Mechanism of Photosubstitution Reactions of Square-planar Platinum(II) Complexes. III. Steric Effects on the Photosubstitution Mechanism of Bromo(1,1,7,7-Tetraethyldiethylenetriamine)Platinum(II) Complex Ion [1]

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The photosubstitution reactions of $Pt(Et_4dien)Br^+$ have been investigated in aqueous solution by irradiation with 313 nm light. $Pt(Et_4dien)H_2O^{2+}$ was always formed in acid or neutral solutions, independently of the presence of Cl^- (up to 1×10^{-2} M) or Br^- (up to 1×10^{-2} M). $Pt(Et_4dien)OH^+$ was formed in alkaline (pH 12) solution. The photoreaction quantum yield was 4.0×10^{-3} in both acid and alkaline solutions, independently of the presence of outer ligands. The results are compared with those of similar unhindered complexes and a general discussion of the photosubstitution mechanism of this class of compounds is given.

Introduction

The photochemical properties of platinum(II) complexes have not been extensively studied in recent years [2, 3]. In particular, as far as the study of intimate mechanisms of photosubstitution reactions of these complexes is concerned, a very limited amount of data is available only. This situation is rather surprising because this field of research is potentially as interesting as that of thermal ligand substitution mechanisms of these complexes [4–6].

The main effect of ligand field excitation lies in the weakening of the metal–ligand bonds which accompanies the promotion of one electron from an essentially non-bonding π orbital to a strongly antibonding σ^* orbital. Since this bond weakening should greatly favor metal–ligand bond dissociation, it is to be expected that dissociative mechanisms are more likely for photosubstitution reactions than for the corresponding thermal processes. In the case of square-planar d^8 metal complexes the excited state behavior is not easily predictable since these complexes react thermally by an associative mechanism [5].

In the previous papers of this series [1, 7] we have performed a study of the mechanism of photosubstitution reactions of some complexes of the Pt(dien)-** X^{n+}** family (X = Br, I, py). The results obtained suggested that, unlike thermal reactions, the photosubstitution reactions of these complexes proceed most likely through an essentially dissociative mechanism [7]. Quite interestingly, a primary intermediate was kinetically detected which contained the co-products of primary dissociation and was able to undergo a geminate recombination process. The recombination process was observed to occur efficiently with the negatively charged Br^- and I^- leaving ligands but not with the neutral pyridine ligand thus suggesting a substantial contribution of electrostatic bonding to the leaving ligand in the formation of the geminate intermediate [1].

In order to obtain further insight into the mechanism of ligand photosubstitution reactions of platinum(II) complexes, we have now studied the photochemical behavior of the $Pt(Et_4dien)Br^{+*}$ complex ion. This complex has some peculiar features which could make it interesting for such a study. It is well known [4–6, 8, 9] that the usual associative path is drastically forbidden at room temperature in the thermal substitution reactions of this type of complexes by the steric axial hindrance of the four ethyl groups. Steric hindrance is also likely to influence to some extent the photosubstitution mechanism possibly through the efficiency of geminate recombination of the primary photodissociation products.

Experimental

Preparation of the Complexes

[Pt(Et₄dien)Br] ClO₄

This complex could not be prepared by the usual Mann's method [10] due to the kinetic inertness of the intermediate products, so that the following procedure was adopted. An excess of Et₄dien·3HBr, previously prepared by standard methods [11], was added to an aqueous solution of K₂PtBr₄; KOH was

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**dien = diethylenetriamine.

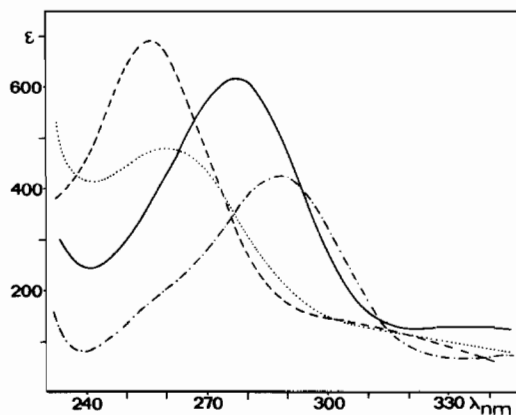*Et₄dien = 1,1,7,7-tetraethyldiethylenetriamine.

