Activation Parameters for Some Substitution Reactions of Acidodiethylenetriamineplatinum(II) Complexes

BY UMBERTO BELLUCO, RENATO ETTORRE, FRED BASOLO, RALPH G. PEARSON, AND ALDO TURCO

The activation energy parameters for the reaction of $[Pt(dien)X]^+$ (dien = $NH_2C_2H_4NHC_2H_4NH_2$; $X^- = Cl^-$, Br^-, I^-, N_3^-, SCN^-, or NO_2^-) in water solution with several different nucleophiles were determined. High rates of reaction parallel low enthalpies of activation. All reactions have an appreciable negative entropy of activation and this is discussed in terms of the nucleophilic displacement mechanism for these reactions.

Introduction

Although extensive investigations on rate of nucleophilic substitutions of low-spin d^8 system such as Pt(II), Pd(II), Ni(II), and Au(III) have been reported,[1] there is, however, relatively little discussion and limited data on the activation parameters of these reactions.

Therefore, it was decided to determine the temperature dependence of the rates of reaction of $[Pt(dien)X]^+$ (X = Cl, Br, I, N_3, SCN, NO_2) with various nucleophiles. This paper reports and discusses the activation parameters estimated from these data.

Experimental and Results

Materials.—The $[Pt(dien)X]X$ and $[Pt(dien)X]NO_3$ complexes were prepared following the method previously reported[2] and were characterized by analysis.

Kinetics.—Rates of all the reactions were determined spectrophotometrically in the ultraviolet region by means of Beckman DK-2A, Beckman DU, and Optica CF-4 spectrophotometers with a cell compartment thermostated at the desired temperature. The reactions studied are represented by eq 1. That the

$$[Pt(dien)X]^+ + Y^- \longrightarrow [Pt(dien)Y]^+ + X^- \qquad (1)$$
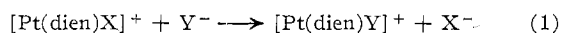
reactions went to completion was checked by comparing the final spectrum obtained for the reacting solution with the spectrum of a solution of the product complex previously isolated and characterized. Reactions which did not go to completion under our experimental conditions were not further investigated.

In most of the experiments the ionic strength was kept constant at 0.1 M by the addition of KNO_3. A few experiments were also done at an ionic strength of 0.02 M. No effect of ionic strength was found for the reaction of $[Pt(dien)Br]^+$ with thiourea.

The kinetic runs were performed with an excess of reagent present (in the range 10^{-2}–10^{-1} M) with respect to the complex ($\gtrsim 10^{-3}$ M) in order to provide pseudo-first-order conditions and to force the reaction to go to completion. In most cases the reagent concentration was varied by at least a factor of five, and measurements were made at three different reagent

concentrations. Duplicate runs were made in many cases with reproducibility being better than 5%.

The rates of the reactions investigated follow the two-term rate law given by eq 2, where k_S is the rate constant for the solvent path and k_Y is for the direct

$$k_{obsd} = k_S + k_Y[Y^-] \qquad (2)$$

reagent path.[3]

For the reaction of $[Pt(dien)Cl]^+$ with Br^- and N_3^- and $[Pt(dien)Br]^+$ with N_3^-, k_S was large enough in comparison to $k_Y[Y^-]$ to be determined accurately; in other cases k_S was too small to be measured.

Rate constants were determined at least at two temperatures in order to calculate the activation parameters, ΔH^* and ΔS^*. The rate constants estimated at 30° and ΔH^* and ΔS^* values are listed in Table I. The error in ΔH^* is ±1 kcal/mole, estimated, and in ΔS^*, ±2 eu.

Discussion

Previous papers report[2–4] the rate data of nucleophilic displacements on $[Pt(dien)X]^+$ with various reagents. The bimolecular reactivity order was found to parallel the order of increasing *trans* effect of the incoming groups. More extensive studies[5] confirm the fact that the nucleophilic strength of a reagent toward a platinum(II) substrate is largely determined by the polarizability of the reagent and not its basicity.

Theoretical discussions of the relative rates of reaction of platinum(II) complexes are usually concerned with energies rather than free energies.[1] Such a discussion makes the assumption that the rate constants are directly paralleled by changes in enthalpies of activation. It is therefore comforting that, for the analogous systems represented in Table I, the data show that high rates of reaction go with low energies of activation. Fortunately, this means that previous discussions[1] of the relative reactivities of these systems are justified.

The data in Table I also suggest that for the same reagent Y, the ease of replacement of X in $[Pt(dien)X]^+$ varies with changes in X^- in the order $Cl^- \sim Br^- \sim I^- \gg N_3^- > SCN^- > NO_2^- > CN^-$. Thus, there

(1) For a review and references see F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 388 (1962); F. Basolo, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

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

(3) H. B. Gray, *ibid.*, **84**, 1548 (1962).

(4) H. B. Gray and T. J. Olcott, *Inorg. Chem.*, **1**, 481 (1962).

(5) U. Belluco, L. Catalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

TABLE I[a]

Rate Constants, k_Y, at 30° and Activation Parameters for the Reactions $[Pt(dien)X]^+ + Y^- \rightarrow [Pt(dien)Y]^+ + X^-$ in Water[a,b]

Complex	Nucleophile, Y^-	Examined temp, °C	$10^3 k_Y^-$, M^{-1} sec^{-1}	ΔH_Y^*, kcal/ mole	ΔS_Y^*, eu/ mole
[Pt(dien)Cl]Cl	H₂O	30, 45	0.0002[c]	20	−18
	Br⁻	30, 45	7	13	−25
	N₃⁻	30, 45	5.2	16	−17
	I⁻	30, 45	170	11	−25
	SCN⁻	20, 35	270[d]	10	−28
		20, 30	420[e]	12[d]	−20[e]
	SeCN	30	2500	...	...
	Thiourea	20, 25, 30	580	8.5	−31
[Pt(dien)Br]Br	H₂O	30, 45	0.0036[c]	19.5	−17
	N₃⁻	30, 45	9.6	15.5	−17
	I⁻	30, 45	320	11	−25
	SCN⁻	20, 35	680[d]	9.5	−27
		20, 30	880[e]	12	−19[e]
	SeCN⁻	30	7000	...	...
	Thiourea	20, 25, 30	1300	8.5	−29
[Pt(dien)I]I	N₃⁻	30, 45	11	15.5	−16
	SCN⁻	20, 35	640[d]	10.5	−25
		20, 30	870[e]	12.5[e]	−18[e]
	SeCN⁻	30	7000	...	...
	Thiourea	20, 30	1300	9	−27
[Pt(dien)N₃]N₃	I⁻	25, 45	8.5[d]	14.5	−19
	SCN⁻	30, 45	5	14	−22
		30, 40	9[e]	15[e]	−18[e]
	SeCN⁻	30, 45	51	13	−21
	Thiourea	30, 45	15	13	−24
	S₂O₃²⁻	30, 40	300	9.5	−29
[Pt(dien)SCN]NO₃	Thiourea	30, 45	20	15.5	−14
[Pt(dien)NO₂]NO₃	Thiourea	30, 45	0.35	13.5	−30

[a] Ionic strength of 0.1 M maintained with KNO₃. [b] Supplementary material (specific kinetic data used to estimate values in this table) has been deposited as Document No. 8717 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks payable to: Chief, Photoduplication Service, Library of Congress. [c] First-order rate constants corrected to second order by dividing by 55.5. [d] Interpolated value. [e] Ionic strength of 0.02 M.

appear to be two types of leaving groups: (1) ligands that are readily replaced and for which the rate of replacement is almost independent of the leaving group, and (2) ligands that are more difficult to displace and for which the rate of displacement depends on the leaving group. This behavior might be surprising if one considers that the halide ions are all replaced with about equal ease, although the Pt–X bond strength increases for changes in X⁻ in the order Cl⁻ < Br⁻ < I⁻.

These observations can be understood if it is assumed that the mechanism of reaction involves the formation of a five-coordinated intermediate. In such a case these reactions can be represented by either reaction profile 1 or 2 of Figure 1. Reaction profile (1) corresponds to leaving groups in category 1 which are replaced at a rate almost independent of the leaving group. It is clear that this follows because the higher activation energy between the ground state and the transition state is that with T.S. (A) which involves chiefly bond formation with the nucleophile Y and little rupture of the Pt–X bond. Thus, the nature of X can have only a secondary effect on the formation of T.S. (A).

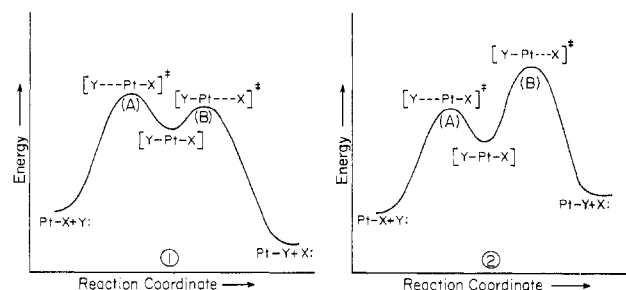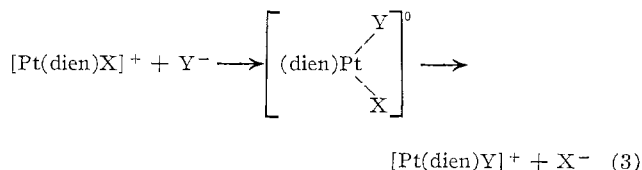In contrast to this, reaction profile 2 of Figure 1 corresponds to leaving groups in category 2 which are

Figure 1.—Reaction profile (arbitrary scale) for SN2 mechanism involving an unstable five-coordinated intermediate in the displacements on $[Pt(dien)X]^+$. (1) For $X^- = Cl^-$, Br^-, I^-, the Pt–X bond rupture is kinetically not important. (2) For $X^- = N_3^-$, NO_2^-, SCN^-, CN^-, the bond rupture Pt–X is kinetically important.

replaced at a rate that depends on the nature of the leaving group. This follows because now the higher activation energy between the ground state and transition state is that with T.S. (B). Since this involves primarily a breaking of the Pt–X bond, the rate of replacement of X will depend on the nature of X.

It is also apparent that the entropies of activation vary for the different reactions. However, the most striking feature of these results is that all of the entropies are appreciably negative. This is a somewhat unexpected result for a displacement process of ths type represented by eq 3. In polar solvents reactione

$$[Pt(dien)X]^+ + Y^- \longrightarrow \left[(dien)Pt \begin{matrix} Y \\ \diagdown \\ X \end{matrix} \right]^0 \longrightarrow$$

$$[Pt(dien)Y]^+ + X^- \quad (3)$$

of this type where there is a neutralization of charge in going from the ground state to the transition state usually have positive entropies of activation.[6] This is because the uncharged activated complex is less solvated than the charged substrate and reagent. Thus, the formation of the transition state is accompanied by an increase in the disorder of the solvent which results in a positive entropy of activation. For large ions, where solvation is small, the normal loss of entropy in forming an activated complex from two reactants in a bimolecular reaction can cancel out the solvation effect. Likewise, the solvation effect may be small if in the transition state the polarity of the bond between platinum(II) and the entering ligand (and/or leaving group) is large. This would mean that the entering group remains largely charged and solvated to much the same extent as it is in the ground state in solution.

The large negative entropies of Table I, and the rather small activation enthalpies, suggest that formation of the transition state is accompanied by a net increase in bonding. Recently,[7] we have suggested that a trigonal bipyramid structure is formed as an

(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 7.

(7) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **4**, 925 (1965).

unstable intermediate in reactions of planar complexes and that the activated complex is somewhere between this structure and a six-coordinated structure containing the complex, the nucleophilic reagent, and a solvent molecule. In any event bond making by the nucleophile has proceeded to a considerable degree, the entire structure is tightened and made more rigid, and a decrease in entropy results.

It may be noted that negative values of $\Delta S°$ are almost invariably found for equilibria in which there is an increased coordination number of a metal ion. For example, Sacconi[8] and his co-workers have published a series of papers reporting thermodynamic data for equilibria of the type represented by eq 4. The

$$\text{NiDBH} + 2\text{base} \rightleftharpoons \text{NiDBH} \cdot 2\text{base} \tag{4}$$

nickel(II) complex, diacetylbis(benzoylhydrazino)-nickel(II), is square-planar, and it adds two molecules of a base to form an octahedral complex. The solvent was benzene and various amine and phosphine bases were used. The values of $\Delta H°$ were in the range 13–17 kcal/mole and of $\Delta S°$ in the range -18 to -42 eu. The values of $\Delta S°$ for this four-coordinated system going to six-coordinated systems are comparable to the ΔS^* values of square-planar complexes undergoing displacement reactions. These reactions are also believed to involve an expansion of coordination number in a process somewhat analogous to that for equilibrium 4.

The values of ΔS^* in Table I are more negative for the reactions of neutral thiourea than for anionic nucleophiles. This could be an indication that solvation effects play some role in the reactions of the anions, making ΔS^* more positive than otherwise. The first-order rate constants, k_S, for the reaction of water as a nucleophilic reagent have been divided by 55.5 to convert them to second-order rate constants in Table I. The entropies of activation are decreased by eight units by this change in standard state. Even so, the values of ΔS^* for neutral water as a reagent are not as negative as would be expected. This may be related to the poor nucleophilic properties of this ligand which may lead to only weak bonding in the transition state. The Pt–OH_2 bond is known to be weak.[4]

Additional data, taken from the literature, on activation parameters for nucleophilic displacement reactions of planar complexes are shown in Table II. In all cases the entropies of activation are negative.

(8) L. Sacconi, G. Lombardo, and R. Ciofalo, *J. Am. Chem. Soc.*, **82**, 4182 (1960); L. Sacconi, G. Lombardo, and P. Paoletti, *ibid.*, **82**, 4185 (1960).

TABLE II

ACTIVATION PARAMETERS FOR NUCLEOPHILIC DISPLACEMENTS ON SOME LOW-SPIN d^8 SYSTEMS

Complex	Nucleophile Y⁻	ΔH^*, kcal/mole	ΔS^*, eu/mole
trans-[Pt(P(C_2H_5)$_3$)$_2$Cl$_2$][a]	NO_2^-	15.1	-31
	N_3^-	15.5	-24
	SCN^-	10.0	-28
	$SeCN^-$	8.5	-27
	Cl^-	23.0	
trans-[Pt(P(C_2H_5)$_3$)$_2$Br$_2$][a]	NO_2^-	12.4	-34
	N_3	13.0	-24
trans-[Pt(P(C_2H_5)$_3$)$_2$I$_2$][a]	NO_2^-	11.0	-30
	N_3	12.5	-16
trans-[Pt(piperidine)Cl$_2$][a]	Cl^-	14.7	-21
	Br^-	13.8	-23
	NO_2^-	13.7	-25
	N_3^-	10.8	-33
	SCN^-	9.1	-30
	$SeCN^-$	8.4	-28
trans-[Pt(As(C_2H_5)$_3$)$_2$Cl$_2$][a]	SCN^-	11.2	-23
	$SeCN^-$	7.9	-28
[Au(dien)Cl]$^{2+}$[b]	Br^-	13	-4
[AuCl$_4$]$^-$[c]	H_2O	4.5	-58^f
	Cl^-	16.5	-2
[Pt(NH$_3$)$_3$Cl]$^+$[d]	H_2O	18	-26^f
	Br^-[e]	17	-16^f
cis-[Pt(NH$_3$)$_2$Cl$_2$][d]	H_2O	20	-22^f
trans-[Pt(NH$_3$)$_2$Cl$_2$][d]	H_2O	20	-19^f
[Pt(NH$_3$)Cl$_3$]$^-$[d]	H_2O	19	-23^f
[PtCl$_4$]$^{2-}$[d]	H_2O	21	-16^f

[a] Reactions in methanol; ionic strength 0.1 M by added LiNO$_3$. Data from U. Belluco, L. Cattalini, R. Ettorre, and M. Martelli, *Gazz. Chim. Ital.*, **94**, 356 (1964); **94**, 733 (1964); **95**, 567 (1965). [b] W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964). [c] R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954). [d] D. S. Martin, *et al.*, *J. Am. Chem. Soc.*, **77**, 2965 (1955); **80**, 536 (1958); **83**, 2457 (1961); *Inorg. Chem.*, **1**, 551 (1962); **2**, 567 (1963). [e] This work. See footnote a of Table I. [f] Rate constant corrected to second-order units.

This is true regardless of the charge on the complex and whether the solvent is water or methanol. It would seem that bond formation with the entering nucleophile is extensive in all these cases. It may be pointed out that stable, five-coordinated platinum(II) complexes are now well known.[9]

(9) See L. M. Venanzi, *Angew. Chem. Intern. Ed. Engl.*, **3**, 453 (1964) for a recent review; R. D. Cramer, R. V. Lindsey, J .C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).