Photochemistry of the Nitrotetraammineamidoplatinum(IV) Ion

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The photochemical behavior of aqueous solutions of $Pt(NH_3)_4(NH_2)(NO_2)^{2+}$ was investigated, using 254 and 313 nm light. Spectrophotometric measurements showed that, besides the photoisomerization reaction to the *nitrito* isomer $Pt(NH_3)_4(NH_2)(ONO)^{2+}$ ($\varphi_{254} = 0.11$; $\varphi_{313} = 0.29$), NO_2^- photoaquation and/or an oxidation-reduction reaction also occurred ($\varphi_{254} = 0.54$; $\varphi_{313} = 0.23$). The relative importance of the last two processes and the nature of the oxidation-reduction reaction was then investigated by means of chemical analyses carried out on solutions irradiated with 254 nm light.

Some results concerning the thermal and photochemical behavior of $Pt(NH_3)_4(NH_2)(ONO)^{2+}$ in its solid state and in aqueous solutions have also been obtained.

Introduction

The NO_2^- ligand has long been known to give rise to *nitro* and *nitrito* isomers when it is coordinated to Co^{III}.[1] The elucidation[2] of the mechanism by which the nitritopentaamminecobalt(III) ion, $Co(NH_3)_5(ONO)^{2+}$, may be prepared starting from $Co(NH_3)_5(H_2O)^{3+}$ has recently allowed the preparation of other $M(NH_3)_5(ONO)^{n+}$ complexes ($M = Rh^{III}$, Ir^{III}, and Pt^{IV}).[3,4] The rearrangement of these *nitrito* complexes to the corresponding *nitro* isomers has also been investigated.[4] More recently, it has been shown that both the *nitrito* and *nitro* isomers of Pt^{IV} are actually in their amido forms $Pt(NH_3)_4(NH_2)(ONO)^{2+}$ and $Pt(NH_3)_4(NH_2)(NO_2)^{2+}$, both in the solid state and in aqueous solution.[5] In this paper we report the results of an investigation on the photochemical behavior of $Pt(NH_3)_4(NH_2)(NO_2)^{2+}$ as well as some related results concerning the *nitrito* isomer.[6]

Experimental Section

Preparation of Compounds. The *nitrito* isomer, $Pt(NH_3)_4(NH_2)(ONO)^{2+}$ (hereafter, Pt–ONO), was prepared as Cl^- salt according to the procedure previously reported.[4,5] We wish to point out that it was impossible to obtain purified samples of this compound.[5] The *nitro* isomer, $Pt(NH_3)_4(NH_2)(NO_2)^{2+}$ (hereafter, Pt–NO₂), was obtained by thermal isomerization of the *nitrito* isomer in the solid state,[4,5] and purified by repeated recrystallizations. The [Pt(NH₃)₅(H₂O)]Cl₄ complex, which is a possible product of the thermal and photochemical reactions of both the isomers, was prepared as indicated in ref. 7. All the other chemicals were of reagent grade.

Apparatus. For the photochemical experiments in solutions, radiations of 254 and 313 nm were obtained using the irradiation equipment previously described.[8] Solutions were irradiated in spectrophotometer cells housed in thermostated cell holders. The intensity of the incident light, measured by means of the ferric oxalate actinometer,[9] was of the order of 10^{-8} Nhν/sec. For the photochemical experiments in the solid state, the irradiation was performed using a Hanau Q 81 high-pressure mercury vapor lamp without any filter.

Spectrophotometric measurements were carried out with an Optica CF 4 NI spectrophotometer, which makes possible both manual measurements and automatic recording. The infrared spectra were recorded with a Hilger and Watts Model H 900 spectrometer.

Chemical Analyses. The following chemical analyses were accomplished on the irradiated solutions: (i) titration of reductant cationic species (Pt^{II} complexes, see later) with potassium permanganate;[10] (ii) determination of the NO_2^- concentration by the method of Vogel,[11] slightly modified; (iii) determination of the NO_3^- concentration with chromotropic acid.[12] In the last determination, the interference due to nitrite was eliminated by reduction with sulphamic

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acid;[13] the reduction with urea[12] did not give satisfactory results (see also ref. 13).

