Models of Chromium(III) Photochemistry. The Photoaquation of *trans*-Bis(ethylenediamine)chlorofluorochromium(III)

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Abstract: The photolysis of *trans*-$Cr(en)_2FCl^+$ has been carried out by irradiation into several of the d–d transitions at several temperatures. The dominant product of this photolysis is *cis*-$Cr(en)_2FH_2O^{2+}$ (ϕ = 0.31 ± 0.01 at 5200 Å, 3°, in 10^{-2} *M* $HClO_4$), but minor yields of *trans*-$Cr(en)_2FH_2O^{2+}$ and a monodentate ethylenediamine complex are also found. The determination of primary products of high absorbance is discussed, and the pertinent equations are derived. The experimental results are examined in terms of several models that predict the axis of labilization; these results also bear on the widely discussed topics of the nature of the leaving group along the activated axis (Adamson's "second rule") and the degree of stereoisomerization that occurs during photolysis. Both subjects are discussed, and a new order of leaving groups is presented.

The photochemistry of Cr(III) complexes offers unusual opportunities to investigate the dependence of various parameters on the quantum yield and, for complexes of less than octahedral symmetry, the course of photoreactions of transition metal ion complexes. Much of the earlier work is summarized in several reviews;[1–5] recent studies have dealt with questions concerning the dominant state from which photoactivity arises,[6–8] the directional nature of the activation process in less than octahedral complexes,[9–15] and more recently the stereochemical course of the photoreaction.[12] It now has become clear that the lowest lying quartet state is photoactive[6–8, 16] and that consideration of its electronic character and how that distribution affects bonds can be used to understand,[9, 14, 17] and perhaps even to predict, the means by which the excited Cr(III) complexes use their energy to photosubstitute.

A previous publication[14] on this latter aspect of the subject was designed to probe the role played by the antibonding nature of the lowest lying quartet state. Spectroscopic investigations of *trans*-$Cr(en)_2F_2^+$ [18] have indicated that fluoride interacts more strongly in a σ fashion with Cr(III) than does ethylenediamine. Within the framework of a one-electron model, this result indicates that the lowest lying excited quartet state is antibonding with respect to the Cr–N bonds. Although electron–electron repulsion mixes this one-electron state with the one antibonding along the *z* axis,[19] the result nevertheless indicates that the Cr–N bond has more antibonding character in the first excited quartet of *trans*-$Cr(en)_2F_2^+$ than in the first excited quartet state of *trans*-$Cr(en)_2Cl_2^+$ [20] because of the relative weakness of the Cr(III)–Cl^- σ interaction. If this conclusion continues to hold for the excited Cr(III) complexes (^4E in C_{4v} notation) after distortion to the lowest vibrational level of the excited state, a level from which photochemistry is presumed to arise, then one might anticipate that the preference for loss of a Cr(III)–N bond in *trans*-$Cr(en)_2F_2^+$ will be greater than in *trans*-$Cr(en)_2Cl_2^+$. Indeed, experiments have shown that the dominant photoproduct of irradiation of each of these molecules into the lowest quartet excited state produces, respectively, $Cr(en)(enH)(H_2O)F_2^{2+}$ [14] and *cis*-$Cr(en)_2H_2OCl^{2+}$.[21] The one-electron argument given above is, of course, simply a molecular orbital approach to Adamson's "rules."[9]

The primary objective in the work reported here was to try to effect an equalizing of these two antibonding tendencies. To achieve this end, the complex *trans*-$Cr(en)_2FCl^+$ was chosen for investigation; the average σ-bonding strength of the ligands along the *z* axis should be approximately intermediate between the *trans*-difluoro- and *trans*-dichlorobisethylenediamine complexes. In addition to this objective, an opportunity to test the "second rule" of Adamson[9] is offered by *trans*-$Cr(en)_2FCl^+$. The rule states that for the axis labilized, the higher ligand field strength ligand will be lost. A molecular orbital interpreta-

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[8] H. F. Wasgestian, *J. Phys. Chem.*, **76**, 1947 (1972).

[9] A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967).

[10] E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, **91**, 1076 (1969).

[11] P. Riccieri and H. L. Schläfer, *Inorg. Chem.*, **9**, 727 (1970).

[12] A. D. Kirk, *J. Amer. Chem. Soc.*, **93**, 283 (1971).

[13] M. F. Manfin, L. Moggi, and V. Balzani, *Inorg. Chem.*, 10, 207 (1971).

[14] S. C. Pyke and R. G. Linck, *J. Amer. Chem. Soc.*, **93**, 5281 (1971).

[15] M. T. Gandolfi, M. F. Manfrin, L. Moggi, and V. Balzani, *J. Amer. Chem. Soc.*, **94**, 7152 (1972).

[16] This conclusion does not rule out participation of the doublet states, although no definitive work has been published that forces one to involve doublet photochemistry.

[17] J. I. Zink, *J. Amer. Chem. Soc.*, **94**, 8039 (1972).

[18] L. Dublicki, M. A. Hitchman, and P. Day, *Inorg. Chem.*, **9**, 188 (1970).

[19] J. R. Perumareddi, *Coord. Chem. Rev.*, 4, 73 (1969).

[20] L. Dubicki and P. Day, *Inorg. Chem.*, 10, 2043 (1971).

