ca.* 3.7 ± 0.7 kcal mol^{-1} higher. Using Skinner and Jones' value of the rate constant for the reaction with bromide, we find that an upper limit for the value for reaction with chloride is *ca.* 5×10^{-5} M^{-1} sec^{-1}. This is about 30% of the rate constant observed[4] in the absence of added $Pt(CN)_4^{2-}$. In view of the uncertainties involved in this estimation, it is possible that the [Pt(II)]-independent reaction is in large part due to the direct reductive attack by chloride rather than to $Pt(CN)_4^{2-}$ impurity.[4] The estimation does show clearly, however, that the direct reductive attack would be much less important than indirect attack through $Pt(CN)_4^{2-}$, so the application of the observed relationship between the substitution kinetics and the reduction thermodynamics is capable of explaining the nonoccurrence of [Pt(II)]-independent reactions as well as their occurrence.

The reaction of bromide with *trans*-$Pt(en)(tet)Cl_2^{2+}$ provides the first example in which a comparison can be made between the kinetic parameters for reduction of a halogenoplatinum(IV) complex by a halide ion both directly and indirectly through a platinum(II) intermediary. The enthalpy of activation for direct attack by bromide is about equal to that for the [Pt(II)]-dependent reduction, but the entropy is very much less favorable. The latter is surprising, since the bridging mechanism requires three ions to be brought together in a rather limited stereochemical arrangement.

Consideration of the kinetic and thermodynamic parameters for direct attack by bromide and iodide enables a value of *c* for the *trans*-$Pt(en)(tet)Cl_2^{2+}\text{–}X^-$ reactions to be calculated. $\Delta(\Delta G_2°)$ will be given by the standard free energy of the reaction $ClBr + I^- \rightarrow ClI + Br^-$ in aqueous solution. Using the same value of the standard free energy of formation of BrCl in aqueous solution as was used above, and values for the other species from ref 21, we find $\Delta(\Delta G_2°) = -14.4 \pm 1$ kcal

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(17) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952, p 207.

(18) Reference 17, p 61.

(19) Reference 17, p 60.

(20) M. C. Day and J. Selbin, "Theoretical Inorganic Chemistry," 2nd ed, Reinhold, New York, N. Y., p 386.

(21) Reference 17, p 63; National Bureau of Science Technical Note 270-1, Washington, D. C., 1965.

mol^{-1}. $\Delta(\Delta G^{\ddagger}) = -7.6$ kcal mol^{-1} so that $c = 0.53 \pm 0.04$. This is a lower value than found for the other systems and suggests a smaller amount of reduction in the transition state. It is clear that c depends on the nature of the complex, and it may be that a relationship $\Delta G^{\ddagger} = c\Delta G_1° + c'\Delta G_2°$ will be found to be more appropriate when more extensive and precise kinetic and thermodynamic data become available.

There is not the same correlation between the values of $\Delta H^{\ddagger}$ and $\Delta H_2°$ for reduction. $\Delta(\Delta H_2°)$ can be estimated from data in ref 21 to be slightly less than -15 kcal mol^{-1}, while $\Delta(\Delta H^{\ddagger})$ is $+5.2$ kcal mol^{-1}. There is also no enthalpy correlation in the reactions of *trans*-$Pt(CN)_4Br_2^{2-}$ with bromide and hydroxide. While $\Delta(\Delta H^{\ddagger})$ = *ca.* 12 kcal mol^{-1}, $\Delta(\Delta H_2°)$ is negligible. Whether this absence of an enthalpy correlation is general or not remains to be seen, but it may be significant that both these examples include reactions for which unusual entropies of activation are obtained. Thus $\Delta S^{\ddagger}$ for the reaction of hydroxide with *trans*-$Pt(CN)_4Br_2^{2-}$ is unusually positive, while that for the reaction of *trans*-$Pt(en)(tet)Cl_2^{2+}$ with bromide is unusually negative. The only other reaction of the latter type for which such a value is observed is that of iodide with *trans*-$Pt(C_2O_4)_2Cl_2^{-}$,[3a] which also has a correspondingly low value of $\Delta H^{\ddagger}$. Both these cases might be exceptional in having much less Pt^{IV}-Cl bond breaking in the transition state coupled with a much less favorable probability of electron transfer of some sort.