Figure 1. Absorption spectra of Pt(Et$_4$dien)Br$^+$ ($-\cdot-\cdot-$), Pt(Et$_4$dien)Cl$^+$ (———), Pt(Et$_4$dien)H$_2$O^{2+} ($\cdots\cdots$) and Pt-(Et$_4$dien)OH$^+$ (- - - - -).

then added to adjust the pH at 6.5 and a fine, cream coloured, unidentified precipitate was obtained. This solid was filtered and extracted with hot water to obtain a yellow solution from which, by evaporation, the pale yellow precipitate of [Pt(Et$_4$dien)Br] Br was obtained. This compound was dissolved in water and treated with AgNO$_3$ (one equivalent) in order to remove the external Br$^-$ anion. After elimination of AgBr by filtration, excess NaClO$_4$ was added to the solution. [Pt(Et$_4$dien)Br] ClO$_4$ was crystallized from the solution by concentration on a steam bath. The salt was twice recrystallized from water and dried *in vacuo*. The absorption spectrum of [Pt(Et$_4$dien)-Br] ClO$_4$ is shown in Fig. 1.

Anal. Calcd. for C$_{12}$H$_{29}$N$_3$PtBrClO$_4$: C, 24.43; H, 4.95; N, 7.12; Pt, 33.07; Br, 13.57; Cl, 6.01; O, 10.85. Found: C, 24.27; H, 5.00; N, 7.04; Pt, 32.86; Br, 13.36; Cl, 6.12; O, 10.91%.

Pt(Et$_4$dien)H$_2$O^{2+} solutions

An aqueous solution of [Pt(Et$_4$dien)Br] ClO$_4$ containing excess AgNO$_3$ was heated for several hours on a steam bath until no spectral variations were observed. The solid AgBr was removed and the solution was used to obtain the UV absorption spectrum of Pt(Et$_4$dien)H$_2$O^{2+} complex ion which is shown in Fig. 1. No attempt was made to isolate this compound in the solid state.

Pt(Et$_4$dien)Cl$^+$ solutions

An aqueous solution of Pt(Et$_4$dien)H$_2$O^{2+} containing large excess of NaCl was heated on a steam bath until no spectral variations were observed; the UV spectrum of the resulting Pt(Et$_4$dien)Cl solution is reported in Fig. 1.

Pt(Et$_4$dien)OH$^+$ solutions

The UV absorption spectrum of Pt(Et$_4$dien)OH$^+$ (Fig. 1) was measured on alkaline (pH 12) solutions of Pt(Et$_4$dien)H$_2$O^{2+}.

Chemicals

All the chemicals used were commercial products of reagent grade.

Apparatus

The light sources and general equipment used to obtain 313 nm radiations were the same as previously described [1, 7]. Spectrophotometric measurements were performed with Perkin–Elmer Mod. 323 (double beam) and Shimadzu QV 50 (single beam) spectrophotometers. The detection of intermediates was attempted with an Applied Photophysics KR-10 Flash-Kinetic spectrophotometer.

Procedures

The irradiation was performed at 20 °C. During the irradiation the solutions were stirred by bubbling pure nitrogen from a glass capillary. The irradiated cells were periodically taken to the spectrophotometer for kinetic measurements. The initial concentration of the reagent complex was selected in order to ensure the maximum light absorption compatible with the spectrophotometric kinetic measurements to be performed. All kinetic runs were carried out under zero-order experimental conditions in order to calculate quantum yield values. The quantum yield calculation was always based on two actinometric measurements [12] performed in the reaction cell before and after each photochemical run.

Results

No thermal aquation of [Pt(Et$_4$dien)Br] ClO$_4$ was observed to occur over several weeks at room temperature (20 °C). No thermal anation was observed after several days in the presence of Cl$^-$ or OH$^-$ (pH 12). This behavior is consistent with previous observations [5] on the thermal substitution behavior of similar hindered platinum(II) complexes.

The irradiation with 313 nm light of aqueous solutions (natural pH) containing 2 × 10^{-3} M [Pt(Et$_4$-dien)Br] ClO$_4$ gives rise to clean spectral changes with an isosbestic point at 274 nm. The observed spectral variations agree well with the absorption spectra of the Pt(Et$_4$dien)Br$^+$ reagent and Pt(Et$_4$dien)H$_2$O^{2+} product (Fig. 1). These experimental results indicate that the only photochemical reaction which occurs is reaction 1:

$$\text{Pt(Et}_4\text{dien)Br}^+ + \text{H}_2\text{O} \xrightarrow{h\nu}$$
$$\text{Pt(Et}_4\text{dien)H}_2\text{O}^{2+} + \text{Br}^- \qquad (1)$$
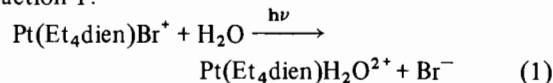
When the irradiation of Pt(Et$_4$dien)Br$^+$ complex ion is carried out in alkaline solution (pH 12), the observed spectral variations indicate the occurrence of photoreaction 2:

