$(CO)_2{}^{2+}$, 69765-89-5; $Fe(TIM)(CH_3CN)_2{}^{2+}$, 49861-52-1; $[Fe(TIM)(N(C_2H_5)_3)_2](PF_6)_2$, 69765-91-9.

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(1) Ligand abbreviations: TIM, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; imid, imidazole.

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(23) The intermediate(s) did not exhibit any redox reactivity—characteristic of species with radical character or metal complexes in abnormal oxidation states—with methanol, 2-propanol, iodide, or oxygen.

(24) Notice that the overall rate constant, k_0, shows *the existence of two parallel and independent pathways* for the decay of the transient absorbances.

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(26) A Bunsen coefficient, $a = 0.12$, was estimated for CO in CH_3CN.

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(28) Notice that the photochemical and thermal formations of these species do not necessarily involve the same intermediates nor precursors with the same nuclear configurations.

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(31) The crossover point occurs for $20Dq > 5(F_2 + 51F_4)$.[30] Therefore, a promotional energy of 10–20 kcal/mol, for a change from low to high spin, is expected for Dq values between 2000 and 2400 cm^{-1}.[32] It is feasible that distortions from an octahedral configuration in $\{Fe(TIM)(CO)_2{}^{2+}\}$ stabilize a high-spin ground state.

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(34) See ref 2 for an assignment of the energies for LF and CTTL transitions.

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Ligand Field Photolysis of *cis*-Tetraamminedichlorochromium(III) and *cis*-α-(Triethylenetetramine)dichlorochromium(III) Cations

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The ligand field photolysis of *cis*-$[Cr(NH_3)_4Cl_5]^+$ in acidic solution results in both amine ($\phi_{H^+} = 0.32$) and chloride ($\phi_{Cl^-} = 0.15$) labilization. The analogous *cis*-α-$[Cr(trien)Cl_2]^+$ ion displays negligible amine loss ($\phi_{H^+} = 0.015$), with chloride aquation dominating ($\phi_{Cl^-} = 0.10$). The photolyses proceed with retention of cis configuration. The total photochemical reactivity ($\phi_{H^+} + \phi_{Cl^-}$) for *cis*-$[CrN_4Cl_2]^+$ is shown to be linearly related to the rate of thermal chloride aquation at 25 °C. The photochemical results are interpreted in terms of the semiempirical photolysis rules and ligand field photolysis models.

Introduction

Among transition metal complexes, the cationic amine complexes of Cr(III) represent one of the most thoroughly studied, if not understood, systems.[1] Elaborate models, both empirical[2] and theoretical,[3,4] have been developed to predict the photolabilized ligand and the relative quantum yields of the photoinduced reaction. The experimental support for these models is surprisingly limited, however, as only complexes of the form $[Cr(N)_5X]^{2+}$ and *trans*-$[Cr(N)_4XY]^+$ (X, Y = halide, pseudohalide, water; N = an amine (NH_3, 1/2(en), etc.)) have been extensively studied.[1] In addition, these models do not account for the stereochemical rearrangements commonly observed upon photolysis of Cr(III) ions.

Theoretical analyses of the stereophotochemistry of d^3 and d^6 systems have recently been presented by Vanquickenborne and Ceulemans,[5,6] in which the chemical processes resulting from ligand field excitation are separated into three distinct steps: (1) ligand labilization, (2) intramolecular distortion of the remaining five-coordinate intermediate, and (3) water attack of the distorted, five-coordinate intermediate. Without discounting the possibility that these processes may be concerted to some extent, a correlation diagram of the second step revealed that for monosubstituted and trans-disubstituted amine complexes of Cr(III), distortion to a trigonal-bipyramidal species was favored for the lowest energy quartet excited state (^4E). In addition, these calculations suggested that cis water attack would be favored over trans attack, accounting for the formation of the cis aquation products generally observed upon ligand field photolysis of these ions.

As part of our investigation of the stereochemistry of ligand field photochemistry of transition-metal complexes, we have investigated the ligand field photochemistry of *cis*-$[Cr(NH_3)_4Cl_2]^+$ and *cis*-α-$[Cr(trien)Cl_2]^+$ (Figure 1). The photochemical behavior of only a few Cr(III) complexes of cis geometry has been reported,[7-9] so an understanding of the photochemistry of these simple ions can provide tests of the photochemical models, as well as allow insight into the stereochemical rearrangements which often accompany Cr(III) photolyses. Photolysis of *cis*-α-$[Cr(trien)Cl_2]^+$ offers a special test of the models which attempt to predict the photolabilized

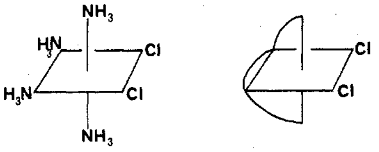

Figure 1. Structural skeleton for *cis*-$[Cr(NH_3)_4Cl_2]^+$ and *cis*-α-$[Cr(trien)Cl_2]^+$.

ligand,[2-4] as they all predict photoinduced labilization will occur in the low-field plane defined by the secondary amines, the chlorides, and the metal, with amine labilization preferred over chloride loss. When the trien ligand is in the cis-α configuration, however, the amines in the photoreactive plane are constrained from leaving the primary coordination sphere by the geometry of the complex. If the regiospecific ligand loss implicit in these models is valid, atypically low amine release quantum yields would be observed upon ligand field excitation of *cis*-α-$[Cr(trien)Cl_2]^+$, despite the presence of unconstrained primary amines above and below the plane of photolabilization.

In addition, study of these ions permits the exploration of an unexplained relationship between the rate of thermal and photoinduced chloride loss observed for a series of *trans*-dichlorotetraaminechromium(III) complexes,[10] as well as a series of *cis*-dichlorotetraaminecobalt(III) ions.[11] A quantum yield is a ratio of the rate of the chemical reaction of an excited state divided by the sum of the rates of all the deactivation processes for that excited state. A parallel between the rate of a thermal (ground-state) reaction and the value of this complex ratio (for an excited state) is not included in any existing photochemical model, and there is no apparent reason such a relationship should exist. If the unexpected connection between photo and thermal reactions proves general, however, new photochemical models would need to account for such a phenomenon.

Experimental Section

Preparation of Complexes. ***cis*-α-(Triethylenetetramine)dichlorochromium(III) Chloride.** The reaction of $[Cr(trien)ox]^+$ with HCl generated in thionyl chloride solution was used to prepare *cis*-α-$[Cr(trien)Cl_2]Cl$.[12] The complex was characterized by electronic and infrared spectra and chloride and chromium analyses.[12]

***cis*-Tetraamminedichlorochromium(III) Chloride.** Finely ground $[Cr(NH_3)_4ox]NO_3$[13] was added to dry methanol, and dry HCl gas was bubbled through the suspension for 6–8 h at room temperature. The purple solid which separated upon cooling was collected by filtration and recrystallized from 6 M HCl. The electronic spectrum and rate of chloride aquation for $[Cr(NH_3)_4Cl_2]^+$, prepared by this simple route, were identical (±2%) with those reported by Jackson et al.[14] Anal. Calcd for $N_4H_{12}Cl_3Cr$: Cl, 47.0; Cr, 23.0. Found: Cl, 45.9; Cr, 22.9.

Instrumentation. Electronic spectra were recorded on a Beckman Acta MIV recording spectrophotometer. A Radiometer PHM 64 (Copenhagen) pH meter with a GK2320C combined electrode (Radiometer) was used for pH measurements, and a F1012Cl Selectrode and K701 calomel reference (Radiometer) were used for determination of chloride ion concentration.

Photolyses. Photolyses were performed on the ions dissolved in 0.1 N perchloric acid solutions at room temperature. A 200-W high-pressure Hg arc lamp (Illumination Industries Inc.) was used for all photolyses. Wavelength selection was effected by an interference filter (Baird Atomic), a hot mirror (to reflect infrared), and a glass UV cutoff filter (Corning CS-54) to absorb any high-energy overtones. Excitation was at 520 nm, which corresponded to the approximate maximum of the lowest energy spin allowed (^4E_g, $^4B_{2g} \leftarrow {}^4A_1$) ligand field absorption.

Unphotolyzed blanks were monitored immediately before and after each pH and chloride determination, and the percent photolysis was kept under 20% to reduce interference from secondary photolysis and inner-filter effects. Chloride release from *cis*-$[Cr(NH_3)_4Cl_2]^+$ was more prone to error, as significant thermal formation of *cis*-$[Cr(NH_3)_4Cl(H_2O)]^{2+}$ during the time of photolysis could not be avoided. The reported ϕ_{Cl^-} for *cis*-$[Cr(NH_3)_4Cl_2]^+$ is the average of 15 separate determinations. A few photolyses of this ion were done with a broad band-pass filter which allowed irradiation of the entire first (^4E_g, $^4B_{2g} \leftarrow {}^4A_1$) ligand field band, at a much higher photon flux. Such conditions permitted short photolysis time, reducing the interference from the thermal reaction, but made determination of the incident photon flux less accurate; quantum yields determined in this manner agreed (within 15%) with the value reported.

The temperatures of photolyzed solutions were monitored and did not rise above the temperature of the blank solution (±0.5 °C).

Results

A general route to complexes of the form *cis*-$[Cr(N_4)Cl_2]^+$ has been reported[12] and was used to prepare the *cis*-α-$[Cr(trien)Cl_2]^+$ used in this study. Despite the apparent simplicity of the ion, the synthesis of *cis*-$[Cr(NH_3)_4Cl_2]^+$ has only recently been reported.[14] The synthesis is complex, however, involving the high-temperature reaction of liquid ammonia with *cis*-$[Cr(py)_4F_2]^+$, followed by reaction of dry HCl gas with the resultant *cis*-$[Cr(NH_3)_4F_2]^+$ in a sealed reaction vessel at high pressure. Seeking a simpler path, we found that a modification of the route used for the chelated amines, the reaction of dry HCl(g) with $[Cr(NH_3)_4ox]^+$ in a nonaqueous environment, allowed the rapid and efficient synthesis of *cis*-$[Cr(NH_3)_4Cl_2]^+$.

Two synthetic methods were reported for the chelated complexes: reaction of $[Cr(N_4)ox]^+$ dissolved in thionyl chloride with the HCl generated by the addition of water to the thionyl chloride solution and the heterogeneous reaction of dry HCl(g) with $[Cr(NH_3)_4ox]NO_3$ suspended in dry methanol. The thionyl chloride reaction is simpler, but when a thionyl chloride solution of $[Cr(NH_3)_4ox]^+$ is reacted with the HCl generated by solvent hydrolysis, a purple solid precipitates which has been identified as *cis*-$[Cr(NH_3)_4Cl(SO_3H)]Cl$. The synthesis, properties, and reactivity of tetraammine(bisulfato)chlorochromium(III) chloride will be reported separately.

The heterogeneous reaction of $[Cr(NH_3)_4ox]NO_3$ suspended in dry methanol with dry HCl gas gave a mixture of the desired *cis*-$[Cr(NH_3)_4Cl_2]Cl$ and an ill-characterized monochlorotetraammine complex, but recrystallization from hydrochloric acid yielded pure *cis*-$[Cr(NH_3)_4Cl_2]Cl$.

All three ions in the series *cis*-$[Cr(N)_4Cl_2]^+$ undergo photoinduced chloride and amine loss. For *cis*-$[Cr(en)Cl_2]^+$, the labilization is concentrated at the higher field amines,[7] although chloride loss is observed ($\phi_{H^+}/\phi_{Cl^-} = 6.5$). In the case of *cis*-α-$[Cr(trien)Cl_2]^+$, the reactivity of the excited states is manifest almost entirely as chloride aquation ($\phi_{H^+}/\phi_{Cl^-} = 0.16$). The parent ion, *cis*-$[Cr(NH_3)_4Cl_2]^+$, ineffectively discriminates between chloride and amine loss, as both aquations are significant ($\phi_{H^+}/\phi_{Cl^-} = 2.1$).

The determination of absolute quantum yields was hindered by thermal aquations, for significant chloride loss occurred during the time of photolysis. Cooling the solution to slow the thermal reaction caused an unacceptable loss of sensitivity of the chloride electrode, so photolyses had to be conducted near room temperature. The thermal reaction of *cis*-$[Cr(NH_3)_4Cl_2]^+$ was especially irksome, and carefully monitored blank runs, coupled with short photolysis times and many repetitions were necessary to obtain reliable quantum yields; the large error limit reflects this experimental difficulty.