The reaction of iodide with *trans*-$Pt(en)_2Cl_2^{2+}$ shows no sign of a [Pt(II)]-independent rate term, and the value of the rate constant for direct attack must, therefore, be less than *ca.* 2 M^{-1} sec^{-1} at 25° and $\mu = 1.0$ M. This is less than one-tenth of the rate constant for direct attack on *trans*-$Pt(en)(tet)Cl_2^{2+}$. As might be expected, the more bulky amine ligand causes more rapid reduction in addition to stabilizing the reduced form thermodynamically, the latter being shown by the nonexistence of *trans*-$Pt(en)(tet)I_2^{2+}$. A similar effect has been noted in the reduction of analogous complexes of platinum(IV) by nitrite.[2b]

The fact that there is no evidence for the formation of *trans*-$Pt(en)(tet)I_2^{2+}$ is probably a consequence of steric factors rather than of electronic ones, since *trans*-$Pt(CN)_4I_2^{2-}$ can be detected in solution although *trans*-$Pt(CN)_4Cl_2^{2-}$ is reduced by iodide about 50 times more rapidly than is *trans*-$Pt(en)(tet)Cl_2^{2+}$.

Finally, there is a strong spectroscopic interaction between *trans*-$Pt(en)(tet)Br_2^{2+}$ and bromide of a similar type to the interactions already observed between bromide and the trans complexes $Pt(en)_2Br_2^{2+}$,[7] Pt-$(NH_3)_4Br_2^{2+}$,[11] Pt(*l*-pn)$_2$Br$_2^{2+}$,[22] and $Pt(CN)_1Br_2^{2-}$.[3b,15] Similar interactions have also been observed between chloride and *trans*-$Pt(en)_2Cl_2^{2+}$ [7] and *trans*-Pt-$(CN)_4Cl_2^{2-}$ [3b] and between iodide and *trans*-Rh-$(en)_2I_2^{+}$.[23] None of these interactions appears to be caused by reduction, and no leveling off of the plots of absorbance against halide concentration (characteristic of finite degrees of ion association) is observed. The existence of these interactions is clearly not charge dependent, and it may be quite general. No really satisfactory explanation of their occurrence has been offered.[3b]

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(22) H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, 42, 1286 (1969).

(23) H. L. Bott, Ph.D. Thesis, London University, 1966.

Pyrolysis of Tetracyclo[5.3.0.0^{2,10}.0^{3,6}]decene-8. A (2′-Vinylcyclopropyl)cyclobutane Rearrangement

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Abstract: Pyrolysis of tetracyclo[5.3.0.0^{2,10}.0^{3,6}]decene-8 (V) (believed to be 3,6-endo) in the vapor phase (~100 Torr) in a static system at 250° gave three isomeric products in the ratio of 4:2:1. The first of these was tricyclo-[5.2.1.0^{4,10}]deca-2,5-diene (VI). The second was found to be the exo stereoisomer (VIII) of the starting material. The third isomer was not further identified. In a fast-flow system at 550° at a pressure of <1 Torr, the products were VI and 1,2-dihydronaphthalene. From kinetic studies and by deuterium labeling, the formation of VI was shown to involve a shift of the C_3C_4 bond in V to the C_8 position. Thus, this reaction can be regarded as the rearrangement of a (2′-vinylcyclopropyl)cyclobutane system to a 1,4-cyclononadiene.

There are numerous examples of thermal rearrangements in which the normal isomerization (or decomposition) pathways of cyclopropane and cyclobutane rings are modified by the presence of a vinyl group on the ring.[1] When two such rings and a vinyl group are suitably placed in a molecule, it should be

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(1) For a recent review, see H. M. Frey and R. Walsh, *Chem. Rev.*, 69, 103 (1969).