[21] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, **49**, 1524 (1971).

tion of this rule[17] offers two other choices for the "strong" ligand: the one with greatest Coulomb integral[22] or the one with the weakest π bonding. Clearly F^- is the ligand that Adamson's rule or Zink's first definition of strong ligand predicts as the leaving group for *z*-axis labilization of *trans*-$Cr(en)_2FCl^+$. (It is not clear whether Cl^- or F^- has the greatest π-donor[23-26] strength toward Cr(III); thus predictions using Zink's latter explanation are difficult.) Our results enable Adamson's second rule to be experimentally investigated.

Experimental Section

Materials. *trans*-$[Cr(en)_2FCl]ClO_4$ was prepared from *trans*-$[Cr(en)_2FH_2O](ClO_4)_2 \cdot H_2O$ by a modification[27] of the published method.[28] The complex was recrystallized from water and dried *in vacuo*. The spectra of these materials were identical with those in the literature[28] (Table II).

Anal. Calcd for $[Cr(en)_2FCl]ClO_4$: Cr, 15.95. Found: Cr, 15.92, 15.96.

Perchloric acid solutions were prepared from G. F. Smith Reagent Grade acid and doubly distilled water. All ion-exchange separations were carried out with Dowex 50W-X2 resin of 200–400 mesh partially screened by flotation and cleaned by treatment with basic peroxide followed by reacidification with HCl and extensive washing with water.

Techniques. The photolyses were performed at three wavelengths using the xenon source and sample block previously described.[14] The wavelengths (half-width 100 Å) were isolated with Oriel interference filters. All light fluxes were measured with Reineke actinometry with corrections applied for the variation in temperature from the data listed in the literature.[29] The temperature was controlled and continuously monitored during photolysis. When the $[H^+]$ was to be followed as a function of photolysis time, a pH electrode was inserted into the sample and the pH read on a Radiometer Model 51 meter. The electrode and meter were standardized with a standard solution of perchloric acid of appropriate $[H^+]$. After the photolysis was complete, the sample was quenched by cooling and frozen (at -10 to $-20°$) until separation by ion-exchange was made. Separations were carried out at 0–5° in the dark. Elution behaviors of the products are described in the Results section.

Each of the products was analyzed by measurement of the visible spectra and determination of the Cr:N:F:Cl ratio. Nitrogen was determined by a micro-Kjehdahl technique; Cr was determined spectrophotometrically after basic peroxide oxidation to CrO_4^{2-}.[30] Fluoride was determined using either the spectrophotometric titration with Th^{4+} [31] or by use of a fluoride sensitive electrode. In the latter procedure, a slight excess of EDTA in a $H_2PO_4^-$–HPO_4^{2-} buffer was first added to a solution of the Cr(III) complex and the mixture was heated until the ethylenediaminetetraacetic acid complex of Cr(III) was formed. This mixture was diluted to volume, and $[F^-]$ was determined by comparing the reading of the ion sensitive electrode with the value obtained from a curve established with standard NaF solution. Chloride was determined by the spectrophotometric method described by Vogel.[32]

Results

Thermal Aquation. In order to correct the observed yields of photoproducts for the amount arising thermally, we measured at frequent intervals the temperature during mixing and separation as well as during photolysis. The temperature–time profile was used to calculate the amount of thermal product according to

$$A = A_0 \prod_{i=1}^{n} e^{-k_i t_i} \qquad (1)$$

where A is the amount of *trans*-$Cr(en)_2FCl^+$ after separation has occurred on the column, A_0 the initial amount, and the product is taken over the various times, t_i, during which the sample was at a temperature T_i. In order to evaluate k_i, as a function of T_i, the thermal aquation of *trans*-$Cr(en)_2FCl^+$ was studied at three temperatures and a log k *vs.* T^{-1} plot constructed. Because there are complications owing to secondary aquation, the details of this system will be reported later.[33] The results of these rate studies are given in Table I.

Table I. Rate of Aquation of *trans*-$Cr(en)_2FCl^+$, 1.0×10^{-2} *M* $HClO_4$

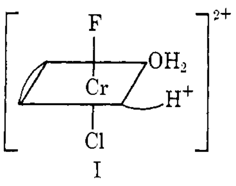
T, °C	*k*, sec^{-1}
18.4	2.29×10^{-5}
25.0	6.20×10^{-5}
36.0	2.59×10^{-4}

From experiments in which *trans*-$Cr(en)_2FCl^+$ is allowed to aquate for short periods of time, two products can be isolated by ion-exchange chromatography. The one that follows *trans*-$Cr(en)_2FCl^+$ off the column (0.75 *N* $HClO_4$ as eluent), complex I, has a Cr:N:F:Cl ratio of 1:4:1:1,[33] but does not correspond to *cis*-$Cr(en)_2FCl^+$ in spectral characteristics[34]—Table II.

Table II. Spectral Characteristics of Complexes

Complex	Wavelength, Å	ϵ, M^{-1} cm^{-1}	Ref
trans-$Cr(en)_2FCl^+$	5505	19.3	27
	4600	21.1	
	3810	27.6	
Complex I	5190	41.6	This work
	3945	30.7	
cis-$Cr(en)_2FCl^+$	5180	62.4	34
	3870	42.8	
trans-$Cr(en)_2FH_2O^{2+}$	5190	23.1	27
	4570	23.9	
	3690	29.9	
Complex II	5110	49.5	This work
	3810	32.4	
cis-$Cr(en)_2FH_2O^{2+}$	5030	72.5	This work
	3730	31.5	

It is believed that this molecule is



I

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[22] It has also been suggested[17] to weight this number in accordance with Mulliken's formula: R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952), see the discussion section.

