

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 $\text{RhCl}(\text{CH}_3)(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)$ to $\text{RhCl}(\text{CH}_3\text{CO})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)$ 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 $\text{RhCl}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)$ 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 $\text{RhCl}(\text{C}_6\text{H}_5)(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)$.¹ At present we are searching for solvents and nucleophiles that will also promote the conversion of this latter σ -carbon-bonded rhodium(III) complex to the corresponding $\text{RhCl}(\text{C}_6\text{H}_5\text{CO})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)$.

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CONTRIBUTION FROM THE INSTITUT FÜR PHYSIKALISCHE CHEMIE DER UNIVERSITÄT, FRANKFURT AM MAIN, GERMANY

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

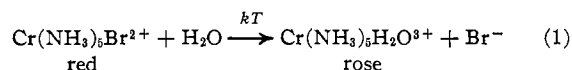
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The photochemical aquation of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ in acid aqueous solution ($10^{-3} M \text{HClO}_4$, $\mu \approx 0.5$) has been studied using light corresponding to absorption in the ligand field and the charge-transfer bands (580–250 m μ). 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 ($\phi_{\text{NH}_3} = 0.34\text{--}0.37$). Simultaneously to a very much smaller extent also the mono-aqua-pentaammine ion and Br^- are photochemically produced ($\phi_{\text{Br}^-} = 0.009\text{--}0.011$). 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 ($\phi_{\text{NH}_3} = 0.17\text{--}0.20$, $\phi_{\text{Br}^-} = 0.18\text{--}0.26$). The possible mechanisms for the photochemical processes are discussed.

I. Introduction

It is well known that $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ in aqueous acid solution undergoes thermal aquation^{2,3} according to



The reaction has been shown to follow first-order kinetics. Its rate constant at 25° is $3 \times 10^{-3} \text{ min}^{-1}$,^{2b} the activation energy is 21.5 kcal/mol.^{2b} The mechanism is supposed to be dissociative.⁴

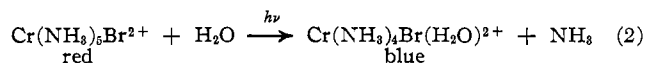
Contrary to the photochemistry of the monochloropentaamminechromium(III) ion⁵⁻⁷ the photochemical behavior of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ has not been investigated. In the case of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ the thermal reaction is analogous to (1). Irradiation in the ligand field bands yields predominantly *cis*- $\text{Cr}(\text{NH}_3)_4\text{Cl}(\text{H}_2\text{O})^{2+}$ and NH_3 with a quantum yield $\phi_{\text{NH}_3} = 0.35\text{--}0.40$, almost wavelength independent. The quantum yield $\phi_{\text{Cl}^-} =$

0.005–0.007 is about two orders of magnitude smaller than ϕ_{NH_3} . Irradiation in the charge-transfer band⁶ 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



as can easily be concluded from spectrophotometric and pH measurements.

Figure 1 shows the change in light absorption when a solution of $10^{-2} M [\text{Cr}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ 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

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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.*, **36**, 1228 (1966).

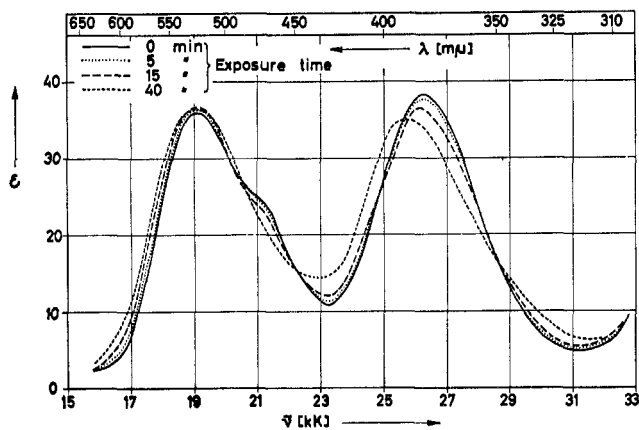


Figure 1.—Change in light absorption of a solution of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ when irradiated with visible light (xenon lamp) ($0.01 M [\text{Cr}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in $0.01 M \text{HClO}_4$ at 0°).

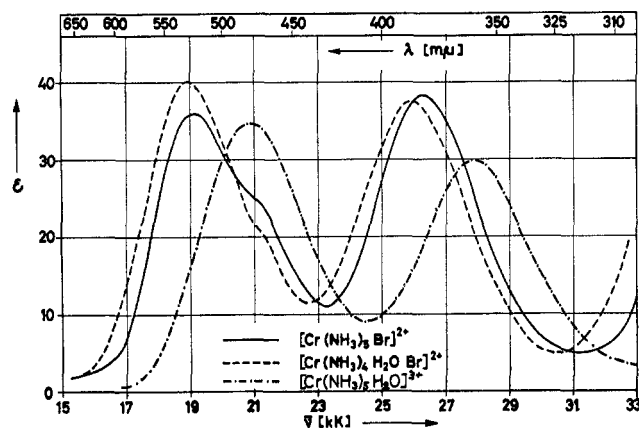


Figure 2.—Absorption spectra of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$, $\text{Cr}(\text{NH}_3)_4\text{Br}(\text{H}_2\text{O})^{2+}$, and $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ ($10^{-2} M [\text{Cr}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$, $[\text{Cr}(\text{NH}_3)_4\text{Br}(\text{H}_2\text{O})]\text{Br}_2$, and $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3$ in $0.1 M \text{HClO}_4$ - $0.37 M \text{NaClO}_4$ at 20°).

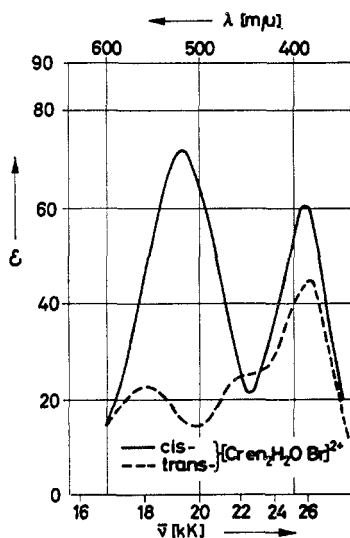
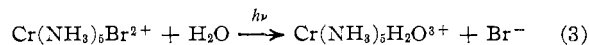


Figure 3.—Absorption spectra of *cis*- and *trans*- $\text{Cr}(\text{en})_2\text{Br}(\text{H}_2\text{O})^{2+}$.⁸

time, because of the protonation of liberated ammonia (*cf.* eq 2). The observed spectral shift is consistent with the position of NH_3 and H_2O in the spectrochemical series ($Dq_{\text{NH}_3} > Dq_{\text{H}_2\text{O}}$).

The absorption spectra of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ and Cr -

$(\text{NH}_3)_4\text{Br}(\text{H}_2\text{O})^{2+}$ are seen in Figure 2. They intersect at 20.4, 22.9, and 26.0 kK. In Figure 1 only at very short exposure times isosbestic points at 20.3 and 22.5 kK are seen. This indicates that another reaction besides eq 2 takes place. Titration of Br^- clearly shows that, in addition to Br^- being produced by the dark reaction eq 1, it is also produced by irradiation with visible light



Comparing Figures 1, 2, and 3 it can be concluded that the aquobromotetraammine ion produced in the photochemical reaction eq 2 exists at least predominantly, if not exclusively, in the *cis* configuration, as was found earlier for the photoproduct of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$.⁵

$[\text{Cr}(\text{NH}_3)_4\text{Br}(\text{H}_2\text{O})]\text{Br}_2$ whose spectrum is seen in Figure 2 is the *cis* compound. This is obvious comparing it with the known spectra of *cis*- and *trans*- $\text{Cr}(\text{en})_2\text{Br}(\text{H}_2\text{O})^{2+}$ ⁸ of Figure 3, which according to the experience with complex ion spectra will be only slightly different from those of the corresponding tetraammines. The *trans* ion shows the long-wavelength band about half as intense as the second d-d band. Also a characteristic splitting is seen. Figure 1 shows an increase of the long-wavelength band and a decrease of the second band during irradiation. This is only consistent with *cis*- $\text{Cr}(\text{NH}_3)_4\text{Br}(\text{H}_2\text{O})^{2+}$ as the predominant product of reaction 2. Zinato, *et al.*,⁹ however, assigned a *trans* configuration to the photoaquation product of $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$. Reasons for this discrepancy will be discussed below.

If one irradiates a solution of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ of the same composition as mentioned above with light of 250 m μ (mercury lamp), one obtains a change in absorption with exposition time as in Figure 4; the

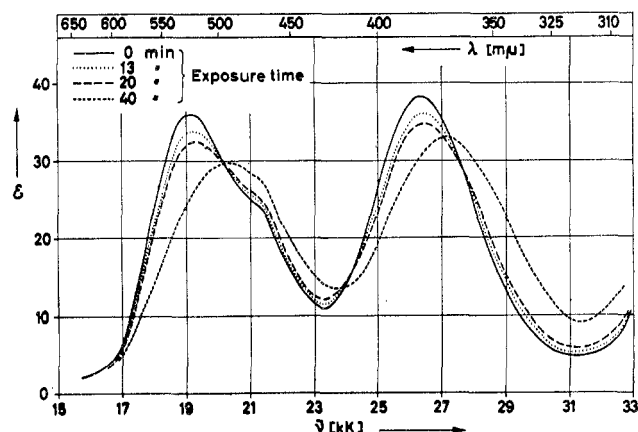


Figure 4.—Change in light absorption of a solution of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ when irradiated with a low-pressure mercury lamp.

behavior is different compared to that of Figure 1. Both d-d bands are shifted to shorter wavelengths, a fact which indicates that mainly reaction 3 proceeds

(8) "Gmelin Handbuch der anorganischen Chemie," 8th ed, Verlag Chemie, Weinheim, Germany, 1965, No. 52, Part C, p 174.

(9) E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Am. Chem. Soc.*, **91**, 1076 (1969).

TABLE I^{a, b}
 ϕ_{NH_3} AT 5° IN THE SPECTRAL RANGE 585–250 m μ

$10^3 a_0$, M	t , min	$10^3 Q_{\text{abs}}$, ein- steins	(% NH ₃) _{phot}	$\phi^{\circ}\text{NH}_3$	ϕ_{NH_3} mol/einstein	$10^3 a_0$, M	t , min	$10^3 Q_{\text{abs}}$, ein- steins	(% NH ₃) _{phot}	$\phi^{\circ}\text{NH}_3$	ϕ_{NH_3} mol/einstein
λ 585 m μ ; Filters: OG 1 (1 mm), GG 18 (2 mm), Interference Filter PAL 757306 (λ_{max} 579 m μ)						Filter: BG 12 (2 mm)					
1.24	20	3.42	4.78	0.347	0.361	1.21	12	2.62	3.92	0.362	0.372
1.21	18	3.20	4.39	0.332	0.344	1.20	12	2.26	3.42	0.364	0.375
1.15	15	2.44	3.56	0.337	0.347	1.17	12	2.36	3.52	0.348	0.358
1.19	15	2.94	4.10	0.332	0.347	1.22	15	2.89	4.28	0.361	0.371
1.12	4°	2.42	3.94	0.363	0.376	Av 0.373 \pm 0.005					
1.35	4°	3.01	3.85	0.346	0.358	λ 400 m μ ; Filter: BG 12 (2 mm)					
Av 0.355 \pm 0.009						1.30	4	2.53	3.65	0.376	0.383
λ 546 m μ ; Filters: BG 18 (3 mm), GG 7 (3 mm)						1.22	4	2.43	3.83	0.381	0.387
1.27	2	4.42	5.63	0.340	0.350	1.21	2	2.14	3.06	0.346	0.352
1.22	2	2.71	3.36	0.323	0.329	1.06	4	4.08	6.74	0.350	0.362
1.35	3	3.94	4.84	0.332	0.340	1.30	4	2.20	2.91	0.343	0.352
1.23	4	2.48	3.34	0.331	0.336	Av 0.367 \pm 0.014					
1.28	4	3.10	4.30	0.335	0.342	λ 380 m μ ; Filter: UG 3 (2 mm)					
1.28	4	3.10	4.30	0.335	0.342	1.21	10	2.42	3.64	0.364	0.369
Av 0.340 \pm 0.005						1.30	15	3.22	4.43	0.358	0.365
λ 530 m μ ; Filters: BG 18 (3 mm), GG 7 (3 mm)						1.23	14	2.95	4.44	0.370	0.377
1.10	3	4.06	6.35	0.334	0.343	Av 0.370 \pm 0.004					
1.05	2	3.60	5.80	0.338	0.347	λ 370 m μ ; Filter: UG 3 (2 mm)					
1.30	2	3.69	4.85	0.341	0.350	1.28	3	4.56	6.34	0.355	0.360
1.00	3	3.70	5.95	0.322	0.333	1.06	3	3.16	5.50	0.37	0.378
1.19	2	2.45	3.68	0.357	0.364	1.23	3	3.58	5.23	0.359	0.364
1.25	3	3.81	5.22	0.343	0.353	Av 0.367 \pm 0.007					
Av 0.348 \pm 0.007						λ 355 m μ ; Filter: UG 3 (2 mm)					
λ 500 m μ ; Filter: BG 18 (3 mm)						1.42	3	4.02	5.31	0.375	0.381
1.15	8	3.16	4.95	0.363	0.375	1.40	3	3.12	4.00	0.358	0.363
1.24	6	2.62	3.63	0.343	0.351	1.48	3	3.22	3.83	0.352	0.359
1.42	8	2.76	3.37	0.344	0.352	Av 0.368 \pm 0.009					
1.34	8	2.56	3.36	0.352	0.360	λ 300 m μ					
1.31	8	2.67	3.44	0.337	0.345	1.20	10	2.52	3.44	0.164	0.165
Av 0.356 \pm 0.008						1.34	15	3.98	2.18	0.147	0.149
λ 470 m μ ; Filter: BG 18 (3 mm)						1.25	25	6.02	4.00	0.166	0.171
1.07	6	2.36	3.84	0.348	0.357	1.20	30	6.62	4.52	0.164	0.170
1.08	8	3.05	4.97	0.350	0.360	1.32	25	5.96	3.86	0.171	0.176
1.02	10	3.65	6.32	0.354	0.368	1.34	20	7.05	4.34	0.165	0.170
1.30	10	3.40	4.48	0.343	0.353	Av 0.167 \pm 0.007					
1.32	10	2.02	2.80	0.366	0.375	λ 250 m μ					
Av 0.363 \pm 0.007						1.52	16	2.25	1.47	0.198	0.200
λ 455 m μ ; Filter: BG 18 (3 mm)						1.17	20	3.00	2.50	0.195	0.198
1.14	6	2.58	4.17	0.368	0.379	1.30	25	3.62	2.62	0.188	0.191
1.18	6	2.65	4.14	0.368	0.378	1.12	30	4.10	3.65	0.200	0.204
1.20	6	2.44	3.74	0.369	0.377	1.08	25	3.93	3.55	0.195	0.199
Av 0.377						1.25	30	4.71	4.15	0.220	0.224
λ 455 m μ ; Filter: BG 18 (3 mm)						1.20	25	4.25	3.32	0.187	0.190
1.14	6	2.58	4.17	0.368	0.379	1.43	25	3.98	2.86	0.206	0.209
1.18	6	2.65	4.14	0.368	0.378	Av 0.202 \pm 0.008					
1.20	6	2.44	3.74	0.369	0.377						

^a Conditions: $[\text{Cr}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in 0.001 M HClO_4 and 0.454 M NaClO_4 ($\mu \approx 0.5$); reaction volume 2 ml. ^b a_0 is the initial concentration of $[\text{Cr}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$, t is the irradiation time, $(\% \text{NH}_3)_{\text{phot}}$ is the NH_3 photochemically produced according to eq 2 in per cent, $(\% \text{NH}_3)_{\text{therm}} = (\Delta c_{\text{H}}/a_0) \times 100$, $(\% \text{Br}^-)_{\text{phot}}$ is the Br^- photochemically produced according to eq 3 in per cent, and $(\% \text{Br}^-)_{\text{therm}}$ is the Br^- thermally produced according to eq 1 in per cent. The filters (Schott, Mainz) indicated in Tables I and II were used to absorb stray light. ^c Only filters OG 1 (1 mm) and GG 7 (3 mm).

($Dq_{\text{Br}^-} < Dq_{\text{H}_2\text{O}}$). Br^- titrations confirm this. Figure 2 shows the spectra of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ which intersect at 20.05, 23.7, and 27.6 kK. Comparison of Figures 2 and 4 leads to the conclusion, because no isosbestic points are seen, that some other process in addition to (3) takes place during irradiation. pH measurements show that also reaction 2 occurs which produces NH_3 . To summarize the qualitative observations one can conclude that irradiation in the d-d bands yields mainly *cis*- $\text{Cr}(\text{NH}_3)_4\text{Br}(\text{H}_2\text{O})^{2+}$ and NH_3 (eq 2) but also $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ to a minor extent (eq 3).

Excitation in the charge-transfer region produces predominantly Br^- and mono-aquo-pentaammine, whereas NH_3 and aquo-bromotetraammine are built up in somewhat smaller quantities than by irradiation with visible light.

III. Quantitative Experiments

Quantum yields ϕ_{NH_3} for production of ammonia in the wavelength region 585–250 m μ are summarized in Table I, column 6. In the region of the d-d bands the ϕ_{NH_3} values are within experimental error almost

TABLE II^{a,b}
 ϕ_{Br^-} AT 3° IN THE d-d BANDS

10 ² a ₀ , M	t, min	10 ² Q _{abs} , ein- steins		(% NH ₃) _{phot}	(% Br ⁻) _{therm}	(% Br ⁻) _{phot}	ϕ_{Br^-} mol/einstein	ϕ_{Br^-}
λ 546 mμ; Filter: GG 3 (4 mm)								
3.10 ^c	7	20.8	12.4	0.82	0.297	0.0088	0.0088	0.0094
1.52	10	20.7	25.0	1.00	0.526	0.0077	0.0077	0.0088
1.52	10	20.7	25.0	1.00	0.526	0.0077	0.0077	0.0088
1.50	10	21.2	26.0	1.20	0.500	0.0071	0.0071	0.0081
1.50	10	20.9	26.0	1.07	0.500	0.0072	0.0072	0.0082
Av 0.0087								
λ 405 mμ; Filter: GG 18 (2 mm)								
4.02 ^c	9	8.85	4.1	0.70	0.124	0.0113	0.0113	0.0116
3.04 ^c	20	21.0	9.9	1.22	0.362	0.0105	0.0105	0.0110
1.65	16	13.9	15.6	1.24	0.472	0.0111	0.0111	0.0124
1.50	18	14.9	18.3	1.07	0.433	0.0088	0.0088	0.0097
1.50	18	14.9	18.3	1.10	0.480	0.0097	0.0097	0.0107
Av 0.0111								

^a Conditions: [Cr(NH₃)₅Br](ClO₄)₂ in 0.05 M HClO₄ and 0.405 M NaClO₄ (μ ≈ 0.5); reaction volume 2 ml. ^b See footnote b of Table I for pertinent information. ^c Solution prepared in 0.05 N HClO₄ without NaClO₄.

 TABLE III^{a,b}
 ϕ_{Br^-} AT 5° IN THE CHARGE-TRANSFER REGION

10 ² a ₀ , M	t, min	V, ml	Q _{abs} , ein- steins		(% NH ₃) _{phot}	(% Br ⁻) _{therm}	(% Br ⁻) _{phot}	ϕ_{Br^-} , mol/einstein
λ 250 mμ								
2.00	20	2.0	1.66	0.83	4.84	1.09	0.264 ^d	
2.00	20	2.0	1.57	0.79	5.43	1.05	0.268 ^d	
1.70	14	2.0	2.02	1.20	5.76	1.41	0.240 ^d	
1.70	16	2.5	2.44	1.16	10.50	1.47	0.256 ^c	
1.22	15	2.5	1.83	1.32	3.85	1.72	0.286 ^c	
1.34	10	2.5	0.907	0.58	1.48	0.82	0.284 ^c	
1.37	15	2.5	1.45	0.86	2.02	0.91	0.216 ^c	
1.55	20	2.5	1.98	1.03	2.30	1.55	0.302 ^c	
1.38	15	2.5	1.49	0.875	2.36	1.11	0.258 ^c	
1.36	15	2.5	1.37	0.81	1.93	1.17	0.292 ^c	
1.32	20	2.5	1.88	1.15	2.35	1.30	0.228 ^c	
1.46	30	2.5	2.74	1.51	2.40	1.99	0.265 ^c	
1.54	30	2.5	2.78	1.45	2.44	1.65	0.230 ^c	
1.49	30	2.5	2.75	1.49	2.52	2.08	0.282 ^c	
Av 0.262 ± 0.020								
λ 300 mμ								
1.70	15	2.0	3.06	1.50	4.25	1.29	0.146 ^d	
2.00	15	2.0	3.25	1.35	4.73	1.20	0.148 ^d	
2.00	15	2.0	3.50	1.46	4.62	1.38	0.157 ^d	
1.90	10	2.0	3.36	1.48	5.25	1.74	0.196 ^d	
2.00	12	2.0	4.26	1.78	5.60	1.90	0.178 ^d	
1.55	10	2.5	2.20	0.92	2.46	2.00	0.176 ^c	
1.02	25	2.5	4.61	3.06	5.40	4.10	0.228 ^c	
0.97	20	2.5	3.40	2.34	5.00	2.92	0.210 ^c	
1.50	15	2.0	3.78	2.10	2.04	2.17	0.174 ^d	
1.45	16	2.0	3.73	2.16	2.26	2.24	0.175 ^d	
1.52	20	2.0	3.24	1.78	2.25	1.76	0.165 ^d	
1.50	20	2.0	3.06	1.71	1.86	1.68	0.165 ^d	
1.59	20	2.0	2.68	1.40	1.81	1.46	0.173 ^d	
Av 0.176 ± 0.016								

^a Conditions: [Cr(NH₃)₅Br](ClO₄)₂ in 0.001 M HClO₄ and 0.454 M NaClO₄ (μ ≈ 0.5). ^b See footnote b of Table I for pertinent information. ^c Titration method used for determination of Br⁻. ^d Concentration cell method used for determination of Br⁻.

independent of the wavelength of the exciting light. In the charge-transfer region a certain decrease of ϕ_{NH_3} takes place.

Quantum yields ϕ_{Br^-} for production of Br⁻ are seen in Table II, column 8, and Table III, column 8. In the d-d band region they are more than one power of ten smaller than ϕ_{NH_3} but attain, in the charge-transfer range at 300 mμ and particularly at 250 mμ, values which are comparable with ϕ_{NH_3} .

One important point in determining the small ϕ_{Br^-}

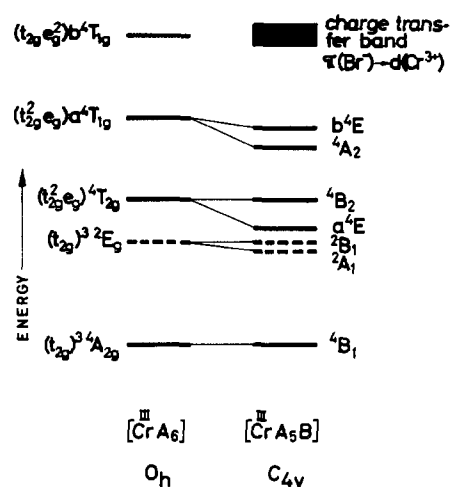


Figure 5.—Term system of [Cr^{III}A₆] and [Cr^{III}A₅B] (schematic; only the lowest doublet level is indicated).

values at 546 and 405 mμ with reasonable accuracy is to change the acid concentration of the solutions from 0.001 M HClO₄, as was used in all other experiments, to 0.05 M. This is necessary because with 0.001 M HClO₄ solutions the apparent quantum yield became a function of exposure time, that is, of quanta absorbed. The reason is that the rate constant k_1 of thermal aquation (eq 1) depends, to some extent, on H⁺ ion concentration. This effect which is of practically no importance if the conversion of Cr(NH₃)₅Br²⁺ is only a few per cent becomes important when conversions of 10–25% occur, as are necessary for determination of ϕ_{Br^-} in the visible range. The greater pH change causes an increase in k_1 . To prevent this effect the acidity has to be increased, so that one obtains solutions with a pH less sensitive to the NH₃ quantities formed. It should be emphasized that this fact is not in total contrast to the results of Levine, *et al.*,³ who investigated the rate of thermal aquation. These authors found that k_1 within the pH range 1–10 is independent of pH, but it is to be considered that they did not prove this “constancy” in very narrow limits. An increase of 30–40% in k_1 is sufficient to give an error of 200% or more in quantum yield measurements.

IV. Discussion

The electronic energy states of Cr(NH₃)₅Br²⁺ can easily be determined on the basis of ligand field theory. The term diagram is shown in Figure 5 (right) together with a diagram for an octahedral chromium(III) complex (left). The splitting of the long-wavelength spin-allowed band which happens when comparing O_h (e.g., Cr(NH₃)₆³⁺) with C_{4v} symmetry is clearly seen in the absorption spectrum of Cr(NH₃)₅Br²⁺ (Figure 2). The splitting of the short-wavelength band should be smaller according to theory and is therefore not observable because it lies within the half-width.

Figure 6 gives the relation determined experimentally between the absorption spectrum and ϕ_{NH_3} as well as ϕ_{Br^-} . The different bands correspond to electronic transitions from the ground state ⁴B₁ to excited states

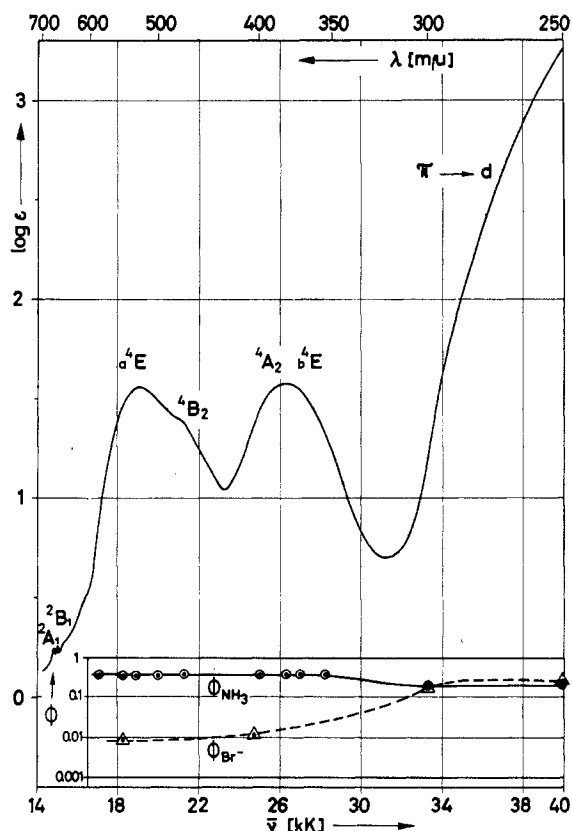


Figure 6.—Absorption spectrum of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$; ϕ_{NH_3} and ϕ_{Br^-} at different wavelengths.

indicated in Figure 6. All ϕ values are smaller than unity. Thus it can be concluded that other processes compete with the photochemical reactions. Because at room temperature in solutions of the complex no luminescence is observed, these processes must be nonradiative.

The question which excited states are responsible for the photoreactions (2) and (3) cannot be answered unequivocally in the present stage of the investigation, but at least some suggestions may be allowed which have a certain plausibility. In principle one has to consider the following different mechanisms:^{10,11} (1) the electronic state which initiates the photochemical reaction is the one populated directly by excitation; (2) internal conversion or intersystem crossing finally leads to an occupation of an electronic state of lower energy which then gives rise to the photochemical reaction; (3) the reaction starts from a "hot" ground state (high vibrational level of the ground state) finally produced by internal conversion (deactivation cascade) from higher electronic states.

Considering ϕ_{NH_3} the almost wavelength independence in the d-d band region seems to indicate that (1) is not likely; excitation with light corresponding to different excited states should most probably give rise to different ϕ_{NH_3} values. Also it is a well-known fact that lifetimes of higher excited states are generally comparatively short. Therefore photochemical re-

actions very seldom originate directly from higher excited states.

The wavelength independence of ϕ_{NH_3} is consistent with (2) and (3). The "hot-molecule" mechanism 3 is supposed to be improbable considering that deactivation of excited vibrations in condensed medium takes place in the time of a few vibrations (*ca.* 10^{-12} sec), that is, three or four powers of ten faster than a fast chemical reaction.

Mechanism 2 still remains and two possibilities have to be discussed. (a) Internal conversion finally yields a population of the thermally equilibrated first excited quartet state a^4E which is responsible for the photo-reaction. (b) The thermally equilibrated lowest doublet (2A_1) is occupied by internal conversion from excited quartet states and becomes the precursor for the photochemistry.

As can be seen from the phosphorescence emission $^2A_1 \rightarrow ^4B_1$ of rigid solutions of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$, when d-d and charge-transfer bands have been irradiated, at least under these conditions a considerable part of the molecules reaches the doublet. The emission occurs at $14,790 \text{ cm}^{-1}$, which is very nearly the wave number where the intercombination band $^4B_1 \rightarrow ^2A_1$ is seen in absorption (*cf.* Figure 6). Fluorescence from the first excited quartet ($a^4E \rightarrow ^4B_1$) is not observed. The lifetime of the doublet state at -193° is $60 \mu\text{sec}$ and at -72° $11 \mu\text{sec}$.¹² The lifetime of the first excited quartet is supposed to be several powers of ten smaller (*ca.* 10^{-8} sec) because the transition to the ground state is only Laporte forbidden, whereas the transition of the doublet to the ground state is in addition also spin forbidden.

From the point of view of lifetimes the doublet is a more likely candidate for the photoreaction. However one has to consider also the structure of the electronic states when discussing their ability for photochemical reactions. Molecules in the doublet have very nearly the same nuclear configuration as molecules in the ground state. This can be seen from the fact that corresponding absorption and phosphorescence emission both occur very nearly at the same wavelengths. Both states in the strong-field approximation arise from the one-electron configuration t_{2g}^3 , that means both potential energy hypersurfaces have minima approximately at the same values of the corresponding normal coordinates. On the other hand complex ions in the first excited quartet have a nuclear configuration expanded in the direction of the central ion-ligand bonds compared to the ground-state configuration. Because the ground state belongs to t_{2g}^3 and the excited quartet to the $t_{2g}^2e_g$ configuration, the potential energy surface has a minimum at greater values of the corresponding normal coordinates than the ground-state surface. If one assumes that such a distorted configuration facilitates the photochemical reaction, then the quartet would probably be favored compared to the doublet.

It is not possible to decide between mechanisms 2a

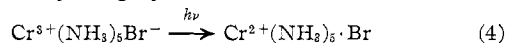
(10) H. L. Schläfer, *J. Phys. Chem.*, **69**, 2201 (1965).

(11) A. W. Adamson, *ibid.*, **71**, 798 (1967).

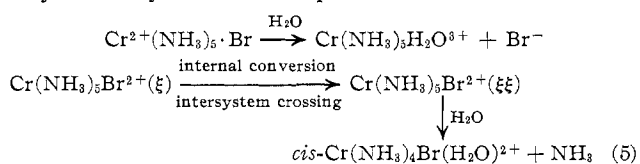
(12) H. U. Zander, Thesis, Frankfurt am Main, 1969.

and 2b and one has to take into account also the possibility that both states are involved in the photochemistry. It should be remembered that in the case of organic molecules some examples are known where both the first excited singlet and the lowest triplet are engaged as precursors of photoreactions.

Before discussing ϕ_{NH_3} in the charge-transfer region, it is useful to consider the nature of the corresponding absorption process. The band is supposed to be of the redox type and related to a transition $\pi(\text{Br}^-) \rightarrow d(\text{Cr}^{3+})$ of an electron from an orbital predominantly localized on Br^- to an orbital mainly localized on Cr^{3+} . This process may roughly be described as



The "excited state" $\text{Cr}^{2+}(\text{NH}_3)_5 \cdot \text{Br}$ with formally bivalent chromium is supposed to react in two different ways which yield different products



One way whose details are unknown finally leads to the same products as the thermal reaction (1). This way must include back-transfer of an electron from chromium to bromine connected with an exchange of bromine against water (probably *via* a dissociation mechanism, that means a pentacoordinated intermediate).

Part of the excited molecules follow another path. They undergo a back-reaction to the original complex ion which is then in a higher excited ligand field state (ξ). [It should be emphasized that another d-d band (in octahedral symmetry ${}^4A_{2g}(t_{2g}^3) \rightarrow {}^4T_{1g}(t_{2g}e_g^2)$) with an intensity somewhat smaller than that of the long-wavelength d-d bands is hidden under the tail of the charge-transfer band. This band is seen in complexes where the charge-transfer band is at shorter wavelength, *e.g.*, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. Therefore by irradiation in the 300–250-m μ region, besides the charge transfer, excitation of this band is expected to occur.] The deactivation cascade finally leads to population of the first excited quartet and the lowest doublet ($\xi\xi$). Consequently photoaquation according to eq 2 occurs.

It is evident that from a given number of excited molecules now a smaller fraction reaches the doublet or the quartet than in the case of d-d excitation. Thus the intersystem crossing yield for the doublet or the intersystem conversion yield for the quartet becomes smaller compared to the values of these yields for excitation into the ligand field bands. The result is a decrease in ϕ_{NH_3} as is observed.

A reasonable conversion to the doublet state at least at low temperatures can be proved considering the luminescence behavior when a rigid solution of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ is excited in the charge-transfer band. One observes a phosphorescence ${}^2A_1 \rightarrow {}^4B_1$ similar to the phosphorescence obtained by irradiation in the d-d bands but with a smaller yield.

It should be of interest to measure the excitation spectrum of the phosphorescence in the ultraviolet region. One should expect in this region a deviation from the normal behavior that the excitation spectrum is very nearly similar to the absorption spectrum. This normal behavior will only hold if all the excitation energy follows the usual deactivation cascade down to the emitting state. In the case of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ only part of the excitation energy will follow this way; another part, at least in solutions of the complex ion at room temperature, undergoes a different deactivation path which finally gives rise to photoaquation (eq 3). Another point which has to be considered is the wavelength dependence of ϕ_{Br^-} , which is essentially the same as that of ϕ_{Cl^-} in the case of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$.⁶ Whereas ϕ_{Br^-} is very small in the d-d band region (*cf.* Figure 6), it becomes remarkably greater in the charge-transfer band, where it is comparable with ϕ_{NH_3} . One explanation which is probably not unreasonable is that the tail of the charge-transfer band extends with small intensity in the visible range. In other words the d-d bands have some charge-transfer character and are not pure d-d bands. ϕ_{Br^-} has its smallest value in the long-wavelength band and increases slightly in the region of the second band which is located closer to the charge-transfer band. The same happens in the case of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+}$ with ϕ_{Cl^-} , where the $\pi(\text{Cl}^-) \rightarrow d(\text{Cr}^{3+})$ band lies at shorter wavelengths than the corresponding band of $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$. For the chloro complex the values (0.005; 0.007⁶) are smaller than the corresponding values of the bromopentaammine.

As another explanation for the small photochemical Br^- production in the d-d band region one may consider a "hot-molecule" mechanism. The photoaquation (eq 3) would then start from a high vibrational level of the ground state reached at the end of the deactivation cascade from excited quartet states. On the other hand population of such a state is also obtained thermally giving rise to the thermal aquation (eq 1). Such a mechanism for photochemically produced Br^- should lead to an almost constant ϕ_{Br^-} in the d-d band region which is not observed. The slight increase of ϕ_{Br^-} with decreasing wavelength which is outside of experimental error leads to the suggestion that a "hot-molecule" mechanism seems to be somewhat unlikely.

The fact that excitation in the d-d band region gives rise predominantly to photoaquation according to eq 2 with release of ammonia is consistent with Adamson's first rule:¹¹ "If one considers the six ligands of an octahedral complex of chromium(III) to lie in pairs at the ends of three mutually perpendicular axes, the axis having the smallest average ligand field will be the one labilized. The total quantum yield will be approximately that for an O_h complex of the same average field." Because $Dq(\text{NH}_3) > Dq(\text{Br}^-)$, predominantly NH_3 aquation should take place, as is observed.

Owing to Adamson's second rule *trans*- $\text{Cr}(\text{NH}_3)_4$ -

$\text{Br}(\text{H}_2\text{O})^{2+}$ should be the primary product of the aquation because the ligand *trans* to Br^- is expected to be subject to photochemical substitution. Similar to the case of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{2+5}$ we did find by means of spectrophotometric measurements that, at least predominantly, the *cis* isomer exists in the irradiated solution. It should be emphasized that *cis* and *trans* isomers can be better distinguished by spectroscopic arguments the more distant the corresponding ligands are located in the spectrochemical series. This we regard as an argument to give more confidence to the isomer assignment in our bromo complex than in the thiocyanato case of Zinato, *et al.*⁹ If this necessitates a modification of Adamson's second rule is a point open for further investigation.

V. Experimental Part

Preparation of Compounds.— $[\text{Cr}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ has been obtained from an aqueous solution of the bromide by precipitation with concentrated HClO_4 . The product was twice recrystallized and washed with ethanol and ether. $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ was prepared from $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3$ by treatment with concentrated HBr .¹³ $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3$ was obtained from chromium alum and concentrated ammonia.¹⁴ *cis*- $[\text{Cr}(\text{NH}_3)_4\text{Br}(\text{H}_2\text{O})]\text{Br}_2$ was prepared by treating $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{NO}_3$ with concentrated HBr .¹⁵ $[\text{Cr}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{NO}_3$ was obtained from $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3$ and oxalic acid.¹⁶ The purity of all compounds was checked by analysis for Cr, NH_3 , and Br.

Solutions.—For the photochemical work (determination of quantum yields) solutions of $[\text{Cr}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$, $c = (1.0-2.0) \times 10^{-2} M$, in $0.001 M \text{HClO}_4$ and $0.454 M \text{NaClO}_4$ ($\mu \approx 0.5$) have been used. In the case of determination of ϕ_{Br^-} at 546 and 405 $m\mu$ $0.05 M \text{HClO}_4$ and $0.405 M \text{NaClO}_4$ ($\mu \approx 0.5$) were used as solvent, and the concentration of the complex was $(1.5-4.0) \times 10^{-2} M$. The thermal aquations of $[\text{Cr}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ and $[\text{Cr}(\text{NH}_3)_4\text{Br}(\text{H}_2\text{O})]\text{Br}_2$ were studied using $0.01 M$ solutions of the complex salts in $0.1 M \text{HClO}_4$ and $0.37 M \text{NaClO}_4$ ($\mu \approx 0.5$).

Spectrophotometric Measurements.—Measurements of optical densities have been done by means of a Cary 14 spectrophotometer using 0.1-, 1-, and 10-cm quartz cells.

pH Measurements.—The H^+ ion concentration was measured with a potentiometer E 353 (Metrohm AG, Herisau, Switzerland), and a micro glass electrode U 9358/81 (Schott, Mainz).

Determination of Br^- .—For determination of Br^- two methods were used.

(a) **Potentiometric Titration.**—Samples of the dark and corresponding irradiated solution (2 ml) were titrated potentiometrically with $0.001 M$ silver nitrate using silver and calomel electrodes connected to a TTT 1b titrator (Radiometer, Copenhagen). During titration the solutions were kept in an ice bath to inhibit thermal reaction.

(b) **Concentration Cell with Ag-AgBr Electrodes.**—Two Ag-AgBr electrodes have been prepared in a similar way as Bates¹⁷ describes for Ag-AgCl electrodes. With these two electrodes a concentration cell was built which consisted of a half-cell with the solution whose Br^- concentration was to be determined and a reference half-cell with a known Br^- concentration, both connected with an agar-potassium nitrate salt bridge. The Br^- concentration of irradiated and dark solutions were found by means of a calibrated graph of $\text{emf vs. log} [\text{Br}^-]$. Emf measurements were made with an electrometer 610B (Keithley Instruments, Munich).

(13) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **266**, 49 (1951).

(14) M. Mori, *J. Inst. Polytechn. Osaka City Univ.*, **3**, 41 (1952).

(15) A. Benrath and H. Steinrath, *Z. Anorg. Allgem. Chem.*, **194**, 351 (1930).

(16) A. Werner and A. Surber, *Ann. Chem.*, **405**, 220 (1914).

(17) R. G. Bates, "Determination of pH," John Wiley and Sons, Inc., New York, N. Y., 1965, p 279.

Determination of Quantum Yields ϕ_{NH_3} and ϕ_{Br^-} .—The quantum yields were determined with an apparatus previously described.¹⁸ The light source was a high-pressure mercury lamp (Osram HBO 200). The light passes a high-intensity grating monochromator (Bausch & Lomb 338602) and filters (to absorb stray light) before it enters the thermostated sample compartment, which contains the holder for three 1-cm quartz cells and the bolometer. The spectral bandpass did in no case exceed 20 $m\mu$. The light intensity which goes through the solution and the pure solvent (the cuvettes can be put alternatively in the light path) is measured by means of the recorded bolometer current. For each measurement a freshly prepared solution of $[\text{Cr}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ was used. Aliquots of the solution (2 or 2.5 ml) were poured into two quartz cells located in the sample compartment together with a third one containing the pure solvent. One of the cells filled with the solution was irradiated; the other one was kept as dark reference.

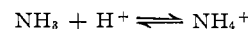
(a) ϕ_{NH_3} .—To determine ϕ_{NH_3} the pH difference ΔpH between irradiated and dark sample was measured. Because of the high ionic strength $\mu \approx 0.5$, it is allowed to assume constant H^+ activity coefficients during irradiation. Therefore

$$\Delta\text{pH} = -\log \frac{c_{\text{H}}}{c_{\text{H}_0}} \quad (6)$$

where c_{H} and c_{H_0} are the concentrations of H^+ after irradiation and in the initial solution (the latter concentration is identical with the concentration of H^+ of the dark solution). One obtains

$$\Delta c_{\text{H}} = c_{\text{H}_0}(1 - 10^{-\Delta\text{pH}}) \quad (7)$$

for the change in H^+ concentration which is identical with the concentration of photochemically produced ammonia, because the equilibrium



is under experimental conditions completely on the side of NH_4^+ . With conversions of up to ca. 6%, H^+ ions released by acid dissociation of the aquated products will not contribute significantly to the measured ΔpH (e.g., for $\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, $\text{p}K_{\text{a}} = 5.2^{19}$).

The experimental quantum yield is given by

$$\phi^{\circ}_{\text{NH}_3} = \frac{\Delta c_{\text{H}} V}{Q_{\text{abs}}} \text{ mol/einstein} \quad (8)$$

if Δc_{H} is measured in moles per liter and Q_{abs} (einstein) is the number of quanta absorbed during irradiation of a volume V (l.) of the solution. $\phi^{\circ}_{\text{NH}_3}$ values obtained according to eq 8 for different wavelengths are seen in Table I, column 5. In column 6 values corrected for the inner light filter effect²⁰ are given. This effect arises from the fact that the product of reaction 2 and also the product of the simultaneous dark reaction 1 both contribute to the absorbance of the irradiated solution. Extinction coefficients and rate constants of thermal aquation necessary for estimation of the inner light filter correction are listed in Tables IV and V.

A typical example for a determination of ϕ_{NH_3} follows. A 2-ml sample of $1.24 \times 10^{-2} M [\text{Cr}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ in $0.001 M \text{HClO}_4$ and $0.454 M \text{NaClO}_4$ was irradiated with light of 585 $m\mu$ for 20 min at 5° . For the absorbed quanta one obtained $Q_{\text{abs}} = 3.42 \times 10^{-8}$ einstein. This value was obtained taking into account a correction for reflected light on the walls of the quartz cells (for details compare ref 5). The pH difference according to the photoaquation (2) was obtained from the following data measured 50 min after preparation of the solution

	pH		
	3.34	3.33	3.33
Irradiated sample	3.34	3.33	3.33
Dark sample	2.94	2.94	2.94
ΔpH	0.40	0.39	0.39

$$\Delta\text{pH} = 0.39$$

(18) H. F. Wastegian and H. L. Schläfer, *Z. Physik. Chem. (Frankfurt)*, **51**, 208 (1966).

(19) See ref 8, p 50.

(20) H. F. Wastegian and H. L. Schläfer, *Ber. Bunsenges. Physik. Chem.*, **71**, 489 (1967).

TABLE IV
MOLAR DECADIC EXTINCTION COEFFICIENTS FOR THE THREE
COMPLEX IONS WHICH HAVE BEEN USED FOR ESTIMATION OF
THE INNER LIGHT FILTER EFFECT

Wave-length, m μ	$\epsilon, M^{-1} \text{ cm}^{-1}$		
	Cr(NH ₃) ₅ Br ²⁺	<i>cis</i> - Cr(NH ₃) ₄ Br(H ₂ O) ²⁺	Cr(NH ₃) ₅ H ₂ O ³⁺
585	8.0	15.2	1.2
546	30.0	35.5	7.5
530	35.5	39.8	14.0
500	31.0	32.5	30.0
470	24.0	20.3	34.0
455	17.5	14.3	28.5
400	27.0	31.5	10.0
380	38.2	36.8	19.0
370	35.0	31.0	26.0
355	22.4	18.4	29.8
300	17.0	34	3.0
250	1740	1780	37

TABLE V
RATE CONSTANTS FOR THERMAL AQUATION

Cr(NH ₃) ₅ Br ²⁺ + H ₂ O $\xrightarrow{k_1}$ Cr(NH ₃) ₅ H ₂ O ³⁺ + Br ⁻			
Temp, °C	$k_1, \text{ min}^{-1}$	Temp, °C	$k_1, \text{ min}^{-1}$
4.0	3.03×10^{-4}	30.0	1.43×10^{-2}
15.0	1.84×10^{-3}		($E_{\text{act}} = 24.7 \text{ kcal/mol}$)
<i>cis</i> -Cr(NH ₃) ₄ (H ₂ O)Br ²⁺ + H ₂ O $\xrightarrow{k_2}$ <i>cis</i> -Cr(NH ₃) ₄ (H ₂ O) ₂ ³⁺ + Br ⁻			
Temp, °C	$k_2, \text{ min}^{-1}$	Temp, °C	$k_2, \text{ min}^{-1}$
8.5	6.50×10^{-4}	20.0	3.63×10^{-3}
16.5	2.03×10^{-3}	25.0	5.48×10^{-3}
			($E_{\text{act}} = 24.7 \text{ kcal/mol}$)

$\Delta p\text{H} = 0.39$ corresponds to $\Delta c_{\text{H}} = 0.593 \times 10^{-3} M$ (eq 7). The experimental quantum yield is then (see eq 8)

$$\phi_{\text{NH}_3}^{\circ} = \frac{(0.593 \times 10^{-3})(2 \times 10^{-3})}{3.42 \times 10^{-6}} = 0.347 \text{ mol/einstein}$$

With the corresponding data of Tables IV and V one obtains the corrected quantum yield $\phi_{\text{NH}_3} = 0.361 \text{ mol/einstein}$.

(b) ϕ_{Br^-} .—To determine ϕ_{Br^-} the Br⁻ concentrations in the irradiated sample (c_{Br^-})_{irr} and in the dark reference (c_{Br^-})_{dark} were measured. The difference between the two values (c_{Br^-})_{irr} - (c_{Br^-})_{dark} = (Δc_{Br^-})_{phot} should give the Br⁻ concentration formed solely by photoaquation (eq 3). Since for Br⁻ determination a certain time is necessary and since reaction 1 is comparatively fast, one has to consider its contribution to Br⁻ concentration during the time needed for the measurements. For determinations in the uv region this contribution is smaller than the precision of the titration, but not so in the visible range (see below).

The scattering of ϕ_{Br^-} values in Table III can be attributed to titration errors, but the average between several determinations is satisfactory. This is proved by measuring the Br⁻ concentration with the more sensitive Ag-AgBr concentration cell. By this method we obtained similar results.

Using Ag-AgBr electrodes one has to take into account that several minutes is required for equilibration with the solution whose Br⁻ concentration is to be determined. Therefore it was necessary to measure Br⁻ concentration as a function of time. After irradiation the irradiated and dark samples were both put in an ice bath. An Ag-AgBr electrode was immersed in the dark sample and measured against a reference Ag-AgBr electrode immersed in a KBr solution of known concentration. This procedure was repeated for the irradiated sample, then again for the dark sample, and so on. The values obtained were plotted *vs.* time. Connecting the different points for the ir-

radiated and dark samples two straight and very nearly parallel lines result. One easily finds (Δc_{Br^-})_{phot} as the vertical distance between these straight lines.

For estimation of the inner light filter effect on ϕ_{Br^-} two cases can be distinguished. (a) In the uv region a light filter correction is not necessary because the amount of photochemical ammonia aquation is always less than 3% (Table III, column 5) and Cr(NH₃)₅H₂O³⁺ produced by photochemical and thermal Br⁻ aquation is always less than 7% of the initial complex and also has a much smaller extinction coefficient than the other ions involved (*cf.* Table IV).

(b) More important on the contrary is the inner-filter effect in the visible range (546 and 405 m μ) because the photochemical aquation (eq 2) reaches values of about 25% (Table II, column 4) whereas the extent of reaction 3 is small (column 6). Therefore we consider only the products of reactions 1 and 2 for estimation of the inner light filter correction. Table II gives the experimental quantum yield $\phi_{\text{Br}^-}^{\circ}$ calculated in the same way as $\phi_{\text{NH}_3}^{\circ}$ (eq 8) (column 7) and the corrected yield ϕ_{Br^-} in column 8. Two typical examples for determinations of ϕ_{Br^-} are given for illustration.

(a) 250 m μ .—A 2.5-ml sample of $1.46 \times 10^{-2} M$ [Cr(NH₃)₅Br](ClO₄)₂ in 0.001 M HClO₄ and 0.454 M NaClO₄ was irradiated for 30 min at 5°. After irradiation 2 ml of the solution was put in an ice bath and titrated with 0.001 M AgNO₃. After 8 min of titrating the irradiated solution, 2 ml of the dark sample was titrated. (Δc_{Br^-})_{phot} = $0.291 \times 10^{-3} \text{ mol/l}$. was obtained. The bolometer gave $Q_{\text{abs}} = 2.74 \times 10^{-6} \text{ einstein}$. Thus one gets

$$\phi_{\text{Br}^-} = \frac{(0.291 \times 10^{-3})(2.5 \times 10^{-3})}{2.74 \times 10^{-6}} = 0.265 \text{ mol/einstein}$$

The increase of Br⁻ concentration due to thermal aquation during titration of irradiated solution is easily seen to be of practically no importance. For the concentration of Br⁻ thus produced one calculates $c_{\text{Br}^-} = a_0 k \Delta t = (1.46 \times 10^{-2})(1.82 \times 10^{-4})(8) = 0.0212 \times 10^{-3} M$ ($k = 1.82 \times 10^{-4} \text{ min}^{-1}$ at 1°, *cf.* Table V). It is obvious that c_{Br^-} is within experimental error of the titration method.

(b) 546 m μ .—A 2-ml sample of $1.52 \times 10^{-2} M$ complex in 0.05 M HClO₄ and 0.405 M NaClO₄ was irradiated 10 min at 3°. After irradiation the light and dark samples both were put in an ice bath. An Ag-AgBr electrode was immersed in the dark solution and after 5 min the emf was measured. From a calibration graph the Br⁻ concentration was obtained. The operation was repeated for the irradiated solution and so on. The data shown in Table VI were obtained.

TABLE VI

Time, min	$10^4 c_{\text{Br}^-}, M$	
	Dark	Irradiated sample
26	1.66	
33		2.57
39	1.90	
45		2.80
51	2.14	
57		3.03

Br⁻ concentration plotted *vs.* time gives two parallel straight lines. The separation between these lines gives (Δc_{Br^-})_{phot} = $0.80 \times 10^{-4} M$. With $Q_{\text{abs}} = 20.7 \times 10^{-6} \text{ einstein}$, one obtains

$$\phi_{\text{Br}^-}^{\circ} = \frac{(0.80 \times 10^{-4})(2 \times 10^{-3})}{20.7 \times 10^{-6}} = 0.0077 \text{ mol/einstein}$$

The inner-filter correction with the corresponding data of Tables IV and V gives the corrected yield: $\phi_{\text{Br}^-} = 0.0088 \text{ mol/einstein}$.

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