Photochemistry of Complex Ions. XI. $Trans$-Pt(NH$_3$)$_4$Br$_2$$^{2+}$

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The net photochemistry of trans-[Pt(NH$_3$)$_4$Br$_2$$^{2+}$ *is that of bromide aquation with quantum yields of 0.11 and 0.06 at 305 and 350 nm, respectively Flash photolysis shows the transient presence of* Br$_2$$^-$, *provided that* Br$^-$ *is present. Formaldehyde is also a photoproduct if the solution contains methanol as well. The results are interpreted to imply that the complex ion undergoes simple photoaquation but also the ion pairs with* Br$^-$, *the ion pair then photolyzing to give aquated complex,* Br$_2$$^-$ *ions and H atoms. The photochemistry of the complex is compared with that of* PtBr$_6$$^{2-}$.

Introduction

The photochemistry of Pt^{IV} complexes has received comparatively little attention only that of the PtX$_6$$^{2-}$ ions (X = Cl, Br, and I) has been studied in any detail.[1,2] Even in these cases the behavior is not simple. Thus an efficient ($\Phi = 0.4$) wavelength independent photoaquation of PtBr$_6$$^{2-}$ has been reported, with the conclusion that the mechanism is one of substitution involving the lowest spin-forbidden state.[3] However, the same complex undergoes photoexchange with Br$^-$ ion with quantum yields which may exceed unity, depending on the light intensity. Such behavior is not explainable in terms of a simple photoaquation mechanism and a chain process was proposed, with a Pt^{III} species as chain carrier.[4] Similarly contrasting observations exist for PtCl$_6$$^{2-}$.[2,5,6] Returning to PtBr$_6$$^{2-}$, flash photolysis experiments failed to show the Br or Br$_2$$^-$ ion transient predicted by the chain mechanism, but did reveal the presence of a relatively long-lived oxidizing species.[7] In subsequent work, the existence of a weakly absorbing transient was confirmed, and assigned as Br$_2$.[8] Some primary photolysis reaction of a redox nature evidently occurs and a two electron reaction involving the concerted departure of vicinal bromine atoms was suggested. A reaction such as (1) is not novel; Pt^{II} species

$$PtBr_6{}^{2-} \xrightarrow{h\nu} [PtBr_4{}^{2-}]^* + Br_2 \qquad (1)$$

are produced in the photolysis of PtX$_2$(NO$_2$)$_2$(NH$_3$)$_2$ (X = Cl or Br)[9] and molecular oxygen is formed directly in the photolysis of MnO$_4$$^-$.[10] It was necessary, however, to regard [PtBr$_4$$^{2-}$]* as a reactive form able to act as chain carrier in Br$^-$ ion exchange. Photoaquation results either from the reoxidation of this reactive form or represents an entirely separate primary reaction mode.

It might be thought that complexities such as the above might be understood in terms of the behavior of octahedral low spin d^6 complexes of other metals, but each family seems to have a different characteristic behavior. The oxidation state of the central metal ion and its stability relative to other oxidation states is undoubtebly important in determining the nature and the extent of photoredox behavior. Thus Fe-(CN)$_6$$^{4-}$ undergoes photoelectron production while Co^{III} complexes photodecompose to give Co^{II}. Rh^{III} complexes show mainly photoaquation, in possible reflection of the instability of Rh^{II} as an oxidation state. The excited state scheme is clearly important as well; in fact, the photochemistry of a complex often helps in assigning an absorption band as ligand field or as having charge transer (CT) character, either to metal or to ligand or to solvent.[1] A complication with heavy transition metal complexes, however, is that excited states may be higly mixed in character.[11]

The above outline underscores both the danger of interpreting Pt^{IV} photochemistry in terms of analogies to other systems and the need for experimental work designed to determine the actual behavior pattern. The present investigation was undertaken to compare the photochemistry of PtBr$_6$$^{2-}$ with that of the acidoammine, $trans$-Pt(NH$_3$)$_4$Br$_2$$^{2+}$. The redov photochemistry should differ in that a concerted departure of two bromine atoms as Br$_2$ should be unlikely for the latter complex. We were also interested in the extent to which photoaquation would occur, and whether it would be of the NH$_3$ or of the Br group. The actual results serve to emphasize the versatility of Pt^{IV} photochemistry.