[23] See, for instance, information in the literature, Co(III)[24] as well as Cr(III).[25,26]

[24] H. Gray, *Advan. Chem. Ser.*, No. 49, 253 (1965).

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[26] J. Glerup and C. E. Schäffer in "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, Amsterdam, 1968, p 500.

[27] G. Wirth, C. Bifano, R. T. Walters, and R. G. Linck, *Inorg. Chem.*, 12, 1955 (1973).

[28] J. W. Vaughn, J. M. DeJovine, and G. J. Seiler, *Inorg. Chem.*, **9**, 684 (1970).

[29] E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, **88**, 394 (1966).

[30] G. Haupt, *J. Res. Nat. Bur. Stand.*, 48, 414 (1952).

[31] C. A. Horton in "Treatise on Analytical Chemistry; II," Vol. 7, I. M. Kolthoff and P. J. Elving, Ed., Interscience, New York, N. Y., 1961, p 307.

[32] A. I. Vogel, "Quantitative Inorganic Analysis," Wiley, New York, N. Y., 1951, p 809.

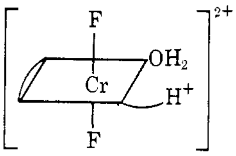
[33] R. G. Linck, unpublished observations.

[34] J. W. Vaughn, O. J. Stvan, and V. E. Magnuson, *Inorg. Chem.*, 7, 736 (1968).

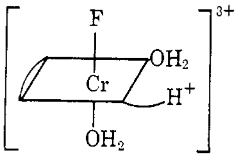
although the geometry is by no means firmly established. The second product of *trans*-$Cr(en)_2FCl^+$ aquation is *trans*-$Cr(en)_2FH_2O^{2+}$ as identified by its spectral characteristics.[27,34]

Products of Photolysis. If a sample of *trans*-$Cr(en)_2FCl^+$ in dilute acidic solution is photolyzed, the initial violet-brown solution turns red. Ion-exchange chromatography of such a solution yields a number of complexes, several of which have been previously reported and several of which are new compounds. In this section each of the dominant five ion-exchange bands are identified. Band 1 is eluted from the column with 0.5 *N* HCl (under our conditions, $HClO_4$ leads to precipitation of band 1 on the column). Band 2 is easily separated from the remainder of the complexes with 0.75 *N* $HClO_4$. The next two bands are difficult to separate. HCl is ineffective in leading to separation, but $HClO_4$ solutions of 0.75–1.0 *N* slowly move and separate bands 3 and 4. Elution of these two compounds with 1.5 *N* $HClO_4$ is convenient after they have been separated. Band 5 is eluted with 2.0 *N* acid. Another band remained on the column after band 5 was eluted; the amount of Cr(III) in this fraction is small and identification of it, or even establishment of a single compound in this sixth band, was not accomplished.

Bands 1 and 3 are readily identifiable by their spectral characteristics. Band 1 is *trans*-$Cr(en)_2FCl^+$, starting material, and band 3 is *trans*-$Cr(en)_2FH_2O^{2+}$, known from earlier studies.[27,34] The fifth band has previously been isolated as a product of the thermal aquation of

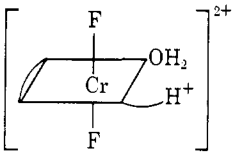


and its spectral characteristics and analytical data (Cr:N:F:Cl of 1:4:1:0) have been obtained.[35] This complex, complex II, was previously assigned[35] as *cis*-$Cr(en)_2FH_2O^{2+}$, but that assignment was erroneous. To establish this, discussion of the other bands recovered from ion-exchange separation is useful. The second band is complex I, the thermal product of aquation of *trans*-$Cr(en)_2FCl^+$ as discussed in the last section. The fourth band, reddish in color and the dominant photoproduct, has spectral characteristics unlike any reported quantitatively in the literature. It is the complex in band 4 that we believe is properly assigned the stoichiometry and geometry of *cis*-$Cr(en)_2FH_2O^{2+}$, whereas complex II, band 5, should be assigned the structure



II

or one of the three remaining stereochemistries of this stoichiometry. The arguments are based to some degree on the tendency of Cr(III)–amine complexes to form, upon substitution, a dominant product of unchanged stereochemistry. (Reference 36 should be consulted for numerous examples.) Our arguments are the following: (1) The analytical data on band 4 give an N to Cr ratio of 3.96 ± 0.02 and a F^- to Cr ratio of 0.97 ± 0.03, indicating that bands 4 and 5 have the same Cr:N:F ratio. This species contains no chloride. (2) Complex II is produced by both the thermal and Hg(II) induced aquation of complex I, as well as by the H^+ induced aquation of



(3) Treatment of a neutral solution of *cis*-$Cr(en)_2Cl_2^+$ with 2 equiv of NH_4F at 60° for 5 min yields a mixture of three products, easily separable by ion exchange. These are spectrally identifiable as *cis*-$Cr(en)_2F_2^+$,[37] band 4 of the photolysis of *trans*-$Cr(en)_2FCl^+$, and *cis*-$Cr(en)_2(H_2O)_2^{3+}$.[38] (4) Anation of a neutralized solution of band 4 with NH_4F leads to production of *cis*-$Cr(en)_2F_2^+$, a substance which we separated by ion exchange and identified spectrally. (5) In photolytic experiments, the change in $[H^+]$ is too small to account for a major process that is H^+ dependent. Thus the proton content of *trans*-$Cr(en)_2FCl^+$ and the major photoproduct, band 4, must be the same. Of the molecules with Cr:N:F content of 1:4:1, only *cis*-$Cr(en)_2H_2OF^{2+}$ fits our requirements.[39] (6) Band 4 has wavelength maxima very close to the values reported for the product of the Ag^+ induced aquation of *cis*-$Cr(en)_2FCl^+$.[34] All attempts to isolate a solid from solutions of band 4 failed, but we believe that the six arguments above are compelling.