Procedures. The photochemical experiments on Pt–NO₂ in aqueous solutions were carried out at 25° and with pH ~ 7. At this pH value the Pt–ONO complex, which is one of the photoreaction products, is sufficiently stable, whereas in acid solution it rapidly undergoes thermal reactions (see later). The reactant concentration $[2 \times 10^{-4}–2 \times 10^{-3} F]$ was such that the light was completely absorbed by this complex for sufficiently long irradiation periods. The general procedure was as follows. Two 1-cm spectrophotometer cells were filled with 3 ml of freshly prepared solution. One of the cells was placed in the thermostated cell holder of the irradiation equipment. During the irradiation, the solution was stirred by the bubbling of a stream of purified N₂. In order to provide a control for possible thermal reactions (which, however, were found to be negligible in the experimental conditions used), 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 using the differential spectrophotometric method in the range 220-320 nm. Chemical analyses were also carried out on the irradiated solutions by the methods described above, using the following procedures (in any case, blank experiments were carried out on analogous samples kept in the dark): (1) The irradiated solution was percolated through the Dovex 1-x8 anionic exchanger in its OH⁻ form and then titrated with potassium permanganate. This method accounted for
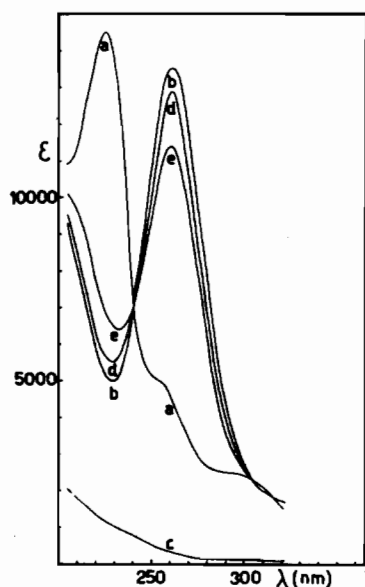
the reductant cationic species produced upon irradiation. (2) The NO₂⁻ analysis was carried out directly in the irradiated solution. This analysis accounted for both the free nitrite ions and the Pt–ONO complex produced upon irradiation; we verified, in fact, that the *nitrito* isomer released quantitatively the NO₂⁻ ligand when the reagents for the nitrite analysis were used. (3) The irradiated solution was percolated through the Dovex 1-x8 anionic exchanger in its OH⁻ form and then the NO₂⁻ ions released by the *nitrito* isomer (see point 2) were determined from the percolate. The NO₃⁻ ion concentration was directly measured in the irradiated solution.

In order to investigate the thermal behavior of [Pt(NH₃)₄(NH₂)(ONO)]Cl₂ in the solid state, a sample of the compound was stored at 50° in the dark and its i.r. and u.v. spectra (the latter recorded after dissolution in water) were measured after suitable periods. The photochemical behavior of this complex was investigated in a similar way by irradiating a powdered sample of the compound at room temperature (see Apparatus). The thermal behavior of Pt–ONO solutions was studied at 30° by means of spectrophotometric measurements in the u.v. spectral region.

Results and Discussion

Spectra. The electronic absorption spectra of the two isomers are shown in Figure 1. As previously mentioned, we were not able to obtain purified samples of the *nitrito* isomer. However, the spectra of samples obtained from three different preparations were nearly in agreement with each other and with the spectrum reported in ref. 4b. The molar extinction coefficients reported in the figure for this complex are mean values evaluated from the spectra of the three samples. As far as the *nitro* isomers is concerned, the spectrum of Figure 1 shows a maximum at 260 nm, as does the spectrum of ref. 4b, but our molar extinction coefficients are very much higher (up to five times) than those reported in ref. 4b; such a difference will be discussed later on.

