Mechanism of Photosubstitution Reactions of Square-Planar Platinum(II) Complexes. I. The Bromodiethylenetriamineplatinum(II)–Nitrite Ion System

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Abstract: The photochemical behavior of $Pt(dien)Br^+$ in aqueous solutions containing various amounts of NO_2^- and Br^- has been investigated. The excitation was performed with 313-nm radiations, corresponding to a ligand field band of the complex. In neutral solutions, the photosubstitution of Br^- with NO_2^- was observed. The quantum yield for the photosubstitution reaction was in the range 0.007–0.04, and it increased with increasing $[NO_2^-]$ and decreased with increasing $[Br^-]$. When the irradiation was carried out in basic solution, only $Pt(dien)OH^+$ was obtained and its quantum yield of formation (ϕ 0.24) was independent of the amounts of NO_2^- and Br^- present in the solution. The results obtained are interpreted on the basis of a photochemical Pt–Br heterolytic bond fission, leading to an ion-pair intermediate (presumably, $Pt(dien)H_2O^{2+}\cdot Br^-$ or $Pt(dien)^{2+}\cdot Br^-$). In neutral solutions, the intermediate can (i) react with NO_2^- to give the product, $Pt(dien)NO_2^+$; (ii) react with external Br^- to give $Pt(dien)Br^+$; and (iii) undergo geminate recombination. The photochemical behavior in alkaline solution is accounted for on the basis of an efficient capture of the intermediate by the OH^- ions.

In the recent development of the photochemistry of coordination compounds,[1–6] much effort has been made in elucidating the stoichiometry of the photochemical processes and identifying the electronic excited states which are responsible for the observed photoreactions. On the contrary, little attention has been devoted to the *intimate* mechanisms of the photochemical processes. In particular, it is unknown whether the photosubstitution reactions really occur, as generally assumed, by a primary dissociative act. On the other hand, although it has been sometimes recognized[7–9] that some electronically excited states of complexes could be particularly inclined to coordinate a new ligand (and thus, to give photosubstitution by an associative-type mechanism), no definite evidence up to now has been obtained in this regard.

The main reason for such a lack of knowledge of the photosubstitution mechanism is presumably due to the fact that the only photosubstitution process which has been extensively investigated is that of photoaquation, *i.e.*, a process that, for obvious reasons, does not lend itself to mechanistic studies. We have recently begun an investigation on the photochemical behavior of square-planar Pt(II) complexes in the presence of various entering ligands with the aim of finding out whether primary photosubstitution reactions other than aquation are possible in aqueous solutions and, if it is so, of obtaining information on their intimate mechanisms. In this paper, we report the results concerning the $Pt(dien)Br^+$–NO_2^- system.

Experimental Section

Materials. [Pt(dien)Br]Br was prepared according to Mann's method[10] and recrystallized from aqueous solutions. The procedure recommended by Watt and Cude[11] was also checked, but in our hands, it did not give higher yields for the product. Solutions of $Pt(dien)NO_2^+$ and $Pt(dien)OH^+$ were prepared according to Gray[12] and Gray and Olcott,[13] respectively, *i.e.*, by aging at room temperature for a period of 3 days solutions containing 10^{-4} *M* [Pt(dien)Br]Br and 10^{-2} *M* $NaNO_2$ or 10^{-1} *M* NaOH. Attempts were also made to prepare solutions of $Pt(dien)Br^+$ which did not contain free Br^- ions. However, both the dissolution of $[Pt(dien)Br]NO_3$ (prepared according to Basolo, *et al.*,[14]) and the use of anionic exchange procedures did not give satisfactory results, presumably because of the rapid thermal hydrolysis of $Pt(dien)Br^+$ that took place in solutions which did not contain Br^- ions.