Photoinduced spectral changes for *cis*-α-$[Cr(trien)Cl_2]^+$ paralleled the thermally induced spectral changes, with the blue shift of the d–d band consistent with the formation of *cis*-$[Cr(trien)Cl(H_2O)]^{2+}$ as the primary photoproduct. The inefficient amine loss eventually caused the loss of the isosbestics characteristic of the thermal reaction, but in the early stages of photolysis, the photoinduced spectral changes are indistinguishable from those observed upon thermal aquation.[15]

Photoinduced spectral changes of *cis*-$[Cr(NH_3)_4Cl_2]^+$ are more complex, as both amine and chloride loss occur at comparable efficiencies. Water is higher on the spectrochemical series than chloride but lower than ammines, so any blue shift due to chloride aquation would be negated by a similar red shift from ammine aquation. Consistent with this consideration, photolysis of *cis*-$[Cr(NH_3)_4Cl_2]^+$ leads to decreased intensity of the d–d bands with no pronounced shift in their position. Isosbestic points are not observed during the photolysis.

The stereochemistry of the photoproducts could be determined, to a limited extent, from the spectral changes. For *cis*-*α*-$[Cr(trien)Cl_2]^+$, the predominant photoproduct was the *cis*-aquochloro ion (the thermal product) with no evidence of any increase in absorbance near 600 nm which would have suggested the formation of *trans*-$[Cr(trien)Cl(H_2O)]^{2+}$. Based upon spectral changes, the maximum percentage of *trans*-$[Cr(trien)Cl(H_2O)]^{2+}$ which could have gone undetected is ca. 3%. The stereochemistry of the amine aquation product is unknown.

The more rapid thermal aquation of *cis*-$[Cr(NH_3)_4Cl_2]^+$ made prolonged photolysis and the accumulation of pure photoproduct impossible, so a determination of photoproduct stereochemistry is difficult. The stereochemistry of photoinduced amine loss is not known, but the spectral changes imply stereoretentive chloride loss. The presence of *trans*-$[Cr(NH_3)_4Cl(H_2O)]^{2+}$ could have been detected by the absorbance band near 600 nm, but no absorption increase in that region was detected. Even when broad band-pass irradiation was used at 2 °C (to reduce thermal aquation), no evidence of any isomerization to the trans aquochloro ion could be detected, and the maximum amount of trans photoproduct which could have gone undetected is estimated to be 8%.

Discussion

The previously reported[7-9] photochemistry of cis tetraamine complexes of Cr(III) has been interpreted in terms of the semiempirical photolysis rules of Adamson.[2] These rules predict photoinduced aquation of either of the equivalent amines trans to the low ligand field strength chlorides (or pseudohalides). In agreement with the rules, the predominant photoreaction of *cis*-$[Cr(en)_2Cl_2]^+$ is amine release,[7] although an inefficient chloride release was observed. A brief study[9] of *cis*-$[Cr(NH_3)_4(NCS)_2]^+$ revealed that amine release ($\phi_{H^+} = 0.6$) was favored by a factor of 15 over thiocyanate release; a wavelength-dependent photochemistry was observed for *cis*-$[Cr(en)_2Cl(NCS)]^+$, with ligand field photolysis producing amine aquation and minor amounts of chloride or thiocyanate release.[8,16] These studies did not indicate whether the aquated amine was originally coordinated on the low field axis, but the results are in agreement with Adamson's rules.

Application of Adamson's rules to *cis*-$[Cr(N)_4Cl_2]^+$ ($N_4 = (NH_3)_4$, $(en)_2$, or trien) leads to a prediction of aquation of an amine trans to a chloride ligand. Amine loss is the dominant photochemical reaction of *cis*-$[Cr(en)_2Cl_2]^+$ (as reported by Kirk[7] and confirmed in this study) but represents the only ion in the series which strictly follows the photolysis rules. Chloride release is significant for the tetraammine complex, being only a factor of 2 less efficient than amine release, while chloride loss dominates the photochemistry of *cis*-*α*-$[Cr(trien)Cl_2]^+$.