Experimental Section

Materials. The complexes [Pt(NH$_3$)$_4$]Cl$_2$ and [*trans*-

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(1) A.W. Adamson, W.L. Waltz, E. Zinato. D.W. Watts, P.D. Fleischauer and R.D. Lindholm, *Chem. Rev.*, 68 541 (1968).

(2) V. Balzani and V. Carassiti, « The Photochemistry of Coordination Compounds », Academic Press, New York, 1970.

(3) V. Balzani, F. Manfrin and L. Moggi, *Inorg. Chem.*, 6, 354 (1967).

(4) A.W. Adamson and A.H. Sporer, *J. Amer. Chem. Soc.*, 80, 3865 (1958).

(5) R.L. Rich and H. Taube, *J. Amer. Chem. Sac.*, 76, 2608 (1954).

(6) R. Dreyer, K. Konig, and H. Schmidt, *Z. Physik. Chem.* (Leipzig), 227, 257 (1964).

(7) S.A. Penkett and A.W. Adamson, *J. Amer. Chem. Soc.*, 87, 2514 (1965).

(8) Paul D. Fleischauer, Ph.D. Dissertation, University of Southern California, *Diss. Abstr. B*, 29, 1317 (1968).

(9) I.I. Chernyaev, G.S. Muravciskaya, and L.S. Korablins, *Russ. J. Inorg. Chem.*, (Eng. Transl.), 11, 728 (1966).
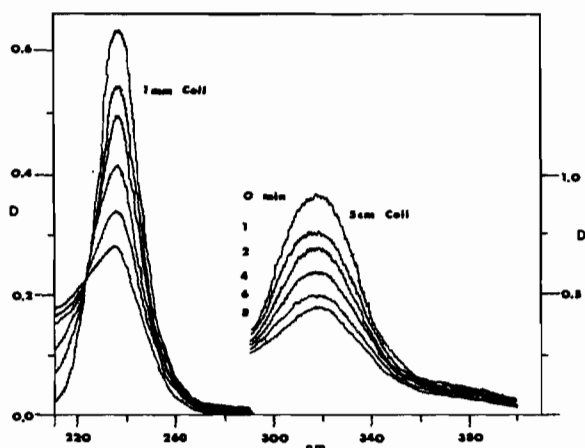
(10) G. Zimmerman, *J. Chem. Phys.*, 23, 825 (1955).

(11) D.L. Swihart and W.R. Mason, *Inorg. Chem.*, 9, 1749 (1970).

Pt(NH₃)₄Br₂]Br₂ were prepared according to literature procedures.[12] In the case of the former complex it was found that fractional precipitation of by-products with a small quantity of a 1:1 mixture of ethanol and acetone before precipitation of the desired product with 4-5 volumes of mixed solvent resulted in a snow-white powder of high purity. This was then used in the preparation of [*trans*-Pt(NH₃)₄Br₂]Br₂. This last was crystallized from water by addition of excess KBr and cooling to 0°C.

[*Trans*-Pt(NH₃)₄Br₂](ClO₄)₂. The perchlorate salt has not previously been reported. It was obtained by dissolving the bromide salt in a minimum amount of warm dilute perchloric acid and filtering through a fine sintered glass suction funnel into an excess of solid lithium perchlorate in the bottom of the filter flask. The resulting slurry was then cooled to 0°C and, after 30 min, mixed with ice cold absolute ethanol, which dissolved the excess solid lithium perchlorate present as well as bromide salts. The product was then separated by filtration, recrystallized from absolute ethanol, vacuum dried at 45°C and stored in a desiccator over calcium chloride. [*Trans*-Pt-(NH₃)₄Br₂](ClO₄)₂ was observed to change color from orange to lemon yellow with decreasing hydration. Chemical analysis of the anhydrous salt gave the following results: Pt, 31.6±0.5%; N, 8.83±0.09%; Br, 24.8±1.0%. Calculated for [Pt(NH₃)₄Br₂](ClO₄)₂: Pt, 31.38%; N, 9.01%; Br, 25.7%. The absorption spectrum, shown in Figure 1, agrees well with the literature,[13] as summarized in Table I.

Table I. Absorption Spectrum of [*trans*-Pt(NH₃)₄Br₂](ClO₄)₂

Feature and wavelength in nm.	Extinction coefficient, $M^{-1}cm^{-1}$ This work	Reported[13]
235 (max)	4.13×10^4	4.2×10^4
318 (max)	1.15×10^3	0.98×10^3
370 (shoulder)	210	—

Figure 1. Spectral changes during the photolysis of *trans*-Pt-(NH₃)₄Br₂²⁺. Broad band 300-380 nm) excitation for times indicated. Initial complex concentration 1.55×10^{-4} M.

Flash photolyses. The flash photolysis apparatus is described in detail elsewhere.[7,8] The kinetic mode of operation was employed in that the spectra of transients were obtained by successive experiments using various filters for the monitoring light source. The 600 joule flash had a decay time of about 15 μsec; ferrioxalate actinometry[14] gave 5×10^{-4} einstein liter⁻¹ per flash in the quartz region and 4×10^{-4} einstein liter⁻¹ in the pyrex region of the flash output. These radiation densities were produced in a photolysis cell 15 cm in length and 1.5 cm in diameter. The latter measurement gives the pathlength for the flash and the former, that for the monitoring beam. Most of the experiments were performed with a pyrex sleeve over the photolysis cell so as to exclude direct excitation of any free bromide ion present, and without exclusion of air. All experiments were conducted at 22-24°C.

Conventional photolyses. Steady illumination experiments were performed with a General Electric Ah-6 high pressure mercury lamp, which could be equipped with either pyrex or quartz components. For irradiations at 305 nm an Optics Technolgy, Inc. interference filter was used (and quartz optics) and for 350 nm irradiations the secondary window of a Bausch and Lomb 500 nm interference filter was used, along with a Schott UB-11 filter.

Solutions were irradiated in a 5 cm cylindrical spectrophotometer cell thermostatted to 22-24°C, and were of concentrations such that 90% to 99% of incident light was absorbed. Ferrioxalate actinometry was again used; absorbed intensities were around 3×10^{-7} einstein liter⁻¹ sec⁻¹ at 305 nm and 8×10^{-7} einstein liter⁻¹ sec⁻¹ at 350 nm. Photolyses were carried only to about 10% reaction to minimize possible secondary reactions.

Analyses. A typical concentration of photoreleased bromide ion was 10^{-4} M and the following analytical procedure was employed.[15] It was first necessary to remove complex ion species and this was done by passing an aliquot of the solution to be analyzed through a Dowex 50W-X4 cation exchange column (in the acid form), of size such that 25 cc of water sufficed to elute the bromide ion present. The eluant was collected in a 50 cc flask and then treated with 3 cc of saturated Hg(SCN)₂ solution and 5 cc each of 0.1 M (Fe(NO₃)₃ in 0.5 M HClO₄ and 4 M HClO₄. After dilution to the mark, ten minutes was allowed for reaction and the absorption by the produced ferric thiocyanate complex measured at 450 nm. The procedure was carried out both on the photolyzed solution and on companion dark or unirradiated solution.

In separate experiments both the water eluant and 25 cc of following 0.5 M HClO₄ wash were analyzed for ammonia by a standard procedure.[16] Long term photolyses in which about 50% of the starting material had undergone reaction were also analyzed for Pt(NH₃)₄²⁺ by titration with standard ceric solution.[17]

(12) R.N. Keller, *Inorg. Syn.*, 2, 251 (1963); « Gmelin's Handbuch der Anorganischen Chemie, » 68D Verlag Chemie, Weinheim/Bergstrasse, 1957, p. 501.
(13) R.R. Rettew and R.C. Johnson, *Inorg. Chem.*, 4, 1565 (1965).

(14) C.A. Parker, *Proc. Roy. Soc.*, (A) 235, 518 (1956).
(15) I.M. Kolthoff, P.J. Elving, and E.B. Sandell, eds., *Treatise on Analytical Chemistry*, pt. II, vol. 7, Interscience Publishers, New York, N.Y., 1961, p. 413.
(16) D.F. Boltz. *Colorimetric Determinations of Nonmetals*, Interscience Publishers, New York, N.Y., 1958, p. 96.
(17) R.C. Johnson, F. Basolo, and R.G. Pearson, *J. Inorg. Nucl. Chem.*, 24, 59 (1962).