Apparatus. The irradiation equipment used to obtain the 313- and 254-nm radiations was the same as previously described.[9,15] The reaction cells were 1-cm standard spectrophotometer cells which were housed in thermostated cell holders. Spectrophotometric measurements were performed with an Optica CF4 NI spectrophotometer. Light intensity measurements were made by means of the ferric oxalate actinometer.[16] The incident light intensities were always of the order of 10^{-7} einstein/min.

Procedures. At room temperature, aqueous solutions of [Pt(dien)Br]Br were fairly stable, but, in the presence of NO_2^- or OH^- ions, appreciable thermal substitution reactions took place.[12,13] In order to minimize these thermal reactions, all the photochemical experiments were carried out at 5°. Two 1-cm spectrophotometer cells were filled with 3 ml of freshly prepared solution. One of the cells was placed in the thermostated cell

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holder of the irradiation equipment. During the irradiation, the solution was stirred by the bubbling of a purified nitrogen stream. In order to provide the control for the concomitant thermal reaction, the other cell was placed in a thermostated cell holder maintained in the dark at the same temperature. After suitable irradiation periods, both of the cells were brought to the spectrophotometer and the changes in absorbance caused by irradiation were measured by the differential spectrophotometric method in the range 250–280 nm. Under the experimental conditions used, the initial light absorption was not complete. The irradiation was only carried on until a small percentage of the initial complex concentration was consumed, so that the rate of light absorption by the reactant remained practically constant during the irradiation. The quantum yield values were calculated from the linear plots of ΔA (difference in the absorbance between irradiated and nonirradiated solution) *vs.* irradiation time, making allowance for the incomplete light absorption. The actinometer measurements were made before and after each photochemical run.

Results

The absorption spectra of Pt(dien)Br$^+$, Pt(dien)NO$_2$$^+$, and Pt (dien) OH$^+$ are shown in Figure 1.

When neutral aqueous solutions of [Pt(dien)Br]Br were irradiated with 254- or 313-nm light, no spectral change was observed. On the contrary, noticeable spectral variations were found when the irradiation was carried out in the presence of NO$_2$$^-$ ions. By means of differential spectrophotometric measurements (see Procedures), it was possible to establish that the only net photoreaction which took place was the substitution of Br$^-$ with NO$_2$$^-$ (*i.e.*, the same reaction which occurs thermally[12]).

$$\mathrm{Pt(dien)Br^+ + NO_2^- \xrightarrow{h\nu} Pt(dien)NO_2^+ + Br^-} \qquad (1)$$

The bulk of the experiments was carried out using 313-nm light. The quantum yield for the substitution reaction was found to depend on the concentration of NO$_2$$^-$ and free Br$^-$ present in the irradiated solutions (Table I).

Table I. Quantum Yield Values for the Photosubstitution Reaction[a]

[NO$_2$$^-$]	[Br$^-$]	ϕ
0.0010	0.0029	0.012
0.0010	0.0050	0.0097
0.0010	0.0070	0.0077
0.0010	0.0090	0.0068
0.0020	0.0029	0.024
0.0020	0.0058	0.019
0.0030	0.0029	0.035
0.0040	0.0029	0.043

[a] Irradiation at 313 nm; [Pt(dien)Br$^+$] = 2.9 × 10^{-3}; reaction shown in eq 1.

Some experiments were also performed irradiating with 254-nm radiations. For a solution 4.5 × 10^{-3} *M* in both [Pt(dien)Br]Br and NO$_2$$^-$, a quantum yield of about 0.06 was obtained. At this wavelength, however, the extinction coefficient of the reaction product was so much higher than that of the reactant, that quantum yield measurements were difficult to perform.

Upon irradiation of [Pt(dien)Br]Br in alkaline solution, differential spectral changes were obtained which indicated that the following photoreaction took place

$$\mathrm{Pt(dien)Br^+ + OH^- \xrightarrow{h\nu} Pt(dien)OH^+ + Br^-} \qquad (2)$$

(the same reaction occurs thermally[13]). Using 313-nm radiations, the quantum yield for reaction 2 was found to be 0.24, independent of the OH$^-$ concentration ($10^{-2} \leqslant [\mathrm{OH^-}] \leqslant 10^{-1}$) and of the presence of NO$_2$$^-$ ions ($0 \leqslant [\mathrm{NO_2^-}] \leqslant 5 \times 10^{-3}$).

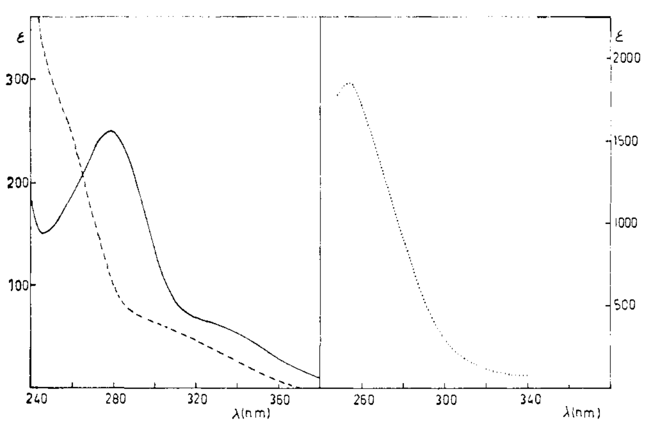

Figure 1. Electronic absorption spectra of: ———, Pt(dien)Br$^+$; - - - -, Pt(dien)OH$^+$; · · · ·, Pt(dien)NO$_2$$^+$.

All of the above results refer to the photodecomposition of only a small percentage of the reactant. For long irradiation periods, other thermal and/or photochemical processes also occurred.

Discussion

The results obtained (Table I) show that the quantum yield for the substitution reaction 1 increases with increasing [NO$_2$$^-$], while it decreases with increasing [Br$^-$]. This indicates that Br$^-$ and NO$_2$$^-$ compete for a common intermediate which is produced as a consequence of photoexcitation. However, such a simple competition is inadequate for explaining the following experimental features: (a) the limiting value of quantum yield for 1/[NO$_2$$^-$] = 0 is higher than that for [Br$^-$] = 0 (see Figures 2 and 3); (b) the quantum yields obtained for solutions containing a fixed [Br$^-$]/[NO$_2$$^-$] ratio increase with increasing [NO$_2$$^-$] (Table I). *It can be shown that the above features require that the intermediate, besides giving second-order substitutions by Br$^-$ and NO$_2$$^-$, undergoes a process converting it back to Pt(dien)Br$^+$ and not involving external Br$^-$* (see eq 9 and 10 below). The results also show that, in alkaline solution, the photoreaction only leads to Pt(dien)OH$^+$, with ϕ 0.24, regardless of the NO$_2$$^-$ concentration. This quantum yield coincides with the limiting quantum yield of reaction 1 for 1/[NO$_2$$^-$] = 0. *This shows that OH$^-$ is 100% efficient in capturing the intermediate.*

In order to account for the above results, two reasonable mechanisms may be considered which differ for the nature of the intermediate that NO$_2$$^-$ and Br$^-$ are thought to compete for.

Mechanism I. The intermediate is an electronically excited state of Pt(dien)Br$^+$. In this case, both the NO$_2$$^-$ substitution and the Br$^-$ exchange should be bimolecular primary photochemical processes and the pathway, which converts the intermediate back to Pt(dien)Br$^+$ without involving external bromide ion, should simply be a physical deactivation process of the excited state.

Mechanism II. The intermediate is the product of a primary photochemical process involving the release of Br$^-$. In order to undergo a process converting it back

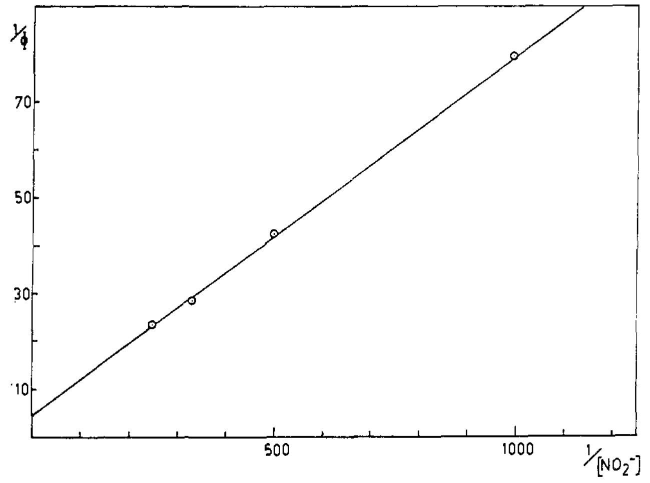

Figure 2. Dependence of the quantum yield on the concentration of NO_2^-.

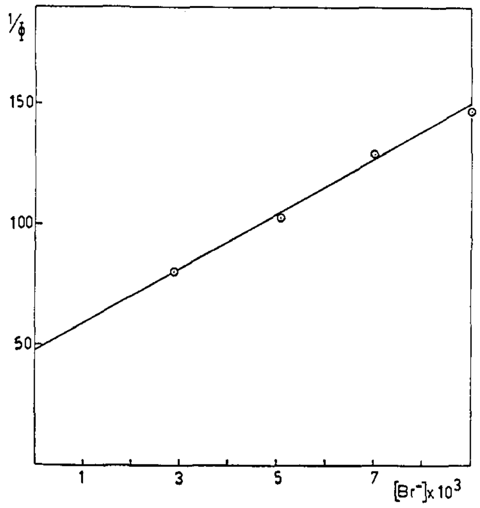

Figure 3. Dependence of the quantum yield on the concentration of Br^-.

to $Pt(dien)Br^+$ and not involving external Br^-, *such an intermediate must still contain the released* Br^-. Therefore, the intermediate can only be an ion pair. According to this mechanism, the reactions of NO_2^- and Br^- with the intermediate should be bimolecular secondary thermal processes, and the pathway, which converts the intermediate to $Pt(dien)Br^+$ without involving external bromide ion, should be a recombination process within the ion pair (geminate recombination). As far as the specific nature of the ion-pair intermediate is concerned, there are only two reasonable possibilities: (a) the ion-pair intermediate contains the coproducts of the primary photodissociation reaction, $Pt(dien)^{2+}$ and Br^-; (b) the ion-pair intermediate contains Br^- and $Pt(dien)H_2O^{2+}$ which results from the occupation of the vacant coordination site of $Pt(dien)^{2+}$ by a water molecule.

Mechanism I can be ruled out on the basis of the experimental observation that, even in the presence of equivalent amounts of NO_2^-, OH^- is 100% efficient in capturing the intermediate (yielding $Pt(dien)OH^+$). It is well known, in fact, that OH^- shows an extremely low entering ability (in comparison with other ligands, such as NO_2^- and Br^-) in the thermal substitution reactions of $Pt(dien)Br^+$,[12] and it does not seem plausible that its entering ability toward a ligand-field excited state of the complex becomes extremely high.

On the contrary, reasonable arguments can be used to justify the high ability of OH^- in capturing the intermediates which are involved in mechanism II. If the intermediate is $Pt(dien)^{2+}\cdot Br^-$ (mechanism IIa), the high nucleophilicity of OH^- should allow it to rapidly coordinate with the unsaturated $Pt(dien)^{2+}$. If the intermediate is $Pt(dien)H_2O^{2+}\cdot Br^-$ (mechanism IIb), a very rapid conversion of $Pt(dien)H_2O^{2+}$ into $Pt(dien)OH^+$ will occur in alkaline media since such a process only requires a proton transfer.[13] Since the occurrence of this last process has been extensively documented,[13] we assume that $Pt(dien)H_2O^{2+}\cdot Br^-$ is the most probable ion-pair intermediate demanded by our kinetic results, even though the possibility of a $Pt(dien)^{2+}\cdot Br^-$ intermediate seems also reasonable. Therefore, we think that the following reaction mechanism is the best suited one for interpreting the experimental results in neutral solutions

$$\mathrm{Pt(dien)Br^+} \xrightarrow{h\nu} \mathrm{{}^*Pt(dien)Br^+} \qquad (3)$$

photoexcitation

$$\mathrm{{}^*Pt(dien)Br^+} \xrightarrow{k_4} \mathrm{Pt(dien)Br^+} \qquad (4)$$

deactivation

$$\mathrm{{}^*Pt(dien)Br^+ + H_2O} \xrightarrow{k_5} \mathrm{Pt(dien)H_2O^{2+}\cdot Br^-} \qquad (5)$$

primary photoreaction

$$\mathrm{Pt(dien)H_2O^{2+}\cdot Br^- + NO_2^-} \xrightarrow{k_6} \mathrm{Pt(dien)NO_2^+ + Br^- + H_2O} \qquad (6)$$

thermal NO_2^- substitution

$$\mathrm{Pt(dien)H_2O^{2+}\cdot Br^- + Br^-} \xrightarrow{k_7} \mathrm{Pt(dien)Br^+ + Br^- + H_2O} \qquad (7)$$

thermal Br^- substitution

$$\mathrm{Pt(dien)H_2O^{2+}\cdot Br^-} \xrightarrow{k_8} \mathrm{Pt(dien)Br^+ + H_2O} \qquad (8)$$

geminate recombination

The expression of the quantum yield of the NO_2^- photosubstitution reaction is

$$\phi = \frac{k_5}{k_4 + k_5}\,\frac{k_6[\mathrm{NO_2^-}]}{k_6[\mathrm{NO_2^-}] + k_7[\mathrm{Br^-}] + k_8} = \phi'\,\frac{k_6[\mathrm{NO_2^-}]}{k_6[\mathrm{NO_2^-}] + k_7[\mathrm{Br^-}] + k_8} \qquad (9)$$

where ϕ' is the primary quantum yield. Rearrangement of eq 9 gives the following expression.

$$\frac{1}{\phi} = \frac{1}{\phi'} + \frac{k_8}{k_6\phi'[\mathrm{NO_2^-}]} + \frac{k_7[\mathrm{Br^-}]}{k_6\phi'[\mathrm{NO_2^-}]} \qquad (10)$$

It can be verified that all the experimental results obtained in neutral solutions are consistent with eq 9 and 10.

The values of the kinetic parameters, which can be calculated from Figures 2 and 3 on the basis of eq 10, are: $\phi' = 0.23$, $k_7/k_6 \sim 3$, $k_8/k_6 \sim 1 \times 10^{-2}$. The value of the quantum yield of the primary photoreaction (ϕ') is in fair agreement with that which was independently obtained from the irradiation of basic solutions (*i.e.*, in conditions where all the Pt (dien) H_2O^{2+} ions, which are formed in the primary photochemical act, are captured as $Pt(dien)OH^+$ ions, *before they are able to undergo any other process*).

It is worthwhile noting that, owing to the relative magnitudes of k_6, k_7, and k_8,[17] in our experimental conditions the order of magnitude of the quantum yield for the photosubstitution reaction is principally determined by the geminate recombination process. We would like to point out that processes of this kind could be of primary importance in other photoreactions of Pt(II) complexes, although in many cases they cannot be experimentally distinguished from the photophysical deactivation processes.

Of course, the question concerning the intimate mechanism of the primary photochemical process (eq 5) is still an unsolved problem. In fact, the formation of $Pt(dien)^{2+} \cdot Br^-$ (mechanism IIa) certainly involves a dissociative photochemical process, but the formation of $Pt(dien)H_2O^{2+} \cdot Br^-$ (mechanism IIb) could follow either dissociative or associative paths. In this last case, however, since it is known that in the thermal substitution reactions (which follow mainly associative-type mechanisms) Br^- and NO_2^- are much better entering ligands than H_2O, one should expect that a direct NO_2^- photosubstitution would also occur. Such a possibility, however, has already been ruled out in the discussion of mechanism I. Therefore, the experimental evidence seems to suggest that the primary chemical reaction proceeds by an essentially dissociative mechanism.

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[17] Note that k_6 and k_7 are second-order rate constants, while k_8 is first order.

Induced Electron Transfer. The Action of One-Electron Oxidants on Pyridinemethanolpentaamminecobalt(III) Complexes

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Abstract: The direct, Ag^+- and Co^{2+}-catalyzed oxidations by Ce(IV) of pentaammine(4-pyridinemethanol)cobalt(III) (A) or pentaammine(3-pyridinemethanol)cobalt(III) (B) yield both the aldehyde complexes of Co(III) and [Co^{2+} + free aldehyde], the ratio of Co(III)–CHO/Co(II) in the products increasing with the concentration of the oxidizing agent. These observations, together with the fact that the rate of consumption of A or B is strictly first order in the concentration of the external oxidizing agent, show that an oxidized intermediate is produced in each system by the external oxidant. The kinetic isotope effects obtained for the CD_2OH derivative of A (k_H/k_D = 2.7 ± 0.2 and 2.2 ± 0.2 for the Ce(IV) and Co^{3+} oxidations in 4 *M* $HClO_4$, respectively) indicate that the rate-determining step involves attack on the alcohol function. A detailed examination of the product ratio as a function of the concentration of external oxidant shows that, in fact, two intermediates are formed which differ in the rate of internal reduction yielding Co(II), relative to reaction with external oxidant yielding Co(III)–CHO (rate ratio k_R/k_T). The ratio k_R/k_T is observed to be significantly greater for the radicals derived from A than for the radicals derived from B, showing that internal electron transfer is more facile from the 4 than from the 3 position. For A, the ratio in which the intermediates are formed varies as the oxidizing agent is changed; this observation suggests that the intermediates are generated by parallel processes. The rates of oxidation by Ce(IV) of A and B and the free but protonated ligands are similar, as are the kinetic isotope effects observed for the $-CD_2OH$ derivative of A and the analogous protonated free ligand, supporting the view that the Co(III) center of the complex does not assist the external oxidant, and the conclusion that radical intermediates of finite lifetime are generated in the rate-determining step of the reaction.

Several investigations[1,2] have shown that when a ligand L in a complex of the type $(NH_3)_5Co^{III}-L$ is oxidized by an external one-electron oxidizing agent, the Co(III) center may be reduced. These reactions are of particular interest when the ligand L has an oxidizable group located at some distance from the atom coordinated to Co(III). If radical intermediates are formed, electron transfer can be induced from various remote positions, and if internal reduction of the cobalt center competes with further reaction of the radical with external oxidant, a measure of the rate of internal reduction from different positions can be obtained.

The investigation by Robson and Taube[2] of the reaction between 4-hydroxymethylbenzoatopentaamminecobalt(III) and one-electron oxidizing agents raised an interesting but incompletely resolved issue. Their evidence showed that the oxidation of this complex by Ce(IV) produces two radical intermediates, one which is not trapped even at high concentrations of Ce(IV) or oxygen, and one which is trapped by both Ce(IV) and oxygen. However, the identity of the two radical intermediates remained obscure.

The present investigation of the reaction of pentaammine(pyridinemethanol)cobalt(III) complexes with various oxidants was initiated in an attempt to study the mechanism of the oxidation processes, particularly the nature of the radical intermediates produced and the relative rate of internal electron transfer from different

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