To apply the more recent ligand field and σ/π bonding models,[3] we set the unique (amine–amine) axis as the z axis, with the identical x and y axes containing an amine and a chloride ligand. On the assumption of no intersystem crossing, the photoreactive state would then be $^4B_{2g}$ (xz, yz, $x^2 - y^2$). Formation of $^4B_{2g}$ would decrease σ donation in the x–y plane and would allow for increased π donation, especially from ligands along the z axis. Amine π donation need not be considered, so photoinduced labilization of σ donors in the x–y plane would be anticipated. Since amines are stronger σ donors than chloride and since the π donation of chloride would not be hindered in the $^4B_{2g}$ state, these models also predict amine loss from the x–y plane. The additive angular overlap model of Vanquickenborne and Ceulemans[4] quantitates these qualitative arguments and predicts that the bond weakening in $^4B_{2g}$ would be most severe in the x–y plane and that the $M{-}(NH_3)_{eq}$ bond would be weaker than the M–Cl bond in the $^4B_{2g}$ state and would thus be preferentially labilized.

Table I. Quantum Yields[a] for the Ligand Field Photolysis of Some Ions of the Form *cis*-$[CrN_4Cl_2]^+$

ion	ϕ_{H^+}	ϕ_{Cl^-}	ϕ_{H^+}/ϕ_{Cl}
$Cr(NH_3)_4Cl_2^+$	0.32	0.15 (±0.05)	2.1
$Cr(en)_2Cl_2^+$ [b]	0.13	0.02	6.5
α-$Cr(trien)Cl_2^+$	0.015	0.10	0.16

[a] Unless otherwise stated, quantum yields are accurate to ±10%.
[b] From ref 6–results confirmed as part of this study.

While the original coordination site of the labilized amine in *cis*-$[Cr(NH_3)_4Cl_2]^+$ is unknown, the atypically inefficient amine release of *cis*-*α*-$[Cr(trien)Cl_2]^+$ supports both Adamson's rules and the prediction of σ labilization in the low-field (x–y) plane. The axial coordination sites in the trien complex contain primary amines, as unconstrained as the photolabile amines in *cis*-$[Cr(en)_2Cl_2]^+$, so the lack of efficient amine loss implies that these sites are not labilized in the $^4B_{2g}$ state. Amine release was monitored by pH changes, so quantum yields can indicate nothing about cage recombinations which might precede protonation of the amines. Proton transfer is exceptionally rapid, however, so that once outside the primary coordination shell, instantaneous protonation would block cage recombinations of any amine. Secondary amines, however, are constrained from leaving the primary coordination sphere, so the predicted labilization of the secondary amine in *cis*-*α*-$[Cr(trien)Cl_2]^+$ may occur but would be undetectable due to the rapid cage recombination.

The efficiency of photoinduced chloride release from both *cis*-$[Cr(NH_3)_4Cl_2]^+$ and *cis*-*α*-$[Cr(trien)Cl_2]^+$ is not predicted by any of the available models and suggests that π donation from Cl^- is less important in these $^4B_{2g}$ states than in other systems[3b] and that chloride loss results from the general σ labilization in the x–y plane. The Vanquickenborne[4] analysis shows that for *cis*-$[Cr(NH_3)_4Cl_2]^+$, $I^*(Cr{-}Cl)$ is 9680 cm^{-1}, while $I^*(Cr{-}N_{eq})$ is 8980 cm^{-1}. The $I^*(Cr{-}X)$ term is related to the Cr–X bond strength in the photoreactive excited state, so the weaker $Cr{-}N_{eq}$ bond strength implies that cleavage of the $Cr{-}N_{eq}$ bond would be the dominant reaction of the excited state. For the chelated amines, the σ parameters were assumed to be identical with the value for ammonia, so that identical photochemical behavior would be predicted.

If the minor differences in the absorption maxima of the (^4E_g, $^4B_{2g} \leftarrow {}^4A_1$) bands in the three *cis*-$[Cr(N)_4Cl_2]^+$ ions are attributed to the differences in the σ parameters, the three $I^*(M{-}N_{eq})$ values are 8980, 9340, and 9160 cm^{-1} for NH_3, en, and trien, respectively. These minor variations do not alter the conclusion that amine labilization in the x–y plane should be the dominant photochemical process. In one complex, *cis*-$[Cr(en)_2Cl_2]^+$, the Cr–Cl and $Cr{-}N_{eq}$ bond energies in the excited state differ only marginally, so an argument could be made for simultaneous chloride and amine loss, with amine loss dominant. It is ironic that this ion has the highest amine to chloride loss ratio (Table I). We conclude that the diversity of photochemical behavior displayed by these three *cis*-$[Cr(N)_4Cl_2]^+$ ions is not adequately predicted by the Vanquickenborne model.

The efficient chloride release from *cis*-*α*-$[Cr(trien)Cl_2]^+$ contrasts with the low chloride release yields for the analogous Co(III)[11] and Rh(III)[17] ions. In these d^6 ions, photoinduced, chloride aquation from *cis*-*α*-$[M(trien)Cl_2]^+$ is several orders

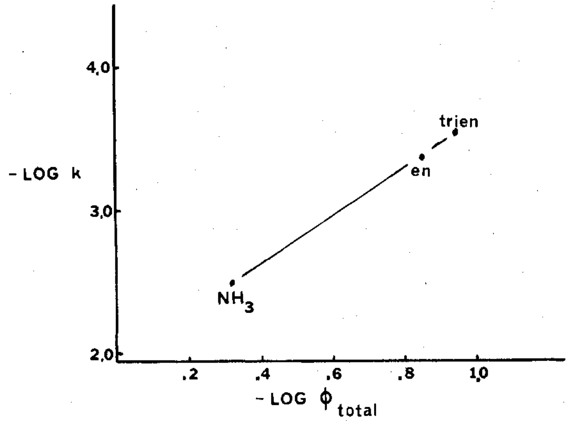

Figure 2. Correlation of ϕ_{total} with k_{Cl^-} (25 °C) for *cis*-$[CrN_4Cl_2]^+$ ions.

of magnitude less efficient than from the bis(ethylenediamine) and cis-β trien complexes. Nor does the quadridentate trien in the α configuration cause the dramatically inefficient chloride loss observed from *trans*-$[Cr(cyclam)Cl_2]^+$.[10] Whatever excited-state distortion is necessary for chloride loss in Cr(III) systems, it is not significantly hindered by linear quadridentates in the cis-α or trans configuration but is severely hindered by the cyclic cyclam ligand.

One trend which does emerge from Table I is that the total photochemical reactivity, defined as the sum of the amine and chloride aquation quantum yields, decreases as the extent of chelation increases. This trend parallels that of the rate of the thermal aquation,[18] and the relationship between the rate of thermal chloride loss (as measured at 25 °C in acidic solution) and the total photochemical reactivity ($\phi_{total} = \phi_{Cl^-} + \phi_{H^+}$) is linear (Figure 2).

Interpretation of this relationship, which has now been observed for three separate sets of complexes,[10,11] remains elusive, for the differences in the thermal and photochemical processes make it clear that the photoreactions occur from states other than the ground state. The recurring parallel between k and ϕ does suggest that some factor has a common effect on both the photochemical and thermal reactions.

The thermal aquation of these cationic Cr(III) complexes is thought to involve an associative interchange between solvent and ligand.[19] An associative mechanism has also been proposed for the ligand field excited states of Cr(III).[20] With an associative mechanism, increased chelation would lead to a decreased rate of aquation, as the hydophobic methylene groups would decrease the attractive interactions between the complex and the solvent shell. Any process which would require attack of a solvent shell water molecule as part of the rate-determining step would be expected to be fastest for $[Cr(NH_3)_4Cl_2]^+$ (hydrophilic, hydrogen-bonding amines) and would become less efficient as the degree of chelation increased. These considerations would apply equally to the ground and excited states, so if increased chelation does not decrease the rates of nonreactivate deactivations to the same extent as it decreases the reactive deactivation path, then these considerations account for the recurring parallel between k and ϕ.

In summary, the inefficiency of photoinduced amine release from *cis*-α-$[Cr(trien)Cl_2]^+$, coupled with the efficient chloride loss, implies that the photochemical reactivity of these ions is concentrated in the low-field plane defined by the metal and the two chlorides. Such a regiospecific excitation pattern is implied by the semiempirical photolysis rules[2] and is contained in the more recent theoretical models.[3,4] The linear relationship between k_{Cl^-} and ϕ_{total} implies that these two ions display a total photochemical reactivity consistent with their thermal reactivity, while the wide range of ϕ_{H^+}/ϕ_{Cl^-} ratios shows that the eventual mode of excited-state reactivity is determined by factors outside the scope of existing models.

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