Table II. Photochemical Behavior of $Trans\text{-}Pt(NH_3)_4Br_2^{2+}$.

Solvent [a]	Type of Irradiation	Analytical Results	Quantum Yield
water	AH-6, pyrex optics	~50% reaction [b] no Pt^{II} no NH_3 Br^- released	$<5 \times 10^{-4}$ $<4 \times 10^{-4}$ (see below)
	AH-6, 305 nm AH-6, 350 nm	Br^- Br^-	0.11 0.060
	flash, pyrex sleeve	~10% reaction [b] no transients Br^- released	
10% CH_3OH	flash, pyrex sleeve	~10% reaction [b] no HCHO no transients	$<10^{-3}$
	AH-6, pyrex optics	~50% reaction [b] HCHO detected gas bubbles observed	
10% CH_3OH 0.01 M NaBr	flash, pyrex sleeve	~10% reaction [b] HCHO formed Br_2^- transient gas bubbles formed	>0.04 [c]
	AH-6, 290-380 nm	HCHO formed gas bubbles observed	~0.04 [d]

[a] Solutions were 10^{-3} M in complex except for aqueous solutions which were 0.001 to 0.002 M in complex; those containing CH_3OH were 0.001 M in complex. [b] Determined from the decrease in absorption at 318 nm. The fractional decrease in optical density at this wavelength was found to be equal to the ratio of Br^- produced to initial complex and hence to the degree of aquation. [c] Estimated from the extinction coefficient for Br_2^{-*} and assuming 10% of incident light to be absorbed by the complex. (*M.S. Matheson, W.A. Mulac, J.L. Weeks, and J. Rabani, *J. Phys. Chem.*, 70, 2092 (1966). [d] Estimated from the observation that HCHO production was half of that of aquated complex.
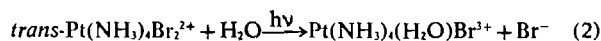
Some experiments were performed in which the solvent contained 10% CH_3OH by volume. In these experiments both the irradiated and the dark solutions were analyzed for formaldehyde by the chromotropic acid method.[18] No ion exchange step was needed in this case. Finally, as with the analyses for bromide ion, all determinations were made by comparison with calibration curves obtained using known amounts of material. These curves showed excellent Beer's law behavior for both the bromide and the HCHO analyses, over the concentration ranges involved.

The thermal back reaction of photolyzed *trans*-$Pt(NH_3)_4Br_2^{2+}$ was followed spectrophotometrically, using a Beckman Model DU spectrophotometer. Other spectral measurements were by means of a Cary Model 14 instrument. Emission at 77°K was examined using an exciting light of 280-380 nm wavelength.

Results

Preliminary experiments showed *trans*-$Pt(NH_3)_4Br_2^{2+}$ to be photosensitive. Irradiation with the full beam of the AH-6 lamp (pyrex optics) produced the changes shown in Figure 1. The isosbestic point at 222 nm was retained to about 60% decomposition, indicating that a single product or that a constant proportion of products was produced; thereafter drift occurred in the spectra, due presumably to secondary photolysis. Quantitative studies using either 305 nm or 350 nm

(18) G.E. Bricker and H.R. Johnson, *Ind. Engin. and Chem. (anal.)*, 17, 400 (1945).

radiation were then carried out and analysis showed only Br^- ion and aquated complex (see later). No ammonia or Pt^{II} species appeared to be produced even on irradiations to about 50% disappearance of initial complex. The various observations are summarized in Table II. The photolysis thus appeared to occur cleanly according to the reaction

$$trans\text{-}Pt(NH_3)_4Br_2^{2+} + H_2O \xrightarrow{h\nu} Pt(NH_3)_4(H_2O)Br^{3+} + Br^- \quad (2)$$

where the aquated product is presumably *trans*, in view of the results of the thermal anation experiments (see later).

Flash photolysis experiments revealed a more complex situation, however. Flashing of $10^{-4} M$ [*trans*-$Pt(NH_4)_3Br_2]Br_2$ with the pyrex sleeve in place produced a transient absorption in the 360-370 nm wavelength region. The transient was not present when an equivalent concentration of aqueous KBr was flashed, nor on the first flashing of the perchlorate salt of the complex (in this last case either with or without the pyrex sleeve in place). The transient was observed, however, if Br^- ion was added to a solution of the perchlorate salt of the complex, and was also observed on successive flashings of a solution of the perchlorate salt alone (with the pyrex sleeve in place). Thus, as summarized in Table II, production of the transient requires the presence both of complex and of bromide ion; it does not occur with either alone.

