Table IV. Summary of Kinetic Data for Reactions of Disubstituted Tetraaquochromium(III) Ions with Chromium(II) at 25 °C and $\mu = 1.0$ M

Entry no.	Oxidant	k, $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
1	*cis*-CrF_2^+	$5.0 \times 10^{-3\ g}$	13	−24	*a*
2	*trans*-CrF_2^+	$7.5 \times 10^{-4\ g}$			*a*
3	$Cr(NCS)_2^+$	$\leq 4.5 \times 10^{-4\ g}$			*b*
4	$Cr(NCS)F^+$	5.4×10^{-2}	14.6	−15	*c*
5	CrF^{2+}	2.6×10^{-2}	13.7	−20	*d*
6	$Cr(NCS)^{2+}$	1.2×10^{-4}			*d*
7	*cis*-$CrCl_2^+$	$1.4 \times 10^{2\ g}$	5.7	−28	*e*
8	*trans*-$CrCl_2^+$	$2.0 \times 10^{2\ g}$	4.9	−30	*e*
9	*cis*-$Cr(N_3)_2^+$	$3.8^{g,h}$	8.1	−27	*f*

[a] References 3 and 4. [b] Calculated from data in footnote 18 of ref 36. [c] This work. [d] Reference 36. [e] J. H. Espenson and S. G. Slocum, *Inorg. Chem.*, **6**, 906 (1967). [f] A. Haim, *J. Am. Chem. Soc.*, 88, 2324 (1966). [g] Corrected for symmetry number factor. [h] Singly bridged pathway.

CrF_2^+ species. All have comparable activation parameters as anticipated for such similar systems. In view of the absence of any trend in rate constants among these species no firm conclusion can be reached concerning the reasonableness of k_2 for $Cr(NCS)F^+$. A comparison of the two constants for entries 5 and 6 indicates clearly that fluoride ion is superior to thiocyanate ion as a bridging group by a factor of ~10^2, a fact consistent with the observed stoichiometry.

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Registry No. $Cr(H_2O)_4(NCS)F^+$, 59110-00-8; Cr^{2+}, 22541-79-3; $[Co(NH_3)_5F](ClO_4)_2$, 36126-23-5; $[Co(NH_3)_5H_2O](ClO_4)_3$, 13820-81-0.

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Photochemistry of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$

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The photochemistry of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$ has been studied in aqueous solution at irradiation wavelengths corresponding to excitation into the ^4E_a (546 nm), $^4B_2$ (436 nm), and $^4A_2$–^4E_b (366 nm) states of the molecule. For irradiation into the lowest energy ^4E state, the photosolvation mode is highly specific, corresponding to loss of ammonia ($\phi = 0.33$) more or less exclusively (100 ± 3%) to yield *cis*-$[Cr(en)_2H_2OCl]^{2+}$ (only 1 ± 2% trans product is found). For irradiation into the higher energy transitions the photochemistry becomes less specific, the quantum yield of ammonia falling somewhat to a constant value ($\phi = 0.30$), while ethylenediamine progressively increases with excitation energy (0.06 at 436 nm, 0.10 at 366 nm). Small temperature dependences of yields were observed. The results are discussed in the framework of existing models of chromium(III) photochemistry.

Introduction

The photochemistry of Cr(III) complexes has been the subject of a number of recent reviews[1-5] which, taken together, draw attention to a number of outstanding questions. Of particular interest to the authors are whether the existing models[6-10] are adequate to predict the reaction modes of chromium(III) complexes, the nature of the excited state(s) from which reaction may occur, and the mechanism of reaction including the nature of the stereochemistry.

In regard to the first two questions, Adamson[6] originally proposed a model in which the strong-field ligand on the weak-field axis would be preferentially labilized, with a loss of discrimination for irradiation at higher energies. Pyke and Linck[7] suggested that this should be modified to reflect that the axis of labilization is more a function of σ-bonding strength than overall ligand field strength. Wrighton[8] et al. and

Zink[9,10] drew attention to the possible role of π bonding in the stabilization or destabilization of a ligand, and Zink[9,10] used MO theory to predict σ- and π-labilization effects for all possible doublet and quartet states, later extending the theory to calculations of the d_{z^2} and $d_{x^2-y^2}$ populations in excited-state wave functions at ground-state geometry.[11]

Much of the data in the literature are consistent with all of the models. Discriminating studies of the trans isomers of $[Cr(en)_2F_2]^+$,[7] $[Cr(en)_2FCl]^+$,[12] $[Cr(en)_2(NCS)_2]$,[13] and $[Cr(en)_2NH_3NCS]^{2+}$ [14] have supported the idea that labilization of the weakest σ-bonding axis is not necessarily exclusive and have thus been more consistent with the general ideas of the molecular orbital theory.

One of the purposes of this study of $[Cr(en)_2NH_3Cl]^{2+}$ was to examine the wavelength dependence of ammonia and ethylenediamine aquation thus yielding information on the degree of axial and in-plane labilization and to examine whether population of the lowest quartet state led to pure axial labilization or a mixed reaction mode. This experiment also arose partly out of an earlier proposal[15] to settle the ambiguity in acidopentaammine photolysis as to the original position of the labilized ammonia by study of a compound such as $[Cr(NH_3)_4{}^{15}NH_3X]^{2+}$. Unfortunately the recent study[16] of $[Cr(NH_3)_4{}^{15}NH_3Cl]^{2+}$ led to ambiguous results due to uncertainty as to the isomeric purity of the starting material.

The second objective of the work was to obtain additional and more precise evidence on the stereochemical nature of axial labilization (this term is used in the sense that reaction is presumed to arise from an excited state in which the σ-antibonding electron resides predominantly in the d_{z^2} orbital). Although the major photoproduct(s) for a large number of Cr(III) complexes of D_{4h} or C_{4v} symmetry has (have) been found to be predominantly (or perhaps exclusively) cis in configuration,[2,17,18] it has been suggested[12] that most of these determinations, based on small absorbance changes, could be in error by up to 10%. Determinations of greater precision require, as a first step, separation of the photolysis products. We report here good chromatographic separations of the possible product isomers resulting from ammonia aquation from *trans*-$[Cr(en)_2NH_3Cl]^{2+}$ and relatively precise ratios of these isomers for the photolyzed samples.

Experimental Section

Materials. Crude *trans*-$[Cr(en)_2NH_3Cl](ClO_4)_2$, containing some bromide as counterion, was prepared.[19] To minimize the residual bromide the product was recrystallized five times, each time by dissolving in a minimum of HCl-acidified water, adding 4 volumes of methanol and 1 volume of 60% perchloric acid, followed by cooling in ice. After the final recrystallization, the filtered crystals were washed with methanol and dried in vacuo. Anal. Calcd for $[Cr(en)_2NH_3Cl](ClO_4)_2$: Cr, 12.28; C, 11.34; N, 16.53; H, 4.52. Found: Cr, 12.5; C, 11.6; N, 16.6; H, 4.6.

Baker Analyzed CGC-241 cation-exchange resin (200–400 mesh), cleaned by warming in a solution of sodium hydroxide and hydrogen peroxide followed by reacidification with HCl and washing with water, was used for the ion-exchange analysis. Ammonia was not used for cleaning since the resin was to be employed in the NH_4^+ analyses.

All other materials used were reagent grade.

Photolysis Apparatus and Procedure. A PEK air-cooled 203-1004 200-W high-pressure Hg lamp with a Bausch and Lomb grating monochromator (set for 20-nm spectral bandwidth) yielded light at 366, 436, and 546 nm, with effective line half-widths of about 6, 7, and 9 nm, respectively. In each case appropriate blocking filters (Corning) were used to remove higher energy scattered light. Light fluxes were measured either by ferrioxalate[20] (366 nm) or by reineckate[21] actinometry. In addition, a constant fraction of the light beam was continuously monitored by a phototube during photolysis runs so that intensity fluctuations or drifts were easily observed and corrected.

Samples were photolyzed in thermostated 1-cm path rectangular glass spectrophotometer cells, with continuous magnetic stirring. For runs involving changes in the hydrogen ion concentration of the solution, the pH was monitored continuously using a Metrohm EA 147 microcombination electrode and Metrohm E 388 potentiometric pH meter.

Chromatography. Ion-exchange chromatograms of chromium(III) complexes were obtained using 12–15-cm columns of cation-exchange resin at 1–2 °C with a Technicon Auto-Analyzer. Best separations were obtained by eluting with a 0.4–1.0 M gradient of ammonium sulfate solution pumped at 150 ml/h (0.15 M/h). A fraction of the eluent was mixed with constant proportions of 1.0 M NaOH and 0.5% H_2O_2 and heated at 95 °C for 20 min to oxidize any Cr(III) species to chromate, and the chromate absorption at 370 nm was continuously monitored and recorded. The remaining fraction of eluent could be collected for spectral or analytical examination.

Run Procedures and Ammonia Analysis. A 1.0×10^{-2} M solution of complex was prepared at an ionic strength of 0.04 ($KClO_4$) and pH 2.8–2.9 ($HClO_4$) with the stock solution precooled to the run temperature. When hydrogen ion concentration was to be followed, a 3-ml sample was pipetted into the photolysis cell and a pH electrode, preequilibrated in a solution of about the same pH and temperature as the sample, was inserted. Thermal equilibration in the dark was followed until pH readings showed a slow steady upward drift due to thermal reaction. The sample was then photolyzed, with monitoring of the pH, to give 3–6% photoreaction. After photolysis, pH monitoring was continued until a steady upward drift was again observed. The initial pH could be determined by extrapolation to time zero. The change in $[H^+]$ due to photolysis was determined by the ΔpH method.[22] Thermal corrections were relatively small and simply determined since photolysis times were very short (100–200 s); equilibrations before and after photolysis were typically 500 and 200 s, respectively.

When liberated ammonia (as NH_4^+) was to be determined, identical 3-ml solutions of starting complex were equilibrated (5 min) and one was irradiated to give 4–7% photolysis while the other was kept in the dark at the photolysis temperature. Each sample was then adsorbed onto a 2-cm ion-exchange column (Na^+ form) cooled to 1–2 °C. To collect any free ammonium ion, the columns were each eluted with acidified 0.7 M NaCl to yield three 10-ml portions.

The collected eluents were then coulometrically titrated as described earlier.[14] The third portions of both the photolyzed and dark samples were always found to give identical titers within uncertainty. The quantity of photoreleased ammonia was calculated from the difference between the titers of the first two 10-ml portions of eluent from the photolyzed and dark samples.

Investigations of Secondary Photolysis. To study the nature and influence of secondary photolysis a few ion-exchange separations were carried out on samples irradiated at 546 nm to give about 8 or 25% photolysis and their duplicate dark samples. Solutions were made up as for the quantum yield runs, but at higher hydrogen ion concentrations, either 2×10^{-3} M (8% photolysis) or 5×10^{-3} M. After irradiation, ion-exchange separation was performed, and when desired, 15-ml samples of the eluent were taken at predetermined elution times (these are reproducible to within about 200 s) and their uv–visible spectra taken (Cary 17 spectrophotometer, 50-mm cells and 0–0.2*A* scale). Quantitative estimates were obtained from the integrated areas of the peaks on chromatograms (representing absorbance of chromate).

Results

Thermal Aquation. Because the thermal reactions of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$ have not been studied, an investigation was a necessary preliminary of this work, with special emphasis on whether the thermal reactions would complicate the photochemical study.

trans-$[Cr(en)_2NH_3Cl]^{2+}$ was found to aquate thermally with proton uptake and release of chloride ion. The rate constant for the first-order (to 10%) proton uptake (corresponding to liberation of ammonia and/or amine groups of ethylenediamine), in the pH range 3.1–3.8 and at ionic strength 0.04 ($KClO_4$), was measured by the same techniques as for the photolysis runs and was found to be 1.2×10^{-5} s^{-1} at 20 °C and 3.8×10^{-5} s^{-1} at 30 °C. At 20 °C, about 25% of the proton uptake was found to correspond to release of ammonia. The first-order rate constant for chloride loss was extremely difficult to measure potentiometrically since the sample was contaminated with traces of free bromide even after elution

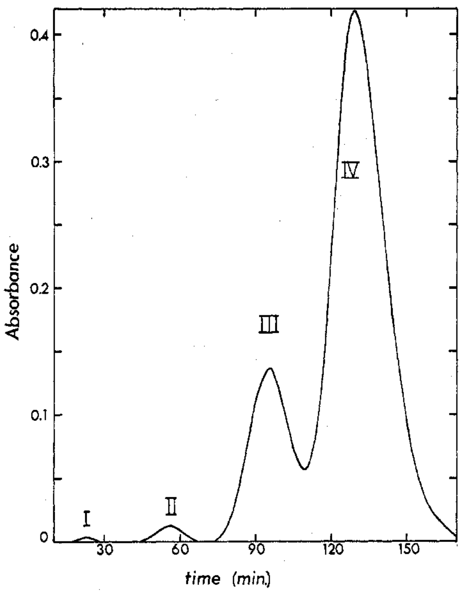

Figure 1. Ion-exchange chromatogram of a sample of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$ photolyzed to about 25% conversion. As discussed in text, band I is a secondary product, band II corresponds to *trans*-$[Cr(en)_2H_2OCl]^{2+}$, band III to *cis*-$[Cr(en)_2H_2OCl]^{2+}$, and band IV to *trans*-$[Cr(en)_2NH_3Cl]^{2+}$.

from a 4-cm column of Rexyn 203 weak-base anion-exchange resin (ClO_4^- form). The effect of bromide was to allow establishment only of an upper limit for the rate constant for chloride release; we found this to be 2.0×10^{-6} s^{-1} at 20 °C, consistent with, but lower than, the value for $[Cr(NH_3)_5Cl]^{2+}$ of 4.5×10^{-6} s^{-1} under similar conditions.[23]

The possible thermal (and photochemical) reaction modes for the complex are

$$trans\text{-}[Cr(en)_2NH_3Cl]^{2+} \xrightarrow{H^+} [Cr(en)(enH)NH_3H_2OCl]^{3+}\ (P) \qquad (1a)$$

$$P \xrightarrow{H^+} [Cr(en)NH_3(H_2O)_2Cl]^{2+} + enH_2^{\ 2+} \qquad (1b)$$

$$trans\text{-}[Cr(en)_2NH_3Cl]^{2+} \xrightarrow{H^+} [Cr(en)_2H_2OCl]^{2+} + NH_4^+ \qquad (2)$$

$$trans\text{-}[Cr(en)_2NH_3Cl]^{2+} \rightarrow [Cr(en)_2NH_3H_2O]^{3+} + Cl^- \qquad (3)$$

That reaction 1 involves a two-step process with a monodentate protonated ethylenediamine-containing intermediate is suggested by experience with other Cr(III) complexes.

Of the four products, those from reactions 1a and 3 are tripositive ions and would not elute from the column under our conditions. Comparisons of ion-exchange chromatograms of thermally aquated *trans*-$[Cr(en)_2NH_3Cl]^{2+}$ and of solutions containing added *cis*- and *trans*-$[Cr(en)_2H_2OCl]^{2+}$ showed that the three dipositive ions were well resolved (see, for example, Figure 1) and that the product of the thermal reaction 2 had the trans configuration; no cis product was observed. In addition, no band corresponding to $[Cr(en)NH_3(H_2O)_2Cl]^{2+}$, which would be expected to elute before these other complexes, was observed. This suggests that reaction 1b did not occur to any large extent in the time of these experiments. Consequently we conclude that the approximate values of the rate constants at 20 °C for the above reactions are $k_{1a} = 9 \times 10^{-6}$ s^{-1}, $k_2 = 3 \times 10^{-6}$ s^{-1}, and $k_3 \leq 2 \times 10^{-6}$ s^{-1}.

These rate measurements show the thermal reactions are sufficiently slow that, under the conditions chosen for the photochemical work, the thermal corrections are generally small and can easily be applied.

Photochemistry of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$. Photolysis of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$ in acidic solution was observed to give rise to an increase in pH of the solution, according to expectation. Preliminary determinations of the quantum yield for proton uptake at 546 nm showed it to be about 0.3 (similar to the value for $[Cr(NH_3)_5Cl]^{2+}$)[22] and to be approximately equal to the yield of free ammonia. Similar determinations at shorter wavelength of irradiation showed that the ratio of ammonia to proton uptake was less than 1, implying a more complex product mixture. The presence of traces of bromide in the sample again precluded the possibility of precise measurement of chloride yields, but by analogy to $[Cr(NH_3)_5Cl]^{2+}$ [22] these are expected to be small at these wavelengths and our measurements did not contradict that expectation.

Table I. Secondary Photolysis of *cis*-$[Cr(en)_2H_2OCl]^{2+}$ Product[a]

				Amt of *cis*-$[Cr(en)_2H_2OCl]^{2+}$, μmol			
Trial	T_1, °C	$10^8 F_0$	t, s	Found[b]	Expected[c]	f[d]	T
1	1	7.3	330	2.16	2.49	0.917	
2	5	7.3	300	2.16	2.26	0.925	
3	15	7.3	1000	5.83	7.26	0.758	1.58
4	5	8.5	1000	5.85	7.60	0.747	1.41
5	5	8.5	1200	6.79	8.79	0.707	1.75

[a] f and T as defined in text; T_1, temperature of photolysis; F_0, incident flux (einstein s^{-1}) on cell containing 3 ml of solution; t, photolysis time. [b] By integration of area under deconvoluted chromatographic bands. [c] Calculated from eq 8 with $\phi_A = 0.30$ (1 and 5 °C) and 0.33 (15 °C). [d] Based on values from column 6; final values resulting from iteration are lower.

These results showed that, of the expected photolysis modes, reaction 2 is predominant at 546 nm, (1a) and (2) are found at the other wavelengths chosen for study, and (3) is always small.

We therefore chose 546 nm as the most uncomplicated wavelength of irradiation to use for studies of the nature and stereochemistry of the reaction products of reaction 2. When irradiations of solutions of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$ at 546 nm were carried out to the 20–25% conversions necessary to yield adequate product for ion-exchange analysis, three products were resolvable from the mixture, Figure 1.

Bands III and IV were *cis*-$[Cr(en)_2H_2OCl]^{2+}$ and *trans*-$[Cr(en)_2NH_3Cl]^{2+}$, respectively, identified both by their elution times and from the uv–visible spectra of collected fractions. The identities of bands I and II were not determinable by spectral means because of the low concentration of the species in the eluent. The elution time of band II was the same, however, as that corresponding to the previously observed product of thermally aquated *trans*-$[Cr(en)_2NH_3Cl]^{2+}$ and also to that of an authentic sample of *trans*-$[Cr(en)_2H_2OCl]^{2+}$ and can therefore be identified (at least in part) as the latter. Band I could be ascribed to a secondary product, photolytic and/or thermal, as it was not observed in solutions photolyzed to lower conversions. Its elution characteristics suggested that it was either a unipositive ion or an easily eluted dipositive ion; the latter is overwhelmingly more probable since no unipositive ion can be formed by solvolysis and photoanation is a rare occurrence. Experience with the chromatography of Cr(III) dipositive ions suggests a polyaquo complex, likely candidates being $[Cr(en)NH_3(H_2O)_2Cl]^{2+}$ and $[Cr(en)(H_2O)_3Cl]^{2+}$.

These observations of secondary photoproducts are not surprising in view of the high conversion used and the greater molar absorptivity of the main photoproduct at 546 nm. Additional evidence is obtained by comparison, Table I, of the quantity of *cis*-$[Cr(en)_2H_2OCl]^{2+}$ found vs. the moles expected from the measured quantum yield for proton uptake. At low

Table II. *trans*- and *cis*-$[Cr(en)_2H_2OCl]^{2+}$ from Photolyzed and Dark Solutions of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$

Trial[a]	T_1, °C	Amt, μmol			Uncor % trans[c]	Amt, μmol		Cor % trans[f]
		I[b]	II[b]	III[b]		III cor[d]	Secondary products[e]	
1, photo	1		0.075	2.16	(1.9)			(1.8)
2, photo	5		0.089	2.16	0.8	2.3	0.14	0.7
dark	5		0.073					
3, photo	15	0.066	0.362	5.83	3.4	8.0	2.2	2.5
dark	15		0.155					
4, photo	5	0.075	0.366	5.85	3.6	8.0	2.3	2.6
dark	5		0.153					
5, photo	5	0.075	0.411	6.79	3.7	10.0	3.2	2.8

[a] The photolytic runs of this table correspond to trials 1-5 of Table I, where the photolysis times etc. are recorded. [b] I, II, and III refer to the chromatographic bands of Figure 1. II corresponds to *trans*-, and III to *cis*-$[Cr(en)_2H_2OCl]^{2+}$. [c] Calculated as μmol of II(photolytic) × 100/(μmol of II(photolytic) + μmol of III). For trial I the dark reaction of trial II, together with an assumed activation energy of 25 kcal mol^{-1}, was used to apply an approximate thermal correction; the result is thus more uncertain. For trial 5 thermal correction was by dark run 4, prorated for the longer photolysis time. [d] Corrected for secondary photolysis using the T values from Table I with eq 8. [e] Micromolar amounts of other unidentified secondary products implied by comparison of columns 5 and 7. [f] Corrected for loss of cis product by secondary photolysis.

conversions (trials 1 and 2) experimentally determined and calculated quantities were in reasonably close agreement, but at higher conversions the experimental values were significantly lower, suggesting losses of *cis*-$[Cr(en)_2H_2OCl]^{2+}$.

The presence of secondary photolysis for irradiation at 546 nm also caused complications in the evaluation of the chromatographic data obtained to examine the cis:trans ratio of $[Cr(en)_2H_2OCl]^{2+}$ from reaction 2, Table II. At low conversions no great secondary photolysis occurs (trials 1 and 2) as evidenced by the absence of band I, Figure 1 and Table II, but the amount of trans product (band II) found is only a small fraction (22%) of that arising from thermal decomposition. Consequently, though less than 1% of photolytic trans product is found, the result is rendered less certain by the need for the large thermal correction. In contrast, photolysis to ≥20% conversion, while enabling better determination of the trans product, gives rise to loss of cis product by secondary photolysis. Table II shows that under these conditions a greater percentage of trans product appears, but this could be an artifact because of both loss of cis product and also possible coincidental elution of a minor secondary product with the small trans peak.

The evaluation of the data of Tables I and II and the proper correction of the quantum yield data discussed later can be carried out using the theory developed by Wirth and Linck.[12] They showed that, for the scheme

$$A \xrightarrow{\phi_A} B \xrightarrow{\phi_B} C \tag{4}$$

$$\frac{-d[A]}{dt} = \phi_A I_0 \frac{\epsilon_A[A]}{\Sigma\epsilon_i[i]}(1 - 10^{-\Sigma\epsilon_i[i]}) \tag{5}$$

$$\frac{d[B]}{dt} = -\phi_B I_0 \frac{\epsilon_B[B]}{\Sigma\epsilon_i[i]}(1 - 10^{-\Sigma\epsilon_i[i]}) - \frac{d[A]}{dt} \tag{6}$$

Hence, dividing (6) by (5), we have

$$\frac{d[B]}{d[A]} = T\frac{[B]}{[A]} - 1 \tag{7}$$

where $T = \epsilon_B\phi_B/\epsilon_A\phi_A$. Solution of this equation to give $[B]_t/[A]_t$ and application of the material balance condition yield the expression given by Wirth and Linck

$$\frac{[C]_t}{[B]_t} = \frac{T - 1 + f^T - Tf}{f - f^T} \tag{8}$$

In these expressions $f = [A]_t/[A]_0$ is the fraction of A photolyzed at time t, ϵ_A and ϵ_B and ϕ_A and ϕ_B are respectively the molar absorptivities and quantum yields for A and B at the irradiation wavelength. I_0 is the incident light intensity. The derivation has been reproduced here to draw attention to the fact that eq 7 does not depend on the solution absorbance, $\sum\epsilon_i[i]$. Thus the final result, in contrast to an implication of the original derivation,[12] is valid for any value of the absorbance and is not influenced should it be time dependent. Therefore, eq 8 is always valid if (4) is a valid description of the system and if it is assumed that the Lambert–Beer law applies, which experience shows to be the case.

Equation 8 can be used in an iterative procedure to find values of T and f that fit an observed $[C]_t/[B]_t$ ratio (Table I) or to correct the Table II values of *cis*-$[Cr(en)_2H_2OCl]^{2+}$ for losses due to secondary photolysis.

For the data of Table I this was done in the following way. Knowing the quantum yield, ϕ_A, for proton uptake (0.30 at 5 °C, 0.33 at 15 °C, 546 nm, obtained from corrected data for low conversion where secondary photolysis and inner filter corrections are small), the expected moles of *cis*-$[Cr(en)_2H_2OCl]^{2+}$ were calculated (Table I, column 6). This yields a value of f and, calculated as (cis expected − cis found)/cis found, a value of $[C]_t/[B]_t$. These values were then used to find the value of T that best satisfies eq 8. Because of the low conversions trials 1 and 2 were too imprecise to yield consistent values, but 3, 4, and 5 yielded the values of T shown in the final column of Table I. Taking T = 1.58 at 15 °C and 1.61 at 5 °C, together with ϵ_A 19.5 and ϵ_B 50.5 M^{-1} cm^{-1} and the above values of ϕ_A, one can calculate ϕ_B = 0.20 and 0.19 at 15 and 5 °C, respectively, with a probable uncertainty of about ±10% due to uncertainty in $[C]_t/[B]_t$ and the indirect nature of the method. The values obtained are in pleasing accord with our expectations based on known quantum yields for analogous *cis*-bis(ethylenediamine) complexes.[17,18,24,25]

Correction of the data of Table II for secondary photolysis could now be accomplished using the above T values and iterating to find a value of f that, together with the calculated value of $[B]_t$, satisfied eq 8 and the stoichiometric condition $[A]_0 = [A]_t + [B]_t + [C]_t$. The resultant f value yielded a corrected value for *cis*-$[Cr(en)_2H_2OCl]^{2+}$ and hence of the percent trans product. In this procedure it was again assumed that no secondary photolysis of *trans*-$[Cr(en)_2H_2OCl]^{2+}$ occurred. The corrected values for the percentage trans product, Table II, still show an increase with percentage conversion, which we suspect is due to a secondary photolysis product eluting coincidentally with the trans. The calculated amounts of secondary products are tenfold larger than that of the trans product. Thus a minor process such as photoisomerization of *cis*-$[Cr(en)_2H_2OCl]^{2+}$ or production of isomers of $[Cr(en)(H_2O)_3Cl]^{2+}$ by photolysis and subsequent thermal loss of ethylenediamine could easily contribute in this way. Unfortunately the quantities of material eluted are too

Table III. Quantum Yields for *trans*-$[Cr(en)_2NH_3Cl]^{2+}$

Wave-length, nm	T, °C	ϕ_{H^+}[a]	ϕ_{NH_3}[b]	ϕ_{en}[c]
366	5	0.348 ± 0.003 (2)	0.275 ± 0.003 (2)	0.07 ± 0.01
	15	0.391 ± 0.001 (2)	0.297 ± 0.007 (2)	0.10 ± 0.01
436	5	0.342 ± 0.002 (2)	0.302 ± 0.006 (2)	0.04 ± 0.01
	15	0.365 ± 0.004 (4)	0.303 ± 0.014 (2)	0.06 ± 0.02
546	5	0.285 ± 0.004 (2)	0.304 ± 0.006 (2)	<0 ± 0.01
	15	0.323 ± 0.007 (6)	0.335 ± 0.012 (4)	<0 ± 0.01

[a] Quantum yield for H^+ uptake. Numbers in parentheses indicate the number of experiments. [b] Quantum yield for photoaquation resulting in loss of NH_3. [c] Quantum yield for solvation of ethylenediamine to give a monodentate enH^+ species.

small for direct investigation of their composition.

In consequence we consider the percentage of trans product found for the higher conversion runs to be high upper limits, and since the lower conversion runs suggest that less than 1% may be the best value, we conclude that the percent trans is 1 ± 2%.

With this background, quantum yields for release of ammonia and proton uptake were obtained for irradiation wavelengths of 546, 436, and 366 nm, Table III. The calculation of precise quantum yields requires consideration of the following effects. Since the molar absorptivity of the starting complex is relatively low, ϵ_{546} 19.5, ϵ_{436} 21.0, and ϵ_{366} 40.8 M^{-1} cm^{-1}, the solution absorbs only a fraction of the incident light, the absorbance changes with the extent of photolysis, and inner filtering occurs, particularly at 546 nm (*cis*-$[Cr(en)_2H_2OCl]^{2+}$ has ϵ_{546} 50.5, ϵ_{436} 21.1, and ϵ_{366} 40.8 M^{-1} cm^{-1}). These effects cause errors in both ϕ_{H^+} and ϕ_{NH_3} if not allowed for, as do thermal corrections. The simplest method of correction[22] assumes that photolysis is linear in time (valid up to about 10% decomposition) and assumes that photolysis occurs instantaneously at the halfway point in time. Then $\phi_i = Q_i/f_{i,mean}I_0t$ where Q_i is the number of moles per liter of i reacted, $f_{i,mean}$ is the mean fraction of the light beam absorbed by component i, I_0 is the incident intensity (einstein l^{-1} s^{-1}), and t is the photolysis time.

More rigorously, and particularly useful for higher conversions, one can integrate the rate law for photolysis of A (eq 5). For runs at 366 and 436 nm A (*trans*-$[Cr(en)_2NH_3Cl]^{2+}$) and B (mainly *cis*-$[Cr(en)_2H_2OCl]^{2+}$) have the same molar absorptivity so that, ignoring second-order errors due to neglect of primary products other than B and absorptivity differences between primary and secondary products (i.e., we assume $\epsilon_B = \epsilon_{cis\text{-}[Cr(en)_2H_2OCl]^{2+}}$ and $\epsilon_B = \epsilon_C$), $\sum\epsilon_i[i]$ is constant. Equation 5 then integrates to

$$\ln(1/f) = \frac{\phi_A I_0 \epsilon_A t}{\Sigma\epsilon_i[i]}(1 - 10^{-\Sigma\epsilon_i[i]}) \tag{9}$$

For runs at 546 nm calculation of the quantity $[A](1 - 10^{-\Sigma\epsilon_i[i]})/\sum\epsilon_i[i]$ shows that, although not constant, it is close to a linear function of f (within 2%) up to $f = 0.75$ for our conditions, i.e.

$$\frac{-d[A]}{dt} = \phi_A I_0 \epsilon_A (mf - c) \tag{10}$$

which integrates to

$$\ln\left(\frac{m - c}{mf - c}\right) = \phi_A I_0 \epsilon_A t \tag{11}$$

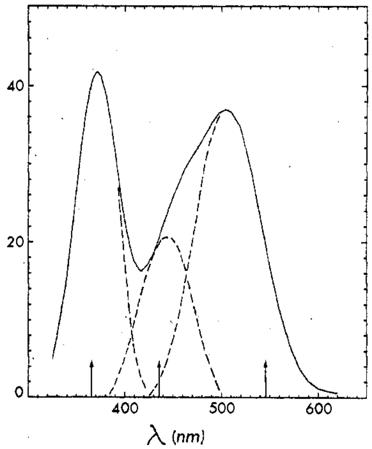

Figure 2. Visible absorption spectrum of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$ with approximate deconvolution to show the splitting of the ^4E and $^4B_2$ bands. The arrows indicate the wavelengths used for excitation.

Equations 9 and 11 were used to evaluate ϕ_{NH_3} and ϕ_{H^+} corrected for transmission and inner filter effects. It is notable that at the 3–8% conversion level the results of the simpler method were the same to three figures at 366 and 436 nm, while at 546 nm they were approximately 1% lower.

Corrections for secondary photolysis effects were then applied using eq 8. For 546 nm the experimental T values of 1.61 (5 °C) and 1.58 (15 °C) were used to calculate $[C]_t/[B]_t = f'$, the ratio of photolyzed to unphotolyzed products. Since at this wavelength the product is *cis*-$[Cr(en)_2H_2OCl]^{2+}$ and this is likely to photolyze to $[Cr(en)(enH)(H_2O)_2Cl]^{3+}$, the process is associated with uptake of a second proton. Consequently

$$[H^+]_{total} = [H^+]_{primary} + [H^+]_{secondary}$$

Since $[H^+]_{primary} = [A]_0 - [A]_t = [B]_t + [C]_t$ and $[H^+]_{secondary} = [C]_t$

$$[H^+]_{primary} = [H^+]_{total}\left(\frac{1 + f'}{1 + 2f'}\right) \tag{12}$$

This equation was used to apply corrections to ϕ_{H^+}. Since secondary photolysis does not contribute ammonia at 546 nm, no correction of ϕ_{NH_3} was required.

At 366 and 436 nm secondary photolysis is fortunately less of a problem as the more complex modes of reaction observed make the corrections more difficult to apply rigorously. ϕ_{H^+} has been corrected in the same manner as outlined above, but using $T = 0.6$ which assumes that ϕ_B shows no wavelength dependence. Any oversimplifications are not serious as the correction amounts only to −1% → −2%. No corrections have been applied to the ammonia quantum yields, even though one of the probable products, $[Cr(en)(enH)NH_3H_2OCl]^{3+}$, could make a small contribution. The error implied by its neglect is, however, negligible.

The final quantum yields obtained by these methods are given in Table III. ϕ_{H^+} is taken to be the sum of the quantum yield of reactions 1a and 2, and ϕ_{NH_3} is the quantum yield of reaction 2, so $\phi_{H^+} - \phi_{NH_3}$ gives the quantum yield for reaction 1a, ϕ_{en}. This value is necessarily less precise than the other values.

Discussion

The spectrum of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$, Figure 2, with its approximate resolution into component bands, shows that irradiation at 546 nm populates the ^4E_a state, while at 436 nm excitation is mainly into the $^4B_2$ state and at 366 nm into an unknown mixture of $^4A_2$–^4E_b. Little definite information is available as to the rates or paths of deactivation of the initially produced states, but it is generally assumed that degradation occurs within about 10^{-11} s to the lowest excited state of a given multiplicity. Recent studies[26] support rates as high as, or even higher than this, not only for internal conversion but also for intersystem crossing. If for the time being, however, one assumes that reactions may occur from states, probably thermally equilibrated excited states ("thexi" states[3]), having the above symmetries, the molecular orbital theory[9] predicts that reaction from ^4E_a and $^4A_2$ would favor axial labilization with predominantly ammonia loss, while reaction from $^4B_2$ or ^4E_b would favor in-plane labilization, i.e., ethylenediamine loss.

The data of Table III show that for irradiation at 546 nm the amine released is largely ammonia, 100 ± 3%, with a somewhat temperature-dependent quantum yield. Since excitation at 546 nm is the least ambiguous case, almost certainly populating the ^4E_a state (and then the $^2A_1$–$^2B_1$ states) and since reaction from a low-lying quartet state is well established in several systems,[1] it is reasonable to accept that the observed reactivity pattern, i.e., almost exclusive (within experimental uncertainty) ammonia loss, is characteristic of the thexi lowest quartet state, $^4E_a{}^0$. The observed reaction mode is completely in accord with the qualitative predictions of the molecular orbital theory as well as with the other models[6,7]), although a recent calculation of orbital character in the excited states of similar complexes,[11] if interpreted literally, might be expected to predict a greater contribution of ethylenediamine loss from $^4E_a{}^0$ than is observed. This supports the opinion of the authors that the molecular orbital model is considerably oversimplified. The most significant aspect of our results is independent of the various models, however, and is simply that the $^4E_a{}^0$ state of this complex exhibits almost pure axial labilization giving rise to ammonia aquation with the quantum yields given for 546 nm in Table III.

In contrast, excitation to higher energies results in products associated both with axial and in-plane labilization, paralleling the behavior observed for other similar complexes.[12,13,16,17] Since the 546-nm results establish the axial labilization reactivity pattern of the $^4E_a{}^0$ state, it is clear that at least one other reactive state also participates in reaction, but from photochemical data alone it is not possible rigorously to decide the detailed mechanism in this region, since there is a hierarchy of progressively more complex mechanisms all consistent with the observations. To consider the two simplest possibilities only, the reaction might occur in part by prompt reaction of an initial state, perhaps even being vibrationally excited or having some charge-transfer character,[22] with the remaining excited molecules internally converting to $^4E_a{}^0$ with subsequent reaction. Such a "hot" molecule might be expected to lose ethylenediamine and ammonia reasonably statistically, consistent with the observed increase in ethylenediamine. There is an uncertain quantitative argument against such a mechanism, however. Since at 15 °C, $\phi_{NH_3}(^4E_a{}^0) = 0.32$ and ϕ_{en} at 436 nm is 0.06, one might expect $(\phi_{NH_3})_{436} = 0.94 \times 0.32 + (0.06/4) = 0.32$ A similar calculation pertains for the 366-nm data.

It is apparent that such a mechanism does not allow for a decrease in ϕ_{NH_3} of the magnitude observed if one requires that all molecules which do not promptly react internally convert to $^4E_a{}^0$. Of course the introduction of a nonreactive deactivation process not leading to $^4E_a{}^0$ removes this inconsistency. The main arguments against the occurrence of a process of this nature are the conventional ones invoking the high rates of the competitive processes. The recent suggestion[27] that prompt heterolytic fission followed by solvation or cage recombination may occur in such photosolvations means, however, that the possibility of such a competitive process should not be rejected out of hand.

The alternative possibility to be considered, and one that seems better to fit the available observations, is that reaction occurs from two (or more) thexi quartet states, produced in differing proportions at different irradiation wavelengths, and of which the higher converts to the lower at a sufficiently slow rate (perhaps with an activation energy) that reaction from the higher state may compete with internal conversion to the lower. An attractive extension of this possibility which would very nicely rationalize the available evidence is that there should be two manifolds of thexi states, one corresponding to axial distortion of the nuclear configuration and the other corresponding to extension of the in-plane bonds. It is then quite reasonable to suppose that there could be a significant activation barrier to interconversion between the lowest in-plane distorted state ($^4B_2{}^0$) and the lowest axially distorted state ($^4E_a{}^0$) but that internal conversion would be rapid within each manifold. On such a model, excitation would lead to an initial state which relaxes to produce $^4B_2{}^0$ and $^4E_a{}^0$ in a proportion that varies with the excitation wavelength.[28] This is represented diagramatically in Figure 3. A further ambiguity remains. Even assuming such a model to be valid, it is not clear how to assign the observed quantum yields to the various processes, due to our ignorance of the reaction mode of the $^4B_2{}^0$ state. For example at 436 nm, where excitation into this state predominates, $\phi_{NH_3} = 0.30$ and $\phi_{en} = 0.06$ (15 °C). On this model this could be interpreted as relaxation into $^4B_2{}^0$ with unit efficiency followed by reaction with the above quantum yields competing with degradation to the ground state. Alternatively, the initial (and/or thexi $^4B_2{}^0$) state might relax 94% into $^4E_a{}^0$ to give $\phi_{NH_3} = 0.94 \times 0.32$ with the remaining 6% relaxing into $^4B_2{}^0$ to give ethylenediamine with unit efficiency. Any intermediate mixture is also possible. These processes are illustrated in Figure 3.

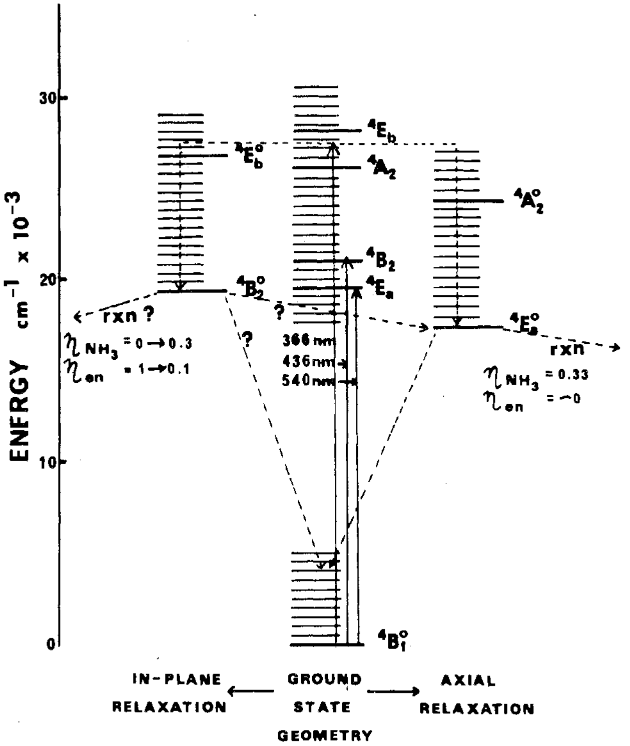

Figure 3. A possible reaction scheme for ammonia and ethylenediamine aquation. The symbol η is used to indicate the fractional efficiency of a particular process. As discussed in the text ambiguity exists as to the decomposition mode of the state(s) arising from excitation at 436 nm, and the possible range of values has been given.

Each extreme has arguments against it. The former assigns $\phi_{en} = 0.06$ and $\phi_{NH_3} = 0.30$ to the $^4B_2{}^0$ state, in poor agreement with the qualitative expectations of the molecular orbital theory. It also leaves no flexibility to account for the further changes in quantum yields observed on excitation at other wavelengths, without invoking participation of other states. The latter requires the $^4B_2{}^0$ state to react with unit efficiency, losing ethylenediamine, unlikely since degradative processes in such excited molecules generally compete favorably with reaction. Consequently a mechanism is favored in which a moderate quantum yield (<1) of ethylenediamine aquation, with perhaps some ammonia, arises from the $^4B_2{}^0$ state.

Our results, and this analysis, illustrate the difficulties involved in obtaining detailed data on excited-state reactivities and the nature of labilization even for very unambiguous systems. It is likely that even more subtle photophysical processes than implied by Figure 3 might play an important role.

Another aspect of ligand field photochemistry which is of interest to us is the stereochemistry of the solvation process. We have shown that, at 546 nm where axial labilization of ammonia occurs, the reaction product appears to be only 1 ± 2% trans. This is consistent with an earlier proposal[2] that photosolvation reactions of Cr(III) might necessarily be associated with stereochemical change, based on data for systems showing axial labilization. In contrast, Linck and co-workers have obtained evidence that the product of in-plane labilization may correspond to retention of stereochemistry, have questioned the degree to which it has been demonstrated that axial labilization is stereomobile, and have claimed that chloride loss from *trans*-$[Cr(en)_2FCl]^+$ gives 9% *trans*-aquofluoro product. In our opinion, due to the complexity of the systems involved and the consequent experimental uncertainties, Linck's data are not unequivocal. The suggestion may well be correct, however, and would represent an interesting stereochemical contrast to that for axial labilization.

The observations supporting stereorententive products for in-plane labilization do not deny, however, the significance of the very large degree of stereochemical change observed earlier for systems showing axial labilization[2,18] and extended in precision here. Whereas random solvation of a trigonal-bipyramidal intermediate or a seven-coordinate intermediate would give 2:1 and 4:1 cis:trans ratios, respectively,[2] the low limit of the range of values found here is 32:1 with a probable value greater than 100:1. We consider this quite significant and support for a stereospecific character for axial labilization. Stereochemical preferences of this magnitude constitute strong evidence for a concerted, associative mode of reaction of the excited state even if they do not totally exclude the possibility of a small amount of trans product being formed.

The results again[2] suggest that an important facet of Cr(III) excited-state reactivity, and therefore of any adequate model of the reactivity, may be the availability of a vacant t_{2g} orbital. Little or no information is available concerning the stereochemistry of reactions of "labile" complexes having vacant t_{2g} orbitals in the ground state. Stereochemical studies of such systems, if possible, might conceivably give evidence for similar stereochemical behavior.

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Registry No. *trans*-$[Cr(en)_2NH_3Cl]^{2+}$, 58560-82-0; *trans*-$[Cr(en)_2H_2OCl]^{2+}$, 14403-90-8; *cis*-$[Cr(en)_2H_2OCl]^{2+}$, 14403-89-5.

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