A Nucleophile-Assisted Methyl Migration in the Reaction of *trans*-Dicarbonylchloro(triphenylphosphine)rhodium with Methyl Iodide

By P. UGUAGLIATI, A. PALAZZI, G. DEGANELLO, and U. BELLUCO

trans-RhCl(CO)$_2$P(C$_6$H$_5$)$_3$ (1) reacts with methyl iodide in dichloromethane under mild conditions to give the acetylrhodium complex RhClI(CO)(COCH$_3$)(P(C$_6$H$_5$)$_3$) (2) which is presumably five-coordinate in the solid. The kinetics and mechanism of this reaction have been studied. The reaction occurs in two stages. The first stage produces a labile intermediate and its rate of formation is first order in metal complex and CH$_3$I. The second stage involves decomposition of the intermediate to final product with a rate law of the type: rate = $k_1{}^{II}$[intermediate] + $k_2{}^{II}$[intermediate][CH$_3$I]. The activation parameters for the first stage are $\Delta H_I{}^* = 11.5 \pm 1.5$ kcal/mol and $\Delta S_I{}^* = -33 \pm 5$ eu; for the second stage $\Delta H_{II}{}^* = 6 \pm 0.5$ kcal/mol and $\Delta S_{II}{}^* = -55 \pm 1.5$ eu for the second-order step. The rate constant of the first-order step, extrapolated from the plot of pseudo-first-order rate constants *vs.* methyl iodide concentration to [CH$_3$I] = 0, is scarcely dependent on temperature over the range examined. The reaction rates of both stages increase markedly with increasing medium polarity. These results are explained by a mechanism involving formation of the intermediate methyl–rhodium(III) complex RhClI(CO)$_2$(CH$_3$)P(C$_6$H$_5$)$_3$ (3) through oxidative addition of CH$_3$I to 1 during the first stage; in the second stage 3 undergoes rearrangement to the final acetyl complex 2 *via* nucleophilic attack by both the solvent and CH$_3$I in a first-order path and a second-order path operating simultaneously.

Introduction

In the course of our studies on the oxidative addition reactions of d^8 transition metal ion complexes we found[1] that the novel Rh^I complex *trans*-RhCl(CO)$_2$-P(C$_6$H$_5$)$_3$[2] (1) gives the acetylrhodium(III) complex RhClI(COCH$_3$)(CO)(P(C$_6$H$_5$)$_3$) (2) when reacting with methyl iodide in dichloromethane at room temperature. With other reagents of the type X–Y 1 gives Rh^{III} complexes of formula RhClXY(CO)$_2$P(C$_6$H$_5$)$_3$ through simple oxidative addition. The reaction leading to 2 may involve "carbon monoxide insertion" (or methyl migration, for that matter) in a step of the overall path. It is reminiscent of the reaction of methyl-manganese pentacarbonyl with Lewis bases which gives substituted acetylmanganese tetracarbonyl derivatives[3] and of the known interconversion of alkyl- and acyl–carbonyl complexes of rhodium and iridium.[4–6] Alternatively, the reaction 1 → 2 may involve direct nucleophilic attack of methyl iodide at the carbon atom of carbon monoxide, in analogy with similar attacks of nucleophiles on metal–carbonyl complexes.[7,8] In view of the mechanistic implications of this interesting reaction we have carried out a kinetic investigation of it and shall report the results here.

Experimental Section

Materials.—*trans*-RhCl(CO)$_2$(C$_6$H$_5$)$_3$ and RhClI(COCH$_3$)-(CO)(P(C$_6$H$_5$)$_3$) were prepared by the methods described pre-

(1) G. Deganello, P. Uguagliati, B. Crociani, and U. Belluco, *J. Chem. Soc., A*, 2726 (1969).

(2) P. Uguagliati, G. Deganello, L. Busetto, and U. Belluco, *Inorg. Chem.*, **8**, 1625 (1969).

(3) (a) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **86**, 3994 (1964); (b) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967); (c) R. F. Heck, *Accounts Chem. Res.*, **2**, 10 (1969).

(4) M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 1347 (1967).

(5) B. L. Shaw, and E. Singleton, *ibid.*, 1683 *A*, (1967).

(6) M. C. Baird, C. J. Nyman, and G. Wilkinson, *ibid.*, *A*, 349 (1968).

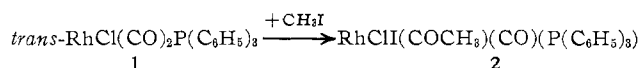(7) L. Malatesta, G. Caglio, and M. Angoletta, *ibid.*, 6974 (1965).

(8) T. Kruck, and M. Noack, *Chem. Ber.*, **97**, 1693 (1964).

viously.[1,2] Reagent grade methyl iodide was extracted with aqueous sodium thiosulfate, dried over phosphorus pentoxide, distilled, and stored over clean mercury. All other chemicals used were reagent grade materials. Prior to use, solvents were freed from oxygen by means of nitrogen.

Kinetic Measurements.—The reaction was followed spectrophotometrically with a Beckman DK-2A double-beam spectrophotometer equipped with a thermostated cell compartment by measuring the rate of disappearance of *trans*-RhCl(CO)$_2$-(P(C$_6$H$_5$)$_3$). The initial concentration of metal complex was generally in the range 3×10^{-4}–8×10^{-4} *M* and the concentration of CH$_3$I was in at least 100-fold excess (0.1–2 *M*). Known volumes of thermostated solutions of the complex and the reagent were mixed in a 1-cm quartz cell placed in the thermostated cell compartment of the instrument. From the recorded near-ultraviolet spectra, a suitable wavelength was chosen and the kinetics were followed by recording the change in optical density as a function of time. Under the prevailing pseudo-first-order conditions the first-order rate constants, k_{obsd}, were calculated from the slopes of the linear plots of log $(A_\infty - A_t)$ *vs.* time (A is the optical density). The reaction proceeded to completion and the infinite spectrum was coincident with that of the product (2) prepared independently.

Results

The reaction

$$\textit{trans-}RhCl(CO)_2P(C_6H_5)_3 \xrightarrow{+CH_3I} RhClI(COCH_3)(CO)(P(C_6H_5)_3)$$
$$\qquad\qquad 1 \qquad\qquad\qquad\qquad\qquad 2$$

proceeds rapidly in dichloromethane at temperatures in the range 15–30° without formation of side products. By scanning the spectrum in the ultraviolet region from time to time during the course of the reaction, it could be seen that there were two observable stages of spectrophotometric change. During the first stage an isosbestic point was developed (353 mμ), whereas in the second, slower stage the optical density increased steadily at any wavelength of the range scanned. Thus, the first stage corresponded to the formation of an intermediate, which decomposed in the second stage to give the product 2. Since the concentration of

TABLE I

RATE CONSTANTS FOR THE REACTION OF
trans-RhCl(CO)$_2$(P(C$_6$H$_5$)$_3$) WITH METHYL IODIDE IN
DICHLOROMETHANE AT VARIOUS TEMPERATURES

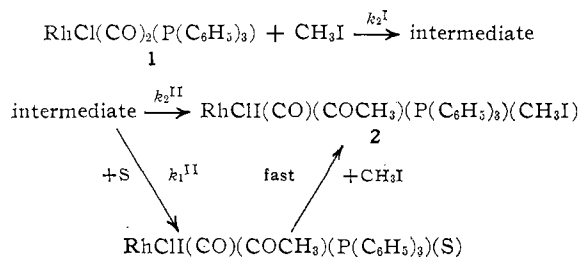| [CH$_3$I], M	Temp, °C	$10^4 k^I_{obsd}$, sec^{-1}	$10^4 k^{II}_{obsd}$, sec^{-1}	$10^4 k_2^I$, M^{-1} sec^{-1}	$10^4 k_2^{II}$, M^{-1} sec^{-1}
0.50	15	2.23	...	4.46	1.13
1.00	15		1.75		
2.00	15		2.80		
2.50	15		3.53		
3.00	15		4.00		
0.50	20	3.63	...	7.26	1.45
1.00	20		2.14		
1.50	20		2.95		
2.00	20		3.60		
0.10	25	0.82		10.20	
0.25	25	2.73			
0.50	25	5.10			
0.75	25	7.55			
0.98	25	10.15			
0.75	25		1.90		1.64
0.98	25		2.30		
1.50	25		3.26		
2.00	25		3.92		
2.50	25		4.70		
2.92	25		5.62		
0.50	30	6.40	...	12.8	2.07
1.00	30		2.60		
1.50	30		3.70		
2.00	30		4.73		

CH$_3$I was always in sufficiently large excess to remain essentially constant, the observed disappearance of RhCl(CO)$_2$(P(C$_6$H$_5$)$_3$) in the first stage obeyed a pseudo-first-order rate law. We established that at one temperature (25°) the pseudo-first-order rate constant, k^I_{obsd}, was proportional to the concentration of CH$_3$I (see Table I). Second-order rate constants of the first stage (k_2^I) for the other temperatures were then calculated from kinetic runs at a single CH$_3$I concentration assuming the second-order rate law to be valid. The k^I_{obsd}'s were actually determined by the use of Guggenheim's method,[9] owing to the uncertainty in locating the infinite spectrum of the first stage caused by the onset of the second stage. The pseudo-first-order rate constants for the second stage, k^{II}_{obsd}, were calculated at 353 mμ and obeyed the rate law

$$k^{II}_{obsd} = k_1^{II} + k_2^{II}[CH_3I]$$

The kinetic data are reported in Table I ($k_1^{II} \simeq 0.7 \times 10^{-4}$ sec^{-1}, extrapolated, scarcely dependent of temperature). The stoichiometric reaction **1** → **2** can therefore be written as in Scheme I.

The k_1^{II} term can be interpreted as a bimolecular

SCHEME I

RhCl(CO)$_2$(P(C$_6$H$_5$)$_3$) + CH$_3$I $\xrightarrow{k_2^I}$ intermediate
1

intermediate $\xrightarrow{k_2^{II}}$ RhClI(CO)(COCH$_3$)(P(C$_6$H$_5$)$_3$)(CH$_3$I)
2

+S $\searrow$ k_1^{II} fast $\nearrow$ +CH$_3$I

RhClI(CO)(COCH$_3$)(P(C$_6$H$_5$)$_3$)(S)

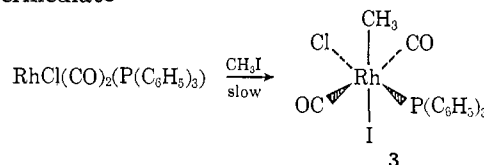(9) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

attack by the solvent (S) on the intermediate followed by fast reaction with CH$_3$I. The molecules of solvent or CH$_3$I that occupy the sixth coordination position in RhClI(CO)(COCH$_3$)(P(C$_6$H$_5$)$_3$)(S) and **2** of Scheme I are probably not firmly bound to the central metal, since the reaction product was isolated under preparative conditions as RhClI(CO)(COCH$_3$)(P(C$_6$H$_5$)$_3$); in the solid, at least, this is a five-coordinate monomer or a halide-bridged six-coordinate dimer[1] and its elemental analysis showed that it was isolated without incorporation of molecules of solvent (CH$_3$I itself). Coordination of iodomethane to a metal ion through the iodine atom as in **2** is not unusual, as witnessed by recently reported examples such as RhClI(CH$_3$)-(P(C$_6$H$_5$)$_3$)$_2$(CH$_3$I)[10] and its Ir analog,[11] although in the latter CH$_3$I appears to be strongly bound to the metal.

The activation parameters for the first stage (k_2^I path) are $\Delta H_I^* = 11.6 \pm 1.5$ kcal/mol and $\Delta S_I^* = -33.4 \pm 5$ eu; for the second stage, only for the methyl iodide dependent path could activation parameters be determined. These are $\Delta H_{II}^* = 6.1 \pm 0.5$ kcal/mol and $\Delta S_{II}^* = -55.2 \pm 1.5$ eu. Therefore the lower reaction rate of the second stage is due to a more negative entropy factor which offsets the more favorable enthalpy. The largely negative activation entropies of both stages indicate that formation of activated states involves either a sizable increase in polarity or a severe stereochemical constraint. That polar transition states are involved is indicated by the marked increase in rates observed on going from benzene through dichlomethane to dimethylformamide: in the first solvent the reaction was too slow to measure, whereas in the last it was too fast to follow by usual spectrophotometric techniques. This is, however, too large an effect to be attributed to simple polarity factors, indicating that the nucleophilic power of the solvent plays some role.

Discussion

The nature of the intermediate in Scheme I is as yet unknown and various attempts to isolate it at low temperatures were unsuccessful. We also tried to follow the reaction by monitoring spectral changes in the infrared spectrum in hopes that changes in the terminal and acyl–carbonyl stretching region would allow us to determine the nature of the reaction stages involved. Unfortunately, under the conditions required for this technique the reaction was too fast to follow. Thus a mechanism of reaction can only tentatively, albeit reasonably, be proposed. We suggest that the first stage is the oxidative addition of CH$_3$I to **1** to give a labile rhodium(III)–methyl complex as intermediate

RhCl(CO)$_2$(P(C$_6$H$_5$)$_3$) $\xrightarrow[\text{slow}]{\text{CH}_3\text{I}}$


3

(10) D. N. Lawson, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 1733 (1966), and ref 7 therein.

(11) M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967).

This is likely to be a *trans* addition, as is commonly found in oxidative addition of alkyl halides on IrCl-(CO)((C$_6$H$_5$)$_2$PCH$_3$)$_2$ and related d^8 metal ion complexes.[12,13] That the first stage is an oxidative addition is supported by the fact that phenyl iodide also was found to add onto RhCl(CO)$_2$(P(C$_6$H$_5$)$_3$) giving the rhodium(III) adduct RhClI(CO)$_2$C$_6$H$_5$(P(C$_6$H$_5$)$_3$); this is stable, however, and does not rearrange to an acyl-rhodium(III) complex, as shown earlier.[1] This interpretation is in agreement with the following experimental observations: (i) Alkyl and aryl chlorides or bromides are unreactive toward 1 even after prolonged heating.[1] This may be due to the lower carbon-iodine dissociation energy, which is likely to play an important role in oxidative additions of this type. These reactions have been shown to involve a highly polar activated complex and should be best considered as bimolecular displacements at carbon by the transition metal acting as a nucleophile.[14] The electrophilic character of the carbon bound to iodide, which is also a better leaving group, should be more pronounced than the other halides, thereby facilitating the replacement reaction

$$\text{Rh} \longrightarrow \text{CH}_3 \overset{\frown}{\rightleftharpoons} \text{I}$$
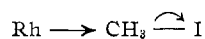
(ii) The entropy of activation for the first stage is largely negative. This is what one would expect for a reaction having a highly polar transition state that would cause "freezing" of solvent molecules at the polar ends of the activated complex Rh$^{\delta+}\cdots$CH$_3\cdots$I$^{\delta-}$. In this regard it may be pertinent to recall that similarly negative activation entropies were found for the oxidative addition of CH$_3$I to IrX(CO)(P-(C$_6$H$_5$)$_3$)$_2$ in various solvents.[14] The lower ΔH^*'s found for this reaction relative to that of 1 with CH$_3$I, moreover, may result from the lower tendency of RhX(CO)$_2$(P(C$_6$H$_5$)$_3$) relative to IrX(CO)(P(C$_6$H$_5$)$_3$)$_2$ to undergo alkylation caused by the stronger π acid CO which is deactivating compared to P(C$_6$H$_5$)$_3$. In other words soft σ-donor ligands make the metal a more effective nucleophile toward carbon. Of course, this order of enthalpy also reflects the lower promotional energy for the process d^8 − 2e → d^6 required by iridium compared to rhodium.

Based on this hypothesis of the nature of the intermediate, the second stage is easily interpreted as a migration of methyl to a coordinated carbonyl group assisted by a nucleophile which may be either the solvent or CH$_3$I itself: these compete for the intermediate RhClI(CH$_3$)(CO)$_2$(P(C$_6$H$_5$)$_3$) in two parallel paths (see Scheme I). In either case the breaking of the rhodium–methyl bond is accompanied, hence facilitated, by partial bond formation of the methyl with an adjacent carbonyl while the entering nucleophile assists this migration by becoming partially bonded to rhodium. The resulting activated com-

plexes are likely to involve rather stringent steric requirements and appreciable charge separation. This is consistent with the largely negative entropy of activation found for the CH$_3$I-dependent path. The striking solvent effect observed for the overall reaction is in line with this mechanism, since the coordinating ability of the solvent plays a major role in the transition state formation. (There must also be a connection between this role and the small dependence of k_1^{II} on temperature, but we cannot rationalize it at this time.) The low value of ΔH^* for the CH$_3$I-dependent path fits well into this simultaneous bond-breaking–bond-forming picture. The competition between solvent and nucleophile CH$_3$I should have been extended to include other nucleophiles of various degrees of coordinating ability; unfortunately, however, RhCl(CO)$_2$(P(C$_6$H$_5$)$_3$) reacts rapidly with most nucleophiles with replacement of either the halide or carbon monoxide. It should be noted that the same rate law for the second stage would have been obtained if another mechanism were operating, namely, fast monomolecular rearrangement of the methyl–rhodium adduct (precursor) to RhClI(COCH$_3$)(CO)(P(C$_6$H$_5$)$_3$) (which then would be the true intermediate) followed by mere occupation of the coordination site thereby made available by the solvent or CH$_3$I. However this route is far less likely, since it could hardly explain the activation parameters and the solvent effect observed.

A solvent-assisted migration of methyl group was also proposed for the mechanism of the reaction CH$_3$-Mn(CO)$_5$ + L → CH$_3$COMn(CO)$_4$.[3a] It appears that most alkyl–acyl conversions involving transition metal–carbonyl complexes are promoted by the entering nucleophiles (CO, PR$_3$, amines, various anions). Such systems proved much more amenable to systematic investigations than ours, and the wide range of nucleophiles and solvents examined resulted in various kinetic patterns being observed.[3c,15,16] The kinetic behavior of RhCl(CO)$_2$(P(C$_6$H$_5$)$_3$) described here is probably a particular case of a more general pattern that might vary considerably depending on the relative nucleophilic power of solvent, CH$_3$I, and entering σ-donor ligand present in the system.

A point of mechanistic interest is whether the methyl group is migrating to a coordinated carbonyl group (methyl migration) or if this latter is shifting to give the acetyl complex (CO insertion). We have chosen the former, more plausible path in our discussion, in line with recent investigations which have shown that no appreciable carbonyl migration occurs during the conversion of CH$_3$Mn(CO)$_5$ to CH$_3$COMn(CO)$_5$ by carbon monoxide. A quite different possible mechanism for the reaction 1 → 2, involving direct nucleophilic attack of methyl iodide on a coordinated carbonyl must be ruled out, as it would involve a one-step, bimolecular path, which is not observed experimentally. Attacks of hard bases at the carbonyl

(12) J. P. Collman and W. R. Roper, *Adv. Organometal. Chem.*, **7**, 53 (1968).
(13) P. J. Collman and C. T. Sears, Jr., *Inorg. Chem.*, **7**, 27 (1968).
(14) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

(15) F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, **1**, 118 (1966).
(16) I. S. Butler, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **6**, 2074 (1967).

carbon in metal carbonyls have been shown to occur in other systems.[7,8]

To the extent that the mechanism proposed here is valid, the conversion of the intermediate $RhClI(CH_3)$-$(CO)_2(P(C_6H_5)_3)$ to $RhClI(CH_3CO)(CO)(P(C_6H_5)_3)$ promoted by bases is a most interesting and unprecedented reaction; no such alkyl–acyl conversions of rhodium–carbonyl complexes have been studied mechanistically so far. The most striking feature of the reaction of $RhCl(CO)_2(P(C_6H_5)_3)$ with CH_3I described here is the instability of the methyl–rhodium derivative toward even so weak a "base" as methyl iodide, especially when compared with the stability of the phenyl–rhodium analog $RhClI(C_6H_5)(CO)_2(P(C_6H_5)_3).$[1] At present we are searching for solvents and nucelophiles that will also promote the conversion of this latter σ-carbon-bonded rhodium(III) complex to the corresponding $RhClI(C_6H_5CO)(CO)(P(C_6H_5)_3)$.

Photochemical Aquation of Monobromopentaamminechromium(III) Ion in Acid Aqueous Solution

By PIETRO RICCIERI[1a] and HANS L. SCHLÄFER[1b]

The photochemical aquation of $Cr(NH_3)_5Br^{2+}$ in acid aqueous solution (10^{-3} M $HClO_4$, $\mu \approx 0.5$) has been studied using light corresponding to absorption in the ligand field and the charge-transfer bands (580–250 mμ). Quantum yields for NH_3 and Br^- production have been determined. Irradiation in the d–d band region yields the aquobromotetraammine ion, mainly in the *cis* configuration, and NH_3 ($\phi_{NH_3} = 0.34$–0.37). Simultaneously to a very much smaller extent also the monoaquopentaammine ion and Br^- are photochemically produced ($\phi_{Br^-} = 0.009$–0.011). Excitation in the charge-transfer band gives a decrease in ϕ_{NH_3} and an increase in ϕ_{Br^-} compared to the values in the d–d band region ($\phi_{NH_3} = 0.17$–0.20, $\phi_{Br^-} = 0.18$–0.26). The possible mechanisms for the photochemical processes are discussed.

I. Introduction

It is well known that $Cr(NH_3)_5Br^{2+}$ in aqueous acid solution undergoes thermal aquation[2,3] according to

$$Cr(NH_3)_5Br^{2+} + H_2O \xrightarrow{kT} Cr(NH_3)_5H_2O^{3+} + Br^- \quad (1)$$
$$\text{red} \qquad\qquad\qquad\qquad \text{rose}$$
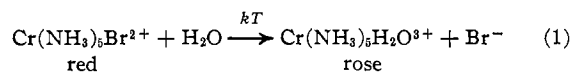
The reaction has been shown to follow first-order kinetics. Its rate constant at 25° is 3×10^{-3} min^{-1};[2b] the activation energy is 21.5 kcal/mol.[2b] The mechanism is supposed to be dissociative.[4]

Contrary to the photochemistry of the monochloropentaamminechromium(III) ion[5–7] the photochemical behavior of $Cr(NH_3)_5Br^{2+}$ has not been investigated. In the case of $Cr(NH_3)_5Cl^{2+}$ the thermal reaction is analogous to (1). Irradiation in the ligand field bands yields predominantly cis-$Cr(NH_3)_4Cl(H_2O)^{2+}$ and NH_3 with a quantum yield $\phi_{NH_3} = 0.35$–0.40, almost wavelength independent. The quantum yield $\phi_{Cl^-} =$

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(2) (a) H. Freundlich and R. Bartels, *Z. Physik. Chem.* (Leipzig), **101**, 177 (1922); (b) E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 95 (1932).

(3) M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, **83**, 2453 (1961).

(4) T. P. Jones, W. E. Harris, and W. J. Wallace, *Can. J. Chem.*, **39**, 2371 (1961).

(5) H. F. Wasgestian and H. L. Schläfer, *Z. Physik. Chem.* (Frankfurt), **57**, 282 (1968).

(6) H. F. Wasgestian and H. L. Schläfer, *ibid.*, **62**, 127 (1968).

(7) L. Moggi, F. Bolletta, and V. Balzani, *Ric. Sci.*, **38**, 1228 (1966).

0.005–0.007 is about two orders of magnitude smaller than ϕ_{NH_3}. Irradiation in the charge-transfer band[6] gives approximately the same ϕ_{NH_3} as in the d–d band region, but a considerable increase in ϕ_{Cl^-} (0.2–0.3).

The present work tends to clarify the photochemical behavior of the monobromopentaamminechromium(III) ion, both for a comparison with the analogous chloro complex and for a further investigation on the possible mechanisms of these photoreactions.

II. Qualitative Experiments

Preliminary experiments show that by irradiation in the d–d band region, similar to the monochloropentaammine, the bromo compound aquates according to

$$Cr(NH_3)_5Br^{2+} + H_2O \xrightarrow{h\nu} Cr(NH_3)_4Br(H_2O)^{2+} + NH_3 \quad (2)$$
$$\text{red} \qquad\qquad\qquad\qquad \text{blue}$$
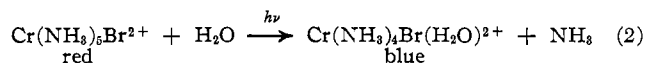
as can easily be concluded from spectrophotometric and pH measurements.

Figure 1 shows the change in light absorption when a solution of 10^{-2} M $[Cr(NH_3)_5Br](ClO_4)_2$ in 10^{-2} M perchloric acid is irradiated for 40 min with a xenon lamp. The temperature was kept at 0° to prevent thermal aquation according to eq 1. Both d–d bands, particularly the band at 26.3 kK, are shifted to longer wavelengths. The short-wavelength band is decreased in intensity; the other one is raised. The pH of the solution increases with increasing exposure