The transient was found to decay exponentially. In a series of experiments with various wavelengths of monitoring light, extrapolation of the linear ,and parallel) log $(D-D_\infty)$ vs. time plots to a common zero time led to the absorption spectrum shown in Figure

2. The same spectral shape was obtained for solutions of various concentrations of complex and of Br^- ion. We believe that the maximum at 350 nm and the width at half-maximum optical density serve to identify the transient as Br_2^-.[19] The mean decay time was about 1 millisec, independent of complex concentration and of whether or not the solvent medium contained 10% CH_3OH or C_2H_5OH. The decay time was affected, however, by dissolved oxygen and by the level of Br^- ion concentration; these effects were not studied in detail. The decay of Br_2^- became second order if the flash energy was increased to much higher values, presumably because the reaction $Br_2^- + Br_2^- \rightarrow Br_3^- + Br^-$ became important. The first order decay law found under our usual flash conditions, and without deaeration, probably corresponds to reaction of Br_2^- with dissolved oxygen.
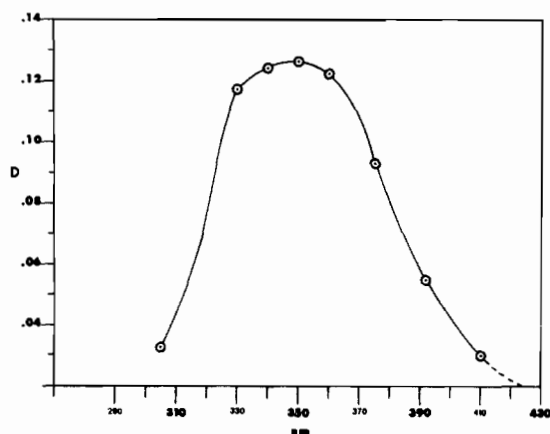

Figure 2. Absorption of Br_2^- transient measured 250 μsec after flashing $trans$-Pt(NH$_3$)$_4$Br$_2^{2+}$ ... Br$^-$; 10^{-4} M complex, 0.01 M NaBr and 600 Joule flashes.

The presence of Br_2^- signals a redox mode of photolysis and of radical production. As a test for the latter, both flash and steady state irardiations were carried out in the presence of 10% by volume of CH_3OH, and HCHO formation was looekd for. As summarized in Table II, HCHO was indeed formed, but only if both Br^- and complex were present.

The above observations suggest that both Br_2^- and HCHO production is associated with ion pair formation and this aspect was therefore investigated. Ion pairing has been reported to occur between Br^- ion and $trans$-Pt(en)$_2$Br$_2^{2+}$ [20] (en denoting ethylenediamine), evidenced by non-additive spectra. Our results are summarized in Figure 3 which shows the absorption spectrum of aqueous $trans$-Pt(NH$_3$)$_4$Br$_2^{2+}$ in various concentrations of added Br^- ion. Conventional algebraic analysis yields a value of 1-2 M^{-1} for the ion pair formation constan, K_{ip}, but the thermodynamic value could be larger since at the higher Br^- ion concentrations the activity coefficient corrections should be appreciable. The value is reasonable for ions of the charge type involved.[21] Figure 3 also shows the

difference between the absorption spectrum of the complex in 0.5 M NaBr and that of the complex alone. This difference spectrum is similar to that found with $trans$-Pt(en)$_2$Br$_2^{2+}$; the absorption maximum is at 260 nm in both cases.
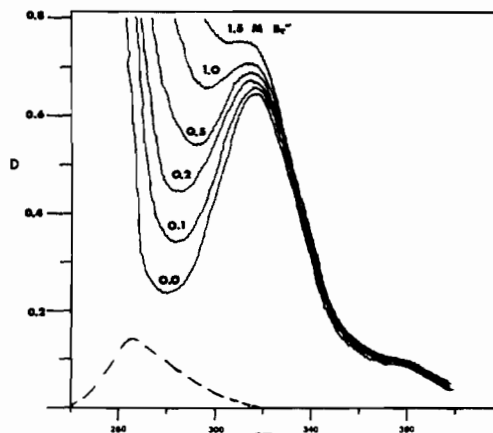

Figure 3. Effects of ion association on the absorption spectrum of [$trans$-Pt(NH$_3$)$_4$Br$_2$](ClO$_4$)$_2$; 1.1×10^{-4} M complex, 5 cm cell and NaBr concentration as indicated. --- difference spectrum between 1.1×10^{-4} M complex + 0.5 M NaBr and 1.1×10^{-4} M complex alone (not to scale).

As noted earlier, the only new form of platinum in the photolyzed solutions appears to be Pt(NH$_3$)$_4$-(H$_2$O)Br^{3+}. Corroborative evidence that Eq. (2) does give the net photolysis reaction is that in the presence of Br^- ion the spectrum of an irradiated solution shows a return in the dark to that of the starting solution. As shown in Figure 4, after irradiation the absorption at 318 nm increased toward the initial value according to first order kinetics, and with an apparent rate constant, k, proportional to the Br^- ion concentration. The value of k approximately doubled in the presence of an amount of added Pt(NH$_3$)$_4^{2+}$ corresponding to 1% of the total complex, but otherwise appeared to depend only on the concentration of Br^- ion present during the rate measurement; that is, it made no difference whether a given concentration of Br^- ion was present during the irradiation or was added subsequent to it. The value of k was the same for our various irradiation conditions; it was not affected by the presence of 10% CH_3OH. No detailed study was made of the effect of Pt(NH$_3$)$_4^{2+}$ on k, but Pt^{II} complexes are known to catalyze Pt^{IV} substitution reactions.[22] As with most preparations of Pt^{IV} complexes, it is likely that ours contained traces of Pt^{II} impurity. Our value for k/(Br$^-$), 0.51 M^{-1} min^{-1}, sould perhaps be written as [(k$_1$ + k$_2$(Pt^{II})], where the k$_1$ and k$_2$ terms denote the uncatalyzed and the catalyzed anation paths, respectively.*

We note that the equilibrium constant for reaction (2) must be small. Solutions of [$trans$-Pt(NH$_3$)$_4$Br$_2$]-(ClO$_4$)$_2$ showed only a slight decrease in optical den-

(19) L.I. Grossweiner and M.S. Matheson, *J. Phys. Chem.*, *61*, 1089 (1957); note the maximum (360 nm) of the published spectrum was corrected to 350 nm because of the spectroplate density conversion factor.
(20) A.J. Poë, *J. Chem. Soc.*, 183 (1963).
(21) W.A. Millen and D.W. Watts, *J. Amer. Chem. Soc.*, *89*, 6858 (1967).

(22) F. Basolo, A.F. Messing, P.H. Wilks, R.G. Wilkins, and R.G. Pearson, *J. Inorg. Nucl. Chem.*, *8*, 203 (1958); F. Basolo and R.G. Pearson, *Adv. Inorg. Chem. Radiochem.*, *3*, 35 (1961).
* We thank one of the reviewers for calling our attention to a recent paper describing anation kinetics for $trans$-Pt(NH$_3$)$_4$(H$_2$O)Br^{3+} in acid, Pt^{II} free solution (W.R. Mason, *Inorg. Chem.*, *10*, 1914 (1971)). Our somewhat different results probably do reflect Pt^{II} catalysis.

sity at 318 nm, even on long standing. Also, of course, photolyzed solutions return almost completely to the unaquated complex.
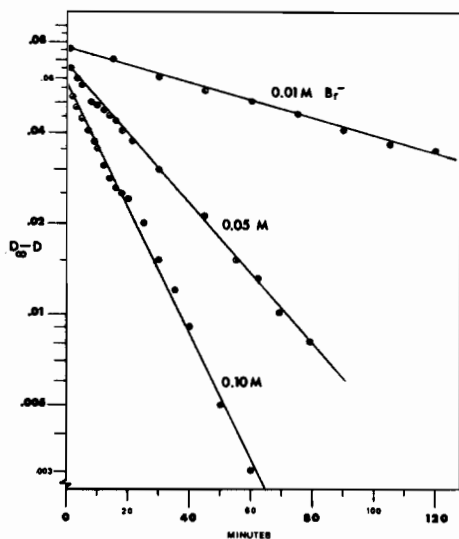

Figure 4. Pseudo first order rate plots for the Br^- anation of the product of photolysis of trans-$Pt(NH_3)_4Br_2^{2+}$; 8×10^{-4} M complex, 27°C and NaBr as indicated.
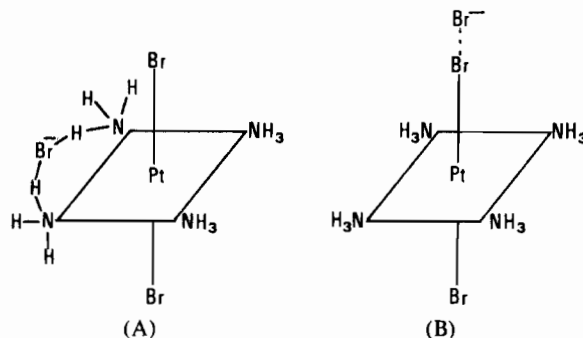
Discussion

We consider first the results obtained in the absence of Br^- ion. The net photolysis reaction, Eq. (2), is probably also the primary reaction of the excited state produced, in view of the lack of any complexities in behavior. Also, the ratio of the quantum yield at 305 nm to that at 350 nm is large enough to suggest that different excited states are populated. For example, irradiation at the former wavelength may produce the state corresponding to the 318 nm absorption maximum, while irradiation at 350 nm may lead to population of the state corresponding to the shoulder at 370 nm. The 318 nm state may be a CT one in view of the intensity of the absorption band, but assignment purely on this last basis is hazardous because of the uncertainty as to the extent to which CT and ligand field states may be mixed in the case of a heavy metal complex,[11] and also in view of the apparent lack of redox character to the photoreaction. The photolysis at 350 nm might be alternatively derived from a ligand field state of energy similar to that corresponding to the first absorption feature in the spectrum of $PtBr_6^{2-}$ (at 525 nm). That is, there is a possibility that a low lying triplet or quintet state is the photochemically active one. Such states, especially if quintet, may not be seen in absorption; their possible role in photochemistry might profitably be investigated by means of sensitization experiments.

Primary photoaquation very likely also occurs in the case of $PtBr_6^{2-}$, the path involving Br_2 production being an alternative and not necessarily major mode of photolysis. In fact, the quantum yields for primary photoaquation may be rather similar for $PtBr_6^{2-}$ and trans-$Pt(NH_3)_4Br_2^{2+}$. Another point of similarity is that both [trans-$Pt(NH_3)_4Br_2$](ClO_4)_2$ and K_2BtBr_6[23]
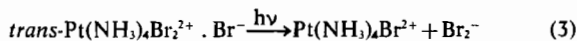
(23) P.D. Fleischauer and P. Fleischauer, Chem. Rev., 70, 199 (1970).

show emission at 77°K. This similarity in behavior is consistent with the rule for d^6 metals that, where d-d transitions are involved, if low temperature emission is observable, the complex will also be photo sensitive, and vice versa.[24]

The photolysis results with added Br^- ion present cannot be explained in terms of aquation as the primary step. Also, it seems necessary to involve the ion pair species [trans-$Pt(NH_3)_4Br_2^{2+} \cdot Br^-$], I, in view of the observation that both Br_2^- and HCHO production increases with increasing Br^- ion concentration. The observed yields of Br_2^- and of HCHO are consistent with a K_{ip} value of about $4\ M^{-1}$ (in low ionic strength media) provided that the quantum efficiency for photolysis of I is close to unity. The alternative to I as a photoactive species is that irradiation of the non ion-paired complex leads in part to Br atoms and some Pt^{III} species. This alternative encounters difficulties (see later).

The excited ion pair species I* must produce (a) Br_2^-, (b) $Pt(NH_3)_4(H_2O)(Br)^{3+}$, (c) no Pt^{II} complexes, and (d) a radical capable of bringing about the conversion of CH_3OH to HCHO. The chemistry implicit in these requirements places some limitation on structures for I. For example, structure A is a

(A)   (B)

reasonable one for I (or I*) on purely electrostatic grounds; it places Br^- ion away from coordinated bromines (whose formal charge should be somewhat negative), and allows hydrogen bonding with ammonia hydrogens. The structure does not suggest, however, why I* should produce Br_2^-, and we therefore prefer the alternative structure B for which the interaction is $Pt-Br-Br^-$. As possibly supporting evidence, the difference spectrum of Figure 3 is similar to that for Br_3^-, (see reference 20). A possible photolysis mode for I is now.

$$trans\text{-}Pt(NH_3)_4Br_2^{2+} \cdot Br^- \xrightarrow{h\nu} Pt(NH_3)_4Br^{2+} + Br_2^- \quad (3)$$

The production of HCHO in the presence of CH_3OH is probably due to the formation of $.CH_2OH$ radicals since these will react with oxygen to give formaldehyde as the ultimate product.[25] The ion Br_2^- does not react efficiently with CH_3OH, however,[26] so the formation of $.CH_2OH$ must be attributed to the reaction $Pt(NH_3)_4Br^{2+} + CH_3OH \rightarrow Pt(NH_3)_4^{2+} + .CH_2OH$. Thus according to mechanism (3) $Pt(NH_3)_4^{2+}$ should

(24) P.D. Fleischauer, A.W. Adamson, and G. Sartori, in Inorg. React. Mech. pt. II, ed. J.O. Edwards, Wiley Interscience Publishers, New York, (1972).
(25) J.H. Baxendale, Rad. Res., 17, 312 (1962).
(26) J. Jortner, M. Ottolenghi, and G. Stein, J. Phys. Chem., 68, 247 (1964).

be a principal photoproduct, arising either from the disproportionation of the Pt^{III} species, or from its reaction with CH$_3$OH. This prediction is contrary to requirements (b) and (c). We find no Pt(NH$_3$)$_4^{2+}$ analytically, and, in addition, the constancy of k/(Br$^-$) for the back anation of variously photophoduced Pt-(NH$_3$)$_3$(H$_2$O)Br^{3+} implies that no Pt^{II} species are formed. That is, according to the probable sequence of events if reaction (3) is correct, the concentration of Pt^{II} species should increase with the degree of photolysis and should also depend on whether or not CH$_3$OH is present, yet no such dependencies are reflected in the behavior of k/(Br$^-$). In summary, reaction (3) does not explain how the net photolysis reaction can be one of aquation only under all of the various conditions tested. The same objections and the same conclusion apply to the supposition that non ion-paired complex undergoes homolytic Pt–Br bond fission to give Br atoms and a Pt^{III} species.

We suggest the alternative possibility that water rather than Pt^{IV} is reduced in the photolysis of I,

$$Pt(NH_3)_4Br_2^{2+} . Br^- + H_2O \xrightarrow{h\nu} Pt(NH_3)_4Br^{3+} + Br_2^- + H + OH^- \quad (4)$$
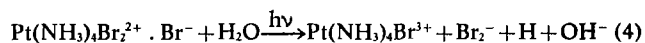
The coordinatively unsaturated species, Pt(NH$_3$)$_4$Br^{3+} should readily coordinate solvent water to yield the observed photolysis product; alternatively, reaction (4) can be written as a concerted process leading directly to Pt(NH$_3$)$_4$(H$_2$O)Br^{3+}. The remaining observations are now accounted for. Hydrogen atoms can abstract H from methanol to produce H$_2$ and .CH$_2$OH,[25] and thus eventually, HCHO. The presence of hydrogen as a photolysis product is also suggested by the observation (see Table II) that gas evolution (not of dissolved air) occurred during irradiations in the presence of added Br$^-$ ion and methanol.

The proposed mechanism adds a certain consistency to the redox photochemistry of Pt^{IV} complexes in that irradiation in the wavelength region of the first absorption features now appears in general not to lead to redox processes involving Pt^{III} products. In the case of PtBr$_6^{2-}$ the photochemistry suggests that the redox reaction mode is one of formation of Pt^{II} and Br$_2$. This mode is not a probable one in the present case and therefore no redox photolysis is observed. On ion pairing of trans-Pt(NH$_3$)$_4$Br$_2^{2+}$, however, two bromines are again adjacent although only one is coordinated. Photolysis now yields Br$_2^-$ but with reduction of water preferred to that of the Pt^{IV} center.