The five identifiable ion-exchange separated products are: band 1, *trans*-$Cr(en)_2FCl^+$; band 2, complex I; band 3, *trans*-$Cr(en)_2FH_2O^{2+}$; band 4, *cis*-$Cr(en)_2FH_2O^{2+}$; band 5, complex II. Spectral data are listed in Table II.

Quantum Yields. We are interested in the products of *trans*-$Cr(en)_2FCl^+$ upon irradiation into the lowest lying quartet state; light of 5200 Å accomplishes this. The dominant product of irradiation at 5200 Å is *cis*-$Cr(en)_2FH_2O^{2+}$. Under normal circumstances, a plot of the concentration of *cis*-$Cr(en)_2FH_2O^{2+}$ produced *vs.* the product of amount of irradiation absorbed (einsteins $l.^{-1}$ sec^{-1}) and time yields a straight line of slope ϕ. Our experiments indicated that this relationship was not obeyed for photolysis of *trans*-$Cr(en)_2FCl^+$ if photolysis was carried out long enough to yield 5–15% photolysis. A comparison of the physical properties of *cis*-$Cr(en)_2FH_2O^{2+}$ and *trans*-$Cr(en)_2FCl^+$ illustrates why this is true. The former absorbs light with ϵ 70 M^{-1} sec^{-1} whereas the latter has ϵ 13.6 M^{-1} cm^{-1} at 5200 Å. Thus when the concentration of *cis*-$Cr(en)_2FH_2O^{2+}$ reaches about 0.2 of that of *trans*-

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(35) S. C. Pyke and R. G. Linck, *Inorg. Chem.*, 10, 2445 (1971).

(36) C. S. Garner and D. A. House, *Transition Metal. Chem.*, **6**, 200 (1970).

(37) K. R. A. Fehrmann and C. S. Garner, *J. Amer. Chem. Soc.*, **82**, 6294 (1960).

(38) F. Woldbye, *Acta Chem. Scand.*, 12, 1079 (1958).

(39) This argument is not as rigorous as it first appears because of the possibility of internal hydrogen bonding between the pendant $-NH_3^+$ group and a hydroxide in the coordination shell or Cr(III). Such interaction should increase the acidity of the Cr(III)–OH_2 system, perhaps sufficiently to cause dominance of the internally bonded system at $[H^+]$ of 10^{-3} *M*.

$Cr(en)_2FCl^+$, the former absorbs half of the photons incident upon the sample. In order to minimize this effect, two courses are open. (1) The photolyses can be carried to only very small conversions so as to reduce the absorptivity of *cis*-$Cr(en)_2FH_2O^{2+}$. This scheme leads to large errors in quantum yield because of the difficulty in separating small amounts of *cis*-$Cr(en)_2FH_2O^{2+}$ from the other components of the spent reaction solution. (2) Any inner-filter effect or secondary photolysis can be taken into account and the appropriate correction applied. If we assume that the reaction scheme[40]

$$A \xrightarrow{h\nu} B \xrightarrow{h\nu} C \tag{2}$$

holds for the *trans*-$Cr(en)_2FCl^+$ system, an assumption that we will show is approximately valid, and if it is assumed that the concentrations are such that all the light is absorbed (net absorbance greater than 2), then the differential equations are[41]

$$\frac{-d[A]}{dt} = \phi_A I_0 \epsilon_A [A](\sum_J \epsilon_J[J])^{-1} \tag{3}$$

$$\frac{-d[B]}{dt} = \phi_B I_0 \epsilon_B [B](\sum_J \epsilon_J[J])^{-1} - \frac{d[A]}{dt} \tag{4}$$

$$\frac{d[C]}{dt} = \phi_B I_0 \epsilon_B [B](\sum_J \epsilon_J[J])^{-1} \tag{5}$$

where the ϕ's are quantum yields for disappearance of reactants, I_0 is the absorbed intensity in einsteins $l.^{-1}$ sec^{-1}, the ϵ's are the appropriate extinction coefficients (including path length), and the sum extends over species A, B, and C. Division of eq 4 by 3 leads to a linear first-order equation that can be integrated. This gives a relationship between [B] and [A] in terms of the extent of photoreaction, $f \equiv [A]/[A]_0$, and the parameter we call T

$$T = \frac{\phi_B \epsilon_B}{\phi_A \epsilon_A} \tag{6}$$

Manipulation of the differential equations (3 and 5) leads to a relationship between [A] and [C]; combination of these two results gives

$$\frac{[C]}{[B]} = \frac{(T + f^T - 1 - Tf)}{(f - f^T)} \tag{7}$$

This result allows us to calculate [C] formed by secondary photolysis of [B] as a function of the extent of primary photoreaction and the parameter T. To apply this correction, estimates of ϕ_A and ϕ_B must be made; we know the former, approximately, by ignoring secondary photolysis. The value of ϕ_B has been measured; a preliminary value is about 0.25 at 5200 Å.[42] The extent of reaction, f, can be estimated with use of ϕ_A and I_0 and the whole procedure reiterated to self-consistency. Our data are not accurate enough to warrant extensive refinement; however, the values we report are not excessively sensitive to T or f. It is to be noted that although theoretically a plot of ϕ *vs.* $1 - f$ should be a curve, the data plotted in this fashion and extrapolated to $(1 - f) = 0$ yield values in close agreement with our method based on eq 7.

Values for the observed quantum yield of *cis*-$Cr(en)_2FH_2O^{2+}$ are given in Table III. The observed quantum yield, ϕ_{obsd} is defined as the [*cis*-$Cr(en)_2FH_2O^{2+}$] observed divided by the absorbed intensity. These values are accompanied by approximate values of the fraction photolyzed as well as values of ϕ_{corr}, the value of ϕ corrected for secondary photolysis by use of eq 7. It is seen there that the correction brings the values of ϕ into agreement with each other. In addition, if *cis*-$Cr(en)_2FH_2O^{2+}$ is undergoing such extensive secondary photolysis, the products of that photolysis should be found when mixtures are ion exchanged. Our preliminary results indicate that bands 5 and 6 are these products.[42] In all cases the amount of secondary products calculated by use of eq 7 is equal to or exceeded by the amount of Cr found in bands 5 and 6. It may be that complex II or the component(s) of band 6 are produced in a primary step or are column induced aquation products, a topic to which we turn below, but their principal source is from photolysis of *cis*-$Cr(en)_2FH_2O^{2+}$.

Table III. Quantum Yields in Photolysis of *trans*-$Cr(en)_2FCl^+$

Fraction photolyzed $(1 - f)$	T, °C	*cis*-$Cr(en)_2FH_2O^{2+}$		*trans*-$Cr(en)_2$-FH_2O^{2+}	Complex I
		ϕ_{obsd}	ϕ_{corr}	ϕ_{trans}	ϕ_I
0.08	3	0.259	0.304	0.00–0.04	0.05–0.08
0.12	3	0.249	0.316	0.05–0.07	0.03–0.06
0.17	3	0.216	0.301	0.03–0.05	0.02–0.06
0.18	3	0.214	0.307	0.01–0.02	0.02–0.04
	Av 3		0.307	0.02–0.045	0.03–0.06
0.06	23	0.304	0.336	0	0–0.06
0.07	23	0.294	0.334	0	0–0.04
0.14	23	0.249	0.325	0	0–0.01
	Av 23		0.332	0	0–0.04

This conclusion leaves us with two bands of the ion-exchange separation, bands 2 and 3, for which to account. These bands contain materials that are also the thermal products of the aquation of *trans*-$Cr(en)_2FCl^+$, and careful thermal correction must be applied in order to determine if an excess of these materials over the expected thermal yield is found. We have used eq 1 to apply this correction where time–temperature profile extends from time of mixing of the solutions until the *trans*-$Cr(en)_2FCl^+$ is separated from other species on the column. Several control experiments (no light) were conducted in order to check our correction and to determine whether or not resin catalyzed aquations took place. In order to put realistic limits on our reported quantum yields, we examine both extremes of thermal correction. Our control experiments never indicated a greater calculated (from eq 1) amount of *trans*-$Cr(en)_2FH_2O^+$ than the amount we observed. In a photolytic experiment, this observed quantity, corrected for the thermal aquation, gives an upper limit to the quantum yield for *trans*-$Cr(en)_2FH_2O^{2+}$, ϕ_t. The biggest deviation between calculated and observed quantities of *trans*-$Cr(en)_2FH_2O^{2+}$ in control experiments was -5 μmol, indicat-

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(40) In eq 2 C represents all of the products of the photolysis of B, not just a single species. This has no effect on our calculations as long as the photolysis of these secondary products is small.

(41) H. F. Wasgestian and H. L. Schläfer, *Ber. Bunsenges. Phys. Chem.*, 71, 489 (1963).

(42) J. A. Doi and R. G. Linck, unpublished observations.

Table IV. Wavelength Dependence of Quantum Yield

λ, Å	T, °C	Conditions, M	ϕ_{cis}[a]	ϕ_{trans}[b]	ϕ_I[c]
5200	3	10^{-2} $HClO_4$	0.307 ± 0.06	0.03	0.04
	6	5×10^{-3} $HClO_4$	0.36 ± 0.03		
	12	10^{-2}–10^{-3} $HClO_4$	0.32 ± 0.04		
	12	0.2 LiCl	0.35 ± 0.03		
	23	10^{-2} $HClO_4$	0.332 ± 0.006	<0.01	0.02
4500	4	10^{-2} $HClO_4$	0.318 ± 0.002	<0.01	0.071
4000	3	10^{-2} $HClO_4$	0.36 ± 0.02	<0.05	0.10

[a] Quantum yield for *cis*-$Cr(en)_2FH_2O^{2+}$. [b] Quantum yield for *trans*-$Cr(en)_2FH_2O^{2+}$ [c] Quantum yield for complex I.

ing some resin catalyzed formation of *trans*-$Cr(en)_2FH_2O^{2+}$. Adding this value to the calculated values gives a lower limit to the photoproduced *trans*-$Cr(en)_2FH_2O^{2+}$. Both of these means of correction still lead to considerable scatter, as can be seen in the values given in Table III. We can find no evidence for photoproduced *trans*-$Cr(en)_2FH_2O^{2+}$ at 23°.

Corrections for thermally produced complex I were determined similarly; in this case our control experiments indicated net destruction of complex I on the resin (see, for instance, ref 21). A lower limit for photoproduced complex I can be determined by neglecting this destruction of complex I. An upper limit can be determined in two ways. Firstly, the amount found in control experiments approached a limit of 5 μmol less than calculated. Thus the amount found in a photolysis experiment can be increased by this amount and then corrected for thermal aquation. Secondly, there is a slight residue of bands 5 and 6 (after compensation for that formed from secondary photolysis of *cis*-$Cr(en)_2FH_2O^{2+}$). Since the likely resin catalyzed decomposition of complex I is complex II, this residue of these products is the maximum unaccounted for amount of complex I. Table III gives these upper and lower limits for the quantum yield of complex I, ϕ_I. (It is to be noted that the quantum yields of both *trans*-$Cr(en)_2FH_2O^{2+}$ and complex I are small compared with ϕ for *cis*-$Cr(en)_2FH_2O^{2+}$. This means the assumption that *trans*-$Cr(en)_2FCl^+$ produces only *cis*-$Cr(en)_2FH_2O^{2+}$, eq 2, for purposes of calculating secondary photolysis yields, is a valid assumption.)

Measurements of quantum yields were made at several other wavelengths and under other conditions. The values for ϕ of *cis*-$Cr(en)_2FH_2O^{2+}$ have been corrected assuming that ϕ for the secondary photolysis is wavelength independent. There is a significant decrease in the correction term because the extinction coefficient difference between *trans*-$Cr(en)_2FCl^+$ and *cis*-$Cr(en)_2FH_2O^+$ decreases.[43] Thus our assumption is not likely to be of great importance. A summary of all our values is to be found in Table IV. The values for ϕ_{trans} and ϕ_I are the means of our data, and, in the cases where limits are given for these two values, we believe they are conservative. (The standard deviations on ϕ_{cis} undoubtedly reflect precision rather than accuracy.)

Discussion

Our purpose in photolyzing *trans*-$Cr(en)_2FCl^+$ was to learn if the simple one-electron molecular orbital model predicted the axis of labilization better than Adamson's[9] first rule (the weak ligand field axis will be labilized). In addition, this molecule has sufficiently low symmetry to allow a multiple number of discernible photoaquation pathways. In particular, the different groups on the z axis allow us to test Adamson's[9] second rule.

The Directional Nature of the Activation Process. Inspection of Table IV indicates that at low temperatures irradiation into the lowest quartet state produces two types of products; *cis*- and *trans*-$Cr(en)_2FH_2O^{2+}$, whose presence would indicate z axis labilization; and complex I, whose presence indicates Cr–N bond breakage, that is, xy activation. It would appear that our simple model[14] does allow one to anticipate the mode of activation. Thus as one moves from *trans*-$Cr(en)_2F_2^+$ to *trans*-$Cr(en)_2FCl^+$, there is an increasing stabilization of d_{z^2} relative to $d_{x^2-y^2}$, resulting in an increasing amount of z axis bond breakage, from within experimental error in *trans*-$Cr(en)_2F_2^+$ to about 90% in *trans*-$Cr(en)_2FCl^+$. It would be most interesting to establish more definitely what the nature of the products in the photolysis of *trans*-$Cr(en)_2Cl_2^+$ is; unforunately, neither Kirk[21] nor we[44] have been able, as yet, to learn about this feature. Certainly the dominant product results from loss of Cl^-.

There are, however, other ways to explain the presence of Cr–N bond-breakage products. The photolysis of *trans*-$Cr(en)_2NCSCl^+$ leads to both H^+ uptake as well as NCS^- and Cl^- loss;[15] but these authors find that the Cr–N bond breakage is more facile when irradiation into the $^4B_2$ is undertaken. It is possible that our studies at 5200 Å involve partial population of this state owing to overlap of the absorption bands, and, in addition, it may be possible that repopulation of this second quartet state ($^4B_2$) from the lowest lying quartet state (^4E) leads to the small yield of complex I. Two other possibilities also exist: the presence of a small yield of complex I could arise from doublet photoreaction[10] or from reaction of the higher of the two states that must, by virtue of the Jahn–Teller theorem, arise from the ^4E state when the complex distorts to satisfy this theorem. Of these four alternative explanations, the second seems unlikely on energetic grounds. At the internuclear distances characteristic of the ground-state molecule, these two states, ^4E and $^4B_2$, are separated by about 10.5 kcal mol^{-1}. Since direct irradiation into the $^4B_2$ state (4500 Å) leads to a value of ϕ_I of only 0.07, it seems unlikely that the entire ϕ_I of 0.04 observed at 5200 Å could arise from a population of the higher state when the energy difference is so large. A similar argument holds with respect to the first alternative explanation. Reasonable analysis of the absorption band shapes indicates that no more than a third of the light at 5200 Å could populate the $^4B_2$ state. No real contribution can be made concerning the third and fourth possibilities, since the nature of the states involved, the magnitude of the energy gaps, and the facility with which interconversons can occur are all unknown. Related to this general uncertainty of the state(s) from which the photoproducts originate is the apparent coupling of the processes leading to complex I and

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(43) The appropriate values of ϵ for *trans*-$Cr(en)_2FCl^+$ and *cis*-$Cr(en)_2FH_2O^{2+}$ are respectively λ 4500 Å (20.4, 25.9 M^{-1} cm^{-1}) and λ 4000 Å (21.6, 23.7 M^{-1} cm^{-1}).

(44) L. Falk and R. G. Linck, unpublished results.

trans-$Cr(en)_2FH_2O^{2+}$, as shown by the temperature dependence at 5200 Å, but the dissimilarity between these two yields upon irradiation at 4500 Å. As far as the available data are concerned it is clear that any of a number of *ad hoc* hypotheses can be formulated to account for the subtleties of our minor products. The simplest model remains however, one in which the two types of products, represented by axial and in plane activation, compete because of a close similarity of the energies of their respective one-electron antibonding states. Comparison of the total yield of products at 5200 Å with that at 4500 Å (both at low temperature) illustrates this point well. In both cases the overall yield is 0.38; the variable distribution of products could arise from the two ways of populating the lowest lying quartet state (directly and by internal conversion), reminiscent of the study of $Cr(en)_3^{3+}$ by Balzani and coworkers.[45] At 4000 Å the total yield increases, mostly because of an increase in *z*-axis activation, that is, in Cl^- loss. A plausible reason for this increase could involve a charge-transfer state as found in the photolysis of $Cr(NH_3)_5Br^{2+}$[10] and $Cr(NH_3)_5Cl^{2+}$.[46] Such a path would be expected to increase Cl^- loss without increase in Cr–N bond breakage. Unfortunately, the molar absorbance of *trans*-$Cr(en)_2FCl^+$ at 3000 Å is only 0.28 M^{-1} cm^{-1}; if a charge-transfer state is responsible for the 4000 Å quantum yield increase, it must arise from a state hidden under the predominant d–d transition (a charge transfer doublet?) or from intersystem crossing into a charge-transfer state from the d–d quartet-state populated by irradiation at 4000 Å.

Stereoisomerization in Fluoroaquo Products. Of the products derived from *z*-axis activation, *cis*-$Cr(en)_2FH_2O^{2+}$ is dominant, but small amounts of *trans*-$Cr(en)_2FH_2O^{2+}$ are found at low temperature when the sample is irradiated at 5200 Å. Under these conditions about 9% of *z*-axis activation thus leads to stereoretentive products. This result is in accord with the arguments developed by Kirk[12] that substantial isomerization accompanies photoaquation in Cr(III) complexes. It differs in a detail, however, that is somewhat crucial. Experimentally the establishment of a >90% stereospecificity is difficult in photolyses of Cr(III) complexes. For instance, our results are relatively uncertain at the 90% stereospecificity level. To the best of our knowledge, the other reports in the literature indicating the level of stereospecificity in Cr(III) photoaquations[10,12,15,47–49] have been based upon differential spectral measurements of small changes in absorbance and are probably also subject to 5–10% errors. But conceptually, there is a significant difference between complete stereoisomerization and production of both isomers, but with one dominating. For instance, generation of a five-coordinate intermediate of trigonal bipyramidal shape from *z*-axis-activated *trans*-$Cr(en)_2FCl^+$ would produce, by random attack of water, 67% *cis*- and 33% *trans*-$Cr(en)_2FH_2O^{2+}$. If the attack to give cis were only slightly preferred, the ratio could easily change from the 2:1 preference to a 9:1 one. Our point is that models of the photoactivation process are very sensitive to changes in product ratios at the level of experimental errors.

In addition to these considerations, two other points merit mention. Firstly, the trans to cis ratio we observe is temperature dependent, indicating that the two photoproducts arise from different origins. Secondly, it is to be noted that the likely geometry of complex I is consistent with the lack of stereochemical change in the photoprocess; the same is true in the case of the dominant photoproduct of *trans*-$Cr(en)_2F_2^+$. Although these results are compatible with a seven coordinate intermediate,[49,50] they require very specific directions of attack to be so.

The Leaving Group and Adamson's Second Rule. Adamson's second rule[9] states that along the activated axis the group with the greater ligand field strength will be the one that is photoactivated. Our results will test this rule as long as we consider only the products of *z*-axis activation. We can find no trace of loss of F^- and estimate ϕ_{F^-} as less than 0.006. This is to be compared with the quantum yield for loss of Cl^-, $\phi_{Cl^-} = 0.38$; chloride ion loss is favored over F^- by a factor of over 60. Clearly this result is inconsistent with Adamson's second rule, which predicts loss of the stronger ligand-field-strength ligand. Another example in which relative leaving group ability has been measured is in the photolysis of *trans*-$Cr(en)_2NCSCl^+$,[15] where both Cl^- and NCS^- are effective leaving groups, although these ligands differ considerably in ligand field strength. There are sufficient data in the literature[10,13,44,47,49,51] to establish a rough order of photoaquation leaving ability from Cr(III) complexes, $NH_3 > H_2O > Cl^- \cong NCS^- > F^-$, $NH_3 > Br^- > F^-$. It remains to be seen how sensitive this *empirical* ordering is to the remaining ligands in the coordination shell; but it is clear that photoactivation is not dictated by the ligand field strength, for which the ordering would be[52] $NH_3 > NCS^- > H_2O > F^- > Cl^- > Br^-$. It is not evident what bonding characteristic, if any simple one at all, can be used to explain the empirical order.

Zink[17] has published a rationalization of Adamson's first two rules. His explanation of our previous result[14] on the photolysis of *trans*-$Cr(en)_2F_2^+$ suffers because, contrary to his assertion, we did not irradiate this species with white light, but rather with light of 5200 ± 50 Å. His model does not, in contradistinction to the simple one-electron model, correctly predict the axis which is activated in photolysis of *trans*-$Cr(en)_2F_2^+$. We reassert our previous conclusion[14] that Adamsons' first rule, as stated,[9] is insufficient to account for the photolysis of *trans*-$Cr(en)_2F_2^+$, but that indeed a redefinition of strong ligand (in terms of σ-bonding interaction) corrects the deficiency.

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(46) H. F. Wasgestian and H. L. Schlafer, *Z. Phys. Chem.* (*Frankfort am Main*), **62**, 127 (1968).

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(48) E. Zinato, C. Furlani, G. Lanna, and P. Riccieri, *Inorg. Chem.*, 11, 1746 (1972); see also footnote 37 in this paper.

(49) (a) A. D. Kirk, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., 1972, No. INOR 22; (b) A. D. Kirk, private communication.

(50) C. Kutal and A. W. Adamson, *J. Amer. Chem. Soc.*, **93**, 5581 (1971).

(51) R. G. Linck, unpublished study of the photolysis of *trans*-$Cr(en)_2FBr^+$.

(52) L. E. Orgel, "An Introduction to Transition Metal Chemistry," Wiley, New York, N. Y., 1966, p 47.

But thus far,[53] only our redefinition is sufficient; Zink's model is not successful.

We turn to consider the rationalization for Adamson's second rule in which it is maintained that the "strong" ligand will be photoaquated, but strong is redefined in terms of the Coulomb integral of the ligand,[17] perhaps weighted by overlap considerations or in terms of the π-bonding ability of the ligand. In the former statement, it is clear that F^- is "stronger" than Cl^-[54] and hence should be the leaving group. It would seem unlikely that overlap effects could change this, since it is necessary to have the Cr–Cl overlap nearly 50% greater than the Cr–F overlap. The second criterion is that the weakest ligand will usually have "the greatest π-bonding character."[17] The available data on the strength of the π-bonding interaction of F^- and Cl^- with Cr(III) allows one to choose either of these ligands as the stronger π-bonding group. For instance, Rowley[25] lists $\delta\pi$ values (the difference between the π interaction of F compared with ethylenediamine) for F^-, Cl^-, and Br^- in *trans*-$Cr(en)_2X_2^+$ as 2017, 473–917, and 705 cm^{-1}, respectively; whereas his values for F^-, Cl^-, and Br^- in $Cr(NH_3)_5X^{2+}$ are −195, 414, and 505 cm^{-1}, respectively. The values are exactly reversed in the two systems. (Some of these values are obtained from room temperature polarization measurements; König[55] has commented on how deceptions can arise in such values. Other values were determined from Gaussian analysis of solution spectra;[56] Yamada[57] has criticized treatments of this type.) On the other hand, Glerup and Schäffer[26] believe that the $\delta\pi$ series goes $F^- > Cl^- > Br^-$. We are uncertain as to which set of data to apply and hence cannot make use of Zink's second measure of "strong" ligand. Any result, however, that predicts that Cl^- is "stronger" than F^- violates the first version of the "strong" ligand.

Our own experience with the chemistry of Cr(III) complexes containing F^- is that the Cr(III)–F^- bond is extraordinarily inert, both thermally and photochemically,[14,51] as long as $[H^+]$ is not too large. The failure of F^- to fit Adamson's second rule may reside in this extraordinary stability which changes excited state wave functions so drastically that MO interpretations based on the energies at the ground-state internuclear distances may not be valid in the vibrationally deactived (distorted) excited state.

Summary. Our results have indicated that *trans*-$Cr(en)_2FCl^+$ photoaquates to give both *z* and *xy* activation with the former dominant. Chloride loss is accompanied by stereoisomerization for 90% of the molecules. This result should be carefully considered in dealing with models of the pathway for photoaquation. The observation of the loss of Cl^- is a violation of Adamson's second rule; a new empirical order of photoactivated groups has been presented.

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Electronic and Steric Control of Reactions of Benzylmagnesium Chloride with Substituted Metal Carbonyls

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Abstract: Kinetic studies are reported for nucleophilic addition of benzylmagnesium chloride to a series of $LM(CO)_x$ complexes, $LM(CO)_x + C_6H_5CH_2MgCl \rightarrow LM(CO)_{x-1}C(CH_2C_6H_5)O^-MgCl^+$, where L = CO, phosphine, or phosphite, M = Fe ($x = 4$) or W, Mo, or Cr ($x = 5$). Nucleophilic reaction occurs at the cis carbonyl ligand of $LM(CO)_5$ complexes except when L is the very bulky ligand tri-*o*-tolylphosphine. For $LFe(CO)_4$ complexes, however, addition is to the trans carbonyl group. Electronic properties of the CO ligand as indicated by the CO stretching force constant or frequency dominate CO reactive sