TABLE II[a]

RATES OF SOLVOLYSIS OF COMPLEXES IN VARIOUS SOLVENTS

First order rate constants in sec.$^{-1}$

Solvent	*trans*-$[Co(en)_2Cl_2]^+$ (35°)	*trans*-$[Co(en)_2NO_2Cl]^+$ (35°)	*trans*-$[Co(en)_2NO_2Br]^+$ (25°)	$[Pt(py)_2Cl_2]$ (25°)
H_2O	1.2×10^{-4} (1)[b]	2.8×10^{-3} (1)	4.2×10^{-3} (1)	3.5×10^{-5} (1)
Dimethyl sulfoxide	3.7×10^{-5} (0.31)	1.4×10^{-4} (0.04)	8.0×10^{-4} (0.19)	3.8×10^{-4} (11)
DMF	5.8×10^{-6} (0.05)	5.4×10^{-5} (0.02)	6.9×10^{-4} (0.16)	$<1 \times 10^{-5}$ (<0.3)

[a] Sources of data given in the text. [b] Numbers in parentheses are relative solvolysis rates (aquation rate = 1.0).

solvent nucleophilicity. (That, perhaps, being measured by the order of solvolysis rates at Pt(II).) Dissociation rates should respond to the ability of the solvent to solvate the ions produced. The similar behavior of the complexes argues for a *single* mechanism for solvolysis. (Comparison with the Pt(II) data suggests that this common response is not to nucleophilicity.)

Parker[17] has given an excellent discussion of the ability of solvents to solvate anions. The solvolysis rates reported here are in the right *order* to suggest that leaving anion solvation is the major determinant of solvolysis rate, but the differences seem a little small. This last point is clearly made in connection with *m* values. Alkyl halides which undergo SN1 solvolysis yield *m* values about five times as large as the ~0.2 reported here. That is, their reactions are more sensitive to "solvent ionizing power." Yet it does not follow that we should exclude a predominantly SN1 mechanism for the solvolysis of cobalt(III) complexes. The Co–X (X = halide) bond is no doubt more ionic than the C–X bond. Thus, the *increase* in anion solvation in the transition state as compared to the ground state may be much greater in the alkyl halide case, leading to a greater "ionizing power" sensitivity in SN1 solvolysis rates.

Note that adoption of a primarily SN1 process as a description of these reactions would agree with a large body of work on the reactions of *trans*-$[Co(en)_2Cl_2]^+$, but would require revision in ideas about the electronic effect of the nitro group.[18] Actually, there is some evidence that electron-withdrawing groups (otherwise known as π-bonding groups with metal to ligand electron donation) may stabilize five-coordinate species similar to the required SN1 intermediate. For example, Haim and Wilmarth[19] have presented strong evidence for a limiting SN1 mechanism in the water exchange reaction of $[Co(CN)_5OH_2]^{-2}$.

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The Photochemical Aquation of Chromium(III)–Ammonia Complexes

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The photochemical aquation of $Cr(NH_3)_6^{+3}$ was shown to proceed in a stepwise manner, and quantum yields were determined for each step. For light absorption by the non-spin-forbidden ligand field bands, the quantum yields for the substitution of a single NH_3 by H_2O were determined to be: 0.32 for $Cr(NH_3)_6^{+3}$, 0.18 for $Cr(NH_3)_5H_2O^{+3}$, 0.15 for $Cr(NH_3)_4(H_2O)_2^{+3}$, 0.018 for $Cr(NH_3)_3(H_2O)_3^{+3}$, and 2.0×10^{-3} for $Cr(NH_3)_2(H_2O)_4^{+3}$. These quantum yields were independent of which of the two main absorption bands were irradiated and also independent of temperature, concentration, light intensity, and acidity in the range 1 to 0.05 *M*. The final product of long irradiation was not $Cr(H_2O)_6^{+3}$. If perchlorate was the only anion present, the final product had a spectrum consistent with that for $Cr(NH_3)(H_2O)_5^{+3}$. If either sulfate or nitrate was present the product appeared to be polynuclear. The photochemical mechanism seems to involve reaction from an excited spin-forbidden (doublet) state. Strong support for the mechanism was found by irradiating $Cr(NH_3)_6^{+3}$ only at the position of its doublet absorption (6500 Å.) and obtaining quantum yield unity.

Earlier studies[2] have concerned the photochemical substitution of solvent water molecules into $Cr(NH_3)_6^{+3}$, $Cr(NH_3)_5H_2O^{+3}$, and $Cr(H_2O)_6^{+3}$. In those cases quantum yields (molecules reacted/quantum absorbed) were found which were significantly smaller than unity and the explanations offered placed great emphasis on a direct involvement of a spin-forbidden (doublet) electronic state. To further test the ideas postulated and to follow the aquation through the entire series of

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[2] R. A. Plane and J. P. Hunt, *J. Am. Chem. Soc.*, **79**, 3343 (1957); M. R. Edelson and R. A. Plane, *J. Phys. Chem.*, **63**, 327 (1959).

TABLE I

QUANTUM YIELDS FOR THE AQUATION OF CHROMIUM AMMINES

Complex	Concn., $M \times 10^3$	Wave length irrad., mμ	Temp., °C.	Quanta abs., mM/min.	Quantum yield, molecule/quantum
$Cr(NH_3)_5(H_2O)^{+3}$	7.87	320–700	25.0	2.16	0.20
$Cr(NH_3)_5(H_2O)^{+3}$	7.71	320–700	25.0	0.325	0.20
$Cr(NH_3)_5(H_2O)^{+3}$	7.87	320–700	0.0	1.87	0.17
$Cr(NH_3)_5(H_2O)^{+3}$	7.65	320–700	0.0	0.325	0.17
$Cr(NH_3)_5(H_2O)^{+3}$	4.54	340–485	25.6	0.242	0.17
$Cr(NH_3)_5(H_2O)^{+3}$	4.42	430–700	25.6	0.891	0.15
$Cr(NH_3)_4(H_2O)_2{}^{+3}$	2.15	320–700	25.6	1.33	0.16
$Cr(NH_3)_4(H_2O)_2{}^{+3}$	0.79	320–700	1.0	0.555	0.16
$Cr(NH_3)_4(H_2O)_2{}^{+3}$	2.22	320–410	25.6	0.063	0.15
$Cr(NH_3)_4(H_2O)_2{}^{+3}$	2.31	380–700	25.6	0.93	0.12
$Cr(NH_3)_3(H_2O)_3{}^{+3}$	9.3	320–700	25.6	5.6	0.014
$Cr(NH_3)_3(H_2O)_3{}^{+3}$	9.3	320–700	0.0	3.7	0.016
$Cr(NH_3)_3(H_2O)_3{}^{+3}$	9.1	340–485	25.6	1.01	0.015
$Cr(NH_3)_3(H_2O)_3{}^{+3}$	9.2	430–700	25.6	2.4	0.019
$Cr(NH_3)_2(H_2O)_4{}^{+3}$	2.94	320–700	25.6	2.1	1.8×10^{-3}
$Cr(NH_3)_2(H_2O)_4{}^{+3}$	3.12	320–700	0.0	2.5	2.0×10^{-3}
$Cr(NH_3)_2(H_2O)_4{}^{+3}$	2.69	340–485	25.6	0.21	2.4×10^{-3}
$Cr(NH_3)_2(H_2O)_4{}^{+3}$	2.86	430–700	25.6	1.28	1.7×10^{-3}
$Cr(NH_3)_6{}^{+3}$	5.1	650	25.6	2.8×10^{-3}	1.3 ± 0.4

ammonia complexes, the present study was undertaken. It includes the preparation and irradiation of $Cr(NH_3)_5(H_2O)^{+3}$, $Cr(NH_3)_4(H_2O)_2{}^{+3}$, $Cr(NH_3)_3(H_2O)_3{}^{+3}$, and $Cr(NH_3)_2(H_2O)_4{}^{+3}$.

The rate of thermal aquation of $Cr(NH_3)_6{}^{+3}$ has been shown to proceed stepwise through the series of lower ammine complexes, producing eventually a solution of spectrum similar to that of $Cr(H_2O)_6{}^{+3}$, with, however, greater extinction coefficients, believed due to formation of some polynuclear species.[3] Photochemical experiments permit a comparison with the thermal process of both the course of the over-all reaction and the ultimate products. In addition, the present study includes an experiment in which $Cr(NH_3)_6{}^{+3}$ is irradiated at only the wave length of its doublet absorption. Determination of quantum yield for this irradiation should give directly information concerning the importance of that spin-forbidden state in the photochemical reaction.

Experimental

The salts used for the studies were $Cr(NH_3)_6(ClO_4)_3$,[4] $Cr(NH_3)_5(H_2O)(NO_3)_3NH_4NO_3$,[5] $Cr(NH_3)_4(H_2O)_2(NO_3)_3$,[6] $Cr(NH_3)_3(H_2O)_3(ClO_4)_3$,[7] and $Cr(NH_3)_2(H_2O)_4(SO_4)_3$.[8] They were prepared by the methods given in the literature cited, with the methods of the German references modified slightly for modern reagents, but with no attempt to isolate or identify isomers.

The irradiation set-up and actinometer procedure were essentially the same as described previously.[2] For determination of the quantum yields for the tetraammine and the lower ammines, $Cr(NH_3)_6(ClO_4)_3$ in 0.05 M $HClO_5$ was used as the actinometer.[2] It was checked against the uranyl oxalate actinometer and was found to give identical values for the light intensity. The irradiation of a solution of a given salt was performed with the General Electric AH-5 and AH-6, using glass filters to isolate appropriate spectral regions. The solutions were kept acidic using 0.05 M $HClO_4$, and studies were undertaken to see if there was a dependence of quantum yield on the concentration of $HClO_4$ used. For some of the determinations of the nitrates and sulfates, solutions of H_2SO_4 and HNO_3 were used as the solvents. The general procedure involved periodically removing the reaction cell from the light source and removing a portion of the solution so that a spectrum could be measured at selected wave lengths with a Beckman DU spectrophotometer. Such measurements allowed identification of the reaction products and permitted measurement of reaction rates.

In the earlier experiments with $Cr(NH_3)_6{}^{+3}$ the rate was followed by measuring the spectral change at 5040 Å.[2] This wave length was picked because it is the isosbestic point for the penta- and tetraammines. However, for subsequent steps in the process a corresponding wave length was not convenient and instead spectral changes at 4700 Å. were followed in every case. This means, however, that a constant first-order rate was observed only during the first half-life. Subsequently, reaction of the product became appreciable.

The doublet irradiation at 650 mμ was difficult because of the low extinction coefficients of the hexaammine solution and the relatively low output of the A-H6 at that wave length. In addition, great care had to be taken to make sure that the lamp intensity was constant, which was made difficult because the lamp tended to become coated by iron oxide deposited from the lamp cooling water. If the water was below 10°, the oxide coating was minimized. This precaution plus the shielding of the cell to keep the stray light of the room from entering the reaction vessel were the main precautions taken for this experiment. While the others runs took at most 3 hr. to complete, this took 56 hr. in order to give sufficient reaction. In this experiment, as in all others, it was assumed that the spectral energy distribution was that supplied by the manufacturer of the lamp. The filtering system used for this experiment consisted of a Corning 2-59 sharp cut-off red filter paired with the Bausch and Lomb interference filter 42-47-59. The combination removed essentially all radiation of wave length shorter than 6300 Å. The filter plus the spectrum of the ammine ensured that light of wave length longer than 6650 Å. was not absorbed.

Results

All aquations studied followed pseudo-first-order kinetics as is usual in photochemistry. The quantum yields calculated from the first-order rate constant and the initial intensity of the lamp are given in Table I. Judging from the mean deviation, quantum yield

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(3) J. Bjerrum and C. G. Lamm, *Acta Chem. Scand.*, **9**, 216 (1955); E. Jørgensen and J. Bjerrum, *ibid.*, **12**, 1047 (1958).

(4) A. L. Phipps and R. A. Plane, *J. Am. Chem. Soc.*, **79**, 2458 (1957).

(5) T. Moeller, *Inorg. Syn.*, **5**, 132 (1957).

(6) P. Pfeiffer, *Ber.*, **38**, 3959 (1905).

(7) A. Werner, *ibid.*, **43**, 2290 (1910).

(8) A. Werner and J. Klein, *ibid.*, **35**, 283 (1902).

TABLE II

ABSORPTION SPECTRA OF CHROMIUM COMPLEXES

	Spin quartet bands				Doublet	
Complexes	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	λ, mμ	ε
$Cr(NH_3)_6^{+3}$	354	33.7	466	40.7	655	0.38
$Cr(NH_3)_5(H_2O)^{+3}$	360	29.0	484	35.0	655	0.25
$Cr(NH_3)_4(H_2O)_2^{+3}$	368	23.1	494	31.4	657	1.1
$Cr(NH_3)_3(H_2O)_3^{+3}$	378	25.9	508	27.0	657	0.66
$Cr(NH_3)_2(H_2O)_4^{+3}$	384	24.3	525	21.4	660	1.5
$Cr(H_2O)_6^{+3}$	408	15.6	574	13.4	669	...

values are probably reliable to ±10%. However, the last experiment quoted, for reasons given in the Experimental section, is subject to the somewhat larger uncertainty noted. The quantum yield for the pentaammine is lower than that reported earlier[2] because the earlier value was based on extinction coefficients of the tetraammine taken from the literature. The present values are based on directly determined extinction coefficients.

From the values given in Table I, it is seen that the quantum yield does not depend for any complex upon whether irradiation is made at the shorter wave length main absorption band (below 400 mμ) or at the longer wave length one (above 460 mμ). The only dependence on wave length is shown by the last experiment in the table, where irradiation at 650 mμ, the wave length of a forbidden doublet band, produces a quantum yield of unity, or about three times the quantum yield found previously for irradiation of the spin-allowed ligand field bands (360 and 460 mμ).[2] Further, the values show that the quantum yields in every case are independent of both temperature and light intensity.

For the experiments noted in Table I, 0.05 *M* $HClO_4$ was present in all solutions. However, it was found that addition of 1.0 *M* $HClO_4$ did not change the quantum yields. Also, the quantum yields were not changed if 0.05 *M* HNO_3 or H_2SO_4 was substituted. However, the final product of the reaction did depend upon the anion present. In no case was the product $Cr(H_2O)_6^{+3}$. If perchlorate was the anion, the spectrum of the final solution had principal peaks at 400 mμ (ε 17.3) and at 552 mμ (ε 18.0) and the spin-forbidden peak at 660 mμ (ε 2.0). Comparison with the spectral data of Table II and the data of Jørgensen and Bjerrum[3] shows that the spectrum of this solution is just that expected for $Cr(NH_3)(H_2O)_5^{+3}$. Attempts to crystallize a product from the dilute solutions after irradiation were unsuccessful. If anions other than perchlorate were present during irradiation, the end product had a different spectrum. For solutions with either sulfate or nitrate, the spectra were identical, with peaks at 418 mμ (ε 14.6) and 580 mμ (ε 16.9). The positions of these peaks resemble those of polynuclear Cr(III) species.[9] Although it could not be shown that anions were not present in the species, the lack of dependence of the spectrum on which of the two anions was present and the correspondence with the spectrum of polynuclear species suggest that hydrolytic polymerization had occurred.

Discussion

The photochemical aquation of $Cr(NH_3)_3^{+3}$ and the lower ammines occurs in a stepwise manner. This stepwise course is ensured by the fact that the quantum yields for the members of the series progressively decrease as water molecules replace ammonia, unlike the thermal reaction, for which successive steps do not become slower. Near the end of the series, the quantum yields become so small that the final step does not occur photochemically. The progressive decrease of quantum yield can be understood in terms of the mechanism previously proposed involving the spin doublet electronic state.

Excitation to either of the spin-allowed ligand field states is followed promptly either by internal conversion to the ground state too rapidly for reaction to occur or, for a fraction of the molecules, by conversion to the low-lying doublet state of longer lifetime. From this longer-lived state, reaction can take place. The spectra quoted in Table II show that substitution of H_2O for NH_3 in the complex narrows the gap between the lower spin-allowed state and the spin-forbidden one. As the spacing narrows, the trapping of an excited molecule in the doublet state for a time sufficient to react prior to its return to the ground state becomes less probable.

Direct evidence for the proposed mechanism is provided by the experiment reported here for irradiation of $Cr(NH_3)_6^{+3}$ at 650 mμ, the position of its low-lying spin-forbidden state. It was found previously that irradiation of either of the spin-allowed bands produced a quantum yield of 0.32.[2] The present result shows that direct excitation to the spin-forbidden state gives a quantum yield of unity. Comparison of the two results indicates that if excitation occurs to a spin-allowed state, only a fraction of the molecules excited are trapped in the spin doublet state before conversion to the ground level.

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(9) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).