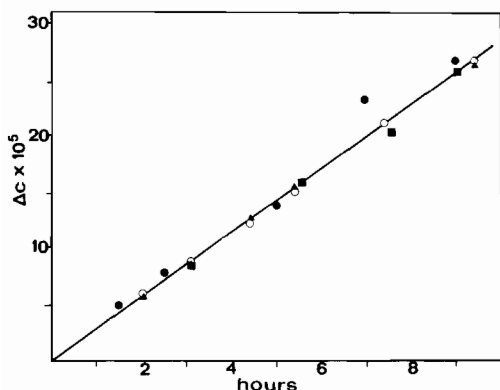$$\text{Pt(Et}_4\text{dien)Br}^+ + \text{OH}^- \xrightarrow{h\nu}$$
$$\text{Pt(Et}_4\text{dien)OH}^+ + \text{Br}^- \qquad (2)$$
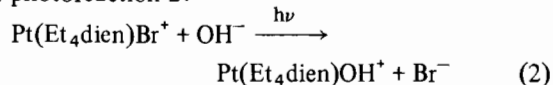
Figure 2. Photoaquation kinetics of Pt(Et$_4$dien)Br$^+$ under various experimental conditions. ○ natural pH; ▲ natural pH, [Br$^-$] 4.0 × 10^{-3}; ■ natural pH, [Cl$^-$] 4.0 × 10^{-3}; ● pH 12.

The presence of NaCl (4 × 10^{-3}–1 × 10^{-2} *M*) or NaBr (4 × 10^{-3}–1 × 10^{-2} *M*) does not affect the spectral changes in either neutral or alkaline solutions.

Quantitative measurements were also performed under various experimental conditions. Fig. 2 shows that the photoreaction rate is independent of pH and of the presence of external Cl$^-$ and Br$^-$ ions. The quantum yield of reactions 1 and 2 is always 4.0 × 10^{-3}.

Discussion

The above reported results show that the only photoproduct which is formed upon irradiation of aqueous solutions of Pt(Et$_4$dien)Br$^+$ complex ion is Pt(Et$_4$dien)H$_2$O^{2+}, independently of the presence of Br$^-$ or Cl$^-$ anions; the photoaquation quantum yield is independent of the concentration of outer anions and pH. This behavior is quite different from that observed for the analogous unhindered Pt(dien)Br$^+$ complex and implies that in the case of Pt(Et$_4$-dien)Br$^+$ neither bimolecular substitution by external ligands nor the previously discussed geminate recombination process [1, 7] compete with the formation of the aquo-product.

This result can be appropriately discussed within the framework of a general mechanism for the photosubstitution reactions of Pt(amine)X^{n+} complexes. All the results obtained on the photosubstitution reactions of these complexes can be accounted for by the following general scheme (Scheme I).
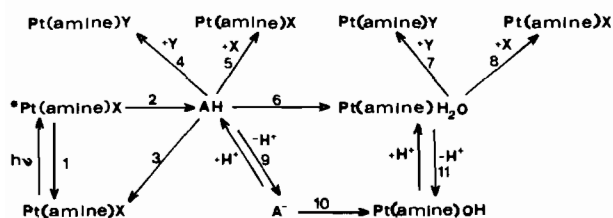
In this scheme, for the sake of simplicity, ionic charges are omitted and the reactions are written without observing stoichiometric rules. The nature of the main photoreaction intermediate, AH, is not specified (*vide infra*). All the systems studied fit into Scheme I with the following specifications.

Case I: amine = dien, X = Br, I, and Y = NO$_2^-$, Br$^-$ [7]. i) in acid solution where the intermediate is completely in the AH form, geminate recombination (Process 3) is a very efficient process and efficiently competes with substitution by X (Process 5) and Y (Process 4) on the intermediate; ii) in alkaline solution equilibrium 9 is completely displaced toward the A$^-$ form of the intermediate which rapidly undergoes process 10; in this case the only product which is formed is Pt(dien)OH$^+$. In both cases (i) and (ii) the formation of aquo-complex (Process 6) is negligible in comparison with the other processes [7].

Case II: amine = dien, X = pyridine and Y = Br$^-$ [1]. In acid solution the AH intermediate converts rapidly to Pt(dien)H$_2$O^{2+} (Process 6) before any other process occurs; in the presence of Y ligand the fast substitution 7 occurs and Pt(dien)Y is formed. In alkaline solution equilibria 9 and/or 11 are completely displaced toward the basic forms and Pt(dien)OH$^+$ is the only product which is observed [1].

Case III: amine = Et$_4$dien, X = Br and Y = Br$^-$, Cl$^-$. In acid solution the aquo-complex is formed (Process 6) while processes 3, 4 and 5 are negligible. Processes 7 and 8 are forbidden by the steric hindrance of the four ethyl groups on the axial positions of the aquo-complex; in this case the only photoproduct is Pt(Et$_4$dien)H$_2$O^{2+}. In alkaline solution Pt(Et$_4$dien)OH$^+$ is formed through 9 and/or 11.

The AH intermediate included in Scheme I is required on kinetic grounds, but escapes direct observation even by fast techniques*. However, its behavior allows us to characterize the intermediate as follows: a) In order to undergo efficient geminate recombination (when amine = dien and X = Br or I) the intermediate has still to contain the released ligand bonded to some extent. b) Since in alkaline solution the AH intermediate is quantitatively converted to Pt(dien)OH$^+$ through equilibrium 9, the intermediate must contain an H$_2$O molecule bonded to platinum. c) The lifetime of the intermediate is strongly dependent on the charge of the leaving ligand and on the degree of steric hindrance in the axial positions of the complex; in fact, when X is negative and the axial positions are free (Case I) substitution by external ligands and geminate recombination occur efficiently during the intermediate lifetime; when X is neutral (Case II) or when amine is

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*Flash photolysis experiments fail to give spectral evidence for the intermediate, presumably because of low quantum yields and small spectral differences between the intermediate and reactants or products.

the bulky Et$_4$dien (Case III), formation of the aquo-product occurs before geminate recombination or substitution by external ligands can take place.

On the basis of these arguments the following structure* can be proposed for the long-lived intermediate of Case I.
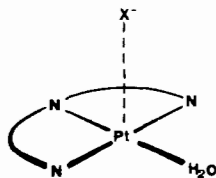
In this intermediate the residual bonding between the released X$^-$ and Pt is predominantly electrostatic, so that the intermediate may be called a *geminate ion pair*. It should be pointed out, however, that this intermediate is substantially different from a conventional *outer-sphere ion pair* (which, for a 2+/1− system, should be quite labile [4]). Here the released anionic ligand occupies a well-defined (axial) position in the *first coordination sphere* of the square-planar complex. In the other cases an analogous geminate intermediate should be extremely labile either for the lack of negative charge on the released ligand (Case II) or for the lack of available axial positions on the complex (Case III).

As far as the nature of the intimate mechanism of the primary photoprocess is concerned, two alternative paths are possible, namely a) dissociative deactivation of the excited state with Pt–X bond splitting followed by H$_2$O substitution, or b) bimolecular attack of H$_2$O on the excited state with consequent labilization of the Pt–X bond. Since the solvent is in any case the entering ligand, kinetic measurements cannot allow any distinction between these mechanisms. A non-kinetic, structural argument which has been used satisfactorily for analogous purposes in the study of the thermal substitution mechanisms of these complexes, is that based on the comparison between reaction rates of axially hindered and non-hindered complexes [4–6]. It should be pointed out, however, that analogous comparisons based on quantum yields for photochemical reactions cannot give any clear-cut indication on the reaction mechanism. In fact, the photoreaction quantum yield, ϕ, is related to excited state reaction rates as follows:

$$\phi = \eta \, \frac{k_r}{k_r + k_d}$$

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*A slightly different structure (involving inverted positions of H$_2$O and X$^-$) has been previously proposed [1]. The present formulation seems to be more appropriate to explain the experimental results of this study.

where η is the efficiency with which the reactive excited state is populated, k_r is the excited state reaction rate constant and k_d is the unimolecular rate constant for photophysical deactivation of the excited state (which in our systems is essentially radiationless). It is clear that variations in ϕ through analogous complexes do not exclusively reflect possible variations in k_r but also in η or k_d. Especially this last quantity, which depends heavily on vibrational factors, is likely to show considerable dependence on the detailed structure of the complex. Thus, it is very difficult to decide whether the low quantum yield of Pt(Et$_4$dien)Br$^+$ photoaquation (4.0 $\times$ 10^{-3} as compared to 0.25 for Pt(dien)Br$^+$) must be ascribed to low excited state reactivity or to short lifetime of the reactive excited state of the complex or both. A low reactivity for the axially hindered complex would support an associative mechanism for water substitution. Comparable reactivities and different lifetimes would, on the contrary, suggest a dissociative mechanism. It may be pointed out that a decrease in excited state lifetimes with increasing alkyl substituent on amine ligands has been observed for other coordination compounds [12], so that the last explanation is not implausible in this system.

Altogether, the strongest argument in favor of a dissociative primary photochemical process in Pt(amine)X^{n+} complexes is still their *antithermal* behavior [7], *i.e.* the preference for water over other entering ligands exhibited by the excited states of these complexes.

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