Thermal Behavior. Before beginning our photochemical studies, we carried out some experiments in order to elucidate the thermal behavior of the prepared isomers. No thermal reaction was observed both in solid state and in solution for the Pt–NO₂ complex. This was in agreement with the results reported in ref. 4. For the Pt–ONO complex in the solid state, we found that, as reported in ref. 4, only the linkage isomerization occurred (Figure 1). As far as the thermal behavior of the *nitrito* isomer in aqueous solution is concerned, we observed that, contrary to what is reported in ref. 4, this complex did not give rise to the linkage isomerization reaction alone. In fact, if this reaction would be the only one that occurred, the absorbance should decrease in the range 220-241 nm and increase in the range 241-304 nm (see Figure 1), while it actually decreased in the entire spectral region examined (Figure 2). The appearance of a well defined maximum at about 260 nm seemed

Figure 1. Electronic absorption spectra of aqueous solutions of: (a), Pt(NH₃)₄(NH₂)(ONO)²⁺; (b), Pt(NH₃)₄(NH₂)-(NO₂)²⁺; (c), Pt(NH₃)₅(H₂O)⁴⁺. Curves (d) and (e) represent the solution spectra of samples of Pt(NH₃)₄(NH₂)(ONO)²⁺ which underwent partial thermal and photochemical isomerization in the solid state, respectively.

(13) A.C. Holler and R.V. Huch, *Anal. Chem.*, *21*, 1385 (1949).

to indicate that some linkage isomerization did really occur; however, the analysis of the spectral changes showed that at least one other reaction took place which caused a decrease in absorbance over the entire spectral region examined. Two possible thermal reactions of Pt–ONO which can cause a decrease in absorbance in the range 220-304 nm are the NO_2^- aquation and an oxidation-reduction reaction. However, on the basis of the observed spectral variations, we could not decide which of these two reactions accompanied the isomerization; in fact, $Pt(NH_3)_5(H_2O)^{4+}$ has practically negligible absorptivities with respect to those of Pt–ONO in the 220-320 nm spectral region (see Figure 1 and ref. 4b), and the oxidation-reduction products would also not absorb in that spectral region. An evaluation of the kinetic data showed that the reaction which took place simultaneously with the linkage isomerization had to be at least three times faster than the isomerization reaction itself. It should be noted that both these reactions were slow in neutral media, but that their rates increased strongly at pH lower than 4. We would also like to note that the spectrum (curve *e* in Figure 2) of an aqueous Pt–ONO solution at the thermal equilibrium (*i.e.*, containing the *nitro* isomer as well as Pt species which do not absorb) was found to be in fair agreement with that reported in ref. 4b, where, however, it was wrongly assigned to the *nitro* isomer alone.
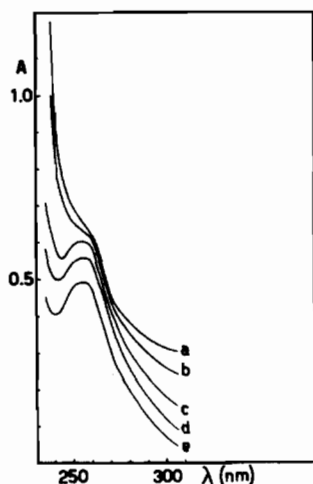

Figure 2. Spectral changes caused by the thermal reactions at 30° of 1.3×10^{-4} *F* $Pt(NH_3)_4(NH_2)(ONO)^{2+}$ in aqueous solution: (a), 0 hr; (b), 9 hr; (c), 23 hr; (d), 32 hr; (e), at the thermal equilibrium.

Photochemical Behavior. $[Pt(NH_3)_4(NH_2)(NO_2)]$-Cl_2. The photochemical behavior of the *nitro* isomer in aqueous solution was investigated, using radiations of 254 or 313 nm. In both cases, it was observed that (i) for short irradiation periods, the changes in absorbance were proportional to the number of einsteins absorbed by the solution (zero order reaction), (ii) the absorbance of the solution increased in the range 225-230 nm, (iii) the absorbance of the solution decreased in the range 235-320 nm, and (iv) no postphotochemical effect took place.

Point (ii) indicates that some nitro→nitrito photo-

isomerization occurred (see Figure 1). However, the absence of the isosbestic points at 241 and 304 nm (point (iii)) suggests that the isomerization reaction had to be accompanied with at least one other photoreaction whose products had lower absorptivities than those of the two isomers at 241 and 304 nm. Two possible photoreactions of Pt–NO₂ which fulfil this last condition are the NO_2^- aquation and an oxidation-reduction reaction; both these reactions, in fact, lead to products which have negligible absorptivities with respect to those of Pt–NO₂ in the 220-320 nm spectral range (see also above). If we assume than, that the photoisomerization and one or both of these two last photoreactions occurred, the spectral changes caused by irradiation should be accounted for by the equation

$$A_o - A = C_1 \varepsilon_{Pt-NO_2} + C_2(\varepsilon_{Pt-NO_2} - \varepsilon_{Pt-ONO}) \quad (1)$$

where A_o is the initial absorbance value of the solution, A is its absorbance value after a given irradiation period, and ε_{Pt-NO_2} and ε_{Pt-ONO} are the extinction coefficients of the *nitro* and *nitrito* isomers, respectively. In this equation, C_1 represents the concentration of the *nitro* isomer which underwent the photoreaction(s) other than the isomerization (hereafter this reaction(s) will be called «decomposition»), and C_2 represents the concentration of the *nitrito* isomer formed. Actually, we observed that the experimental spectral changes fit very well (within 5%) with the above equation, and therefore on can conclude that photoisomerization and «decomposition» reactions occur simultaneously. For each run quantum yield values for the «decomposition», φ_d, and for the photoisomerization, φ_i, were calculated from the mean values of C_1 and C_2, which were obtained at 10 different wavelengths from equations of the type of equation 1. The means of the quantum yields obtained for 5 runs, and their uncertainties are as follows:

254 nm: $\varphi_d = 0.54 \pm 0.05$ $\varphi_i = 0.11 \pm 0.01$

313 nm: $\varphi_d = 0.23 \pm 0.02$ $\varphi_i = 0.29 \pm 0.03$

Further information regarding the nature of the «decomposition» reaction was obtained from the chemical analyses carried out on solutions irradiated with 254 nm light. The results obtained were as follows: 1) The irradiated solutions contained cationic species which released NO_2^- due to the action of the reagents used for the NO_2^- determination (this result agrees with the occurrence of the photoisomerization reaction); 2) A cationic reducing species and NO_3^- were present in the irradiated solutions. Considering the cationic reducing species as a two electron reductant (*e.g.*, divalent platinum), its concentration after a given irradiation period was about twice that of NO_3^- ($\varphi_{Pt^{II}} \sim 0.4$, $\varphi_{NO_3^-} \sim 0.2$); 3) The irradiated solutions contained free NO_2^- ions. Their concentration after a given irradiation period was about twice as great as that of NO_3^- ($\varphi_{NO_2^-} \sim 0.4$).

Point 2 indicates that a photooxidation-reduction reaction takes place in our system. The experimentally observed 2:1 ratio between $\varphi_{Pt^{II}}$ and $\varphi_{NO_3^-}$ rules out the possibility of a simple two-electron transfer from the NO_2^- ligand to the central metal (which

stoichiometrically requires $\varphi_{Pt^{II}} = \varphi_{NO_3^-}$), and moreover, it suggests that the NO_2^- ligand contributes only one electron to the reduction of the platinum ion. Therefore, it seems logical to assume that the photooxidation-reduction process of Pt–NO$_2$ is analogous to that observed in the photochemistry of Co-$(NH_3)_5(NO_2)^{2+}$,[8] *i.e.*, that it should involve a one-electron transfer from the NO_2^- ligand to the central ion, followed by the disproportionation of the NO_2 radical and the reduction of Pt^{III} by some other chemical species present in the solution. If this oxidation-reduction reaction alone represents the «decomposition» process, it should result that $\varphi_{Pt^{II}} = \varphi_d$ and $\varphi_{NO_3^-} = \varphi_{NO_2^-}$. However, since we have experimentally observed that $\varphi_{Pt}^{II} < \varphi_d$ and $\varphi_{NO_3^-} < \varphi_{NO_2^-}$, one could conclude that some NO_2^- photoaquation also occurs, whose quantum yield should be about 0.1-0.2.

Pt(NH$_3$)$_4$(NH$_2$)(ONO)Cl$_2$. Since it was impossible to obtain purified samples of this compound,[5] only qualitative experiments were carried out. The u.v. irradiation of the complex in the solid state caused the nitrito→nitro linkage isomerization. In fact, both the i.r. and u.v. spectral changes obtained upon irradiation of a powdered sample of the compound were identical to those observed for the thermal isomerization in the solid state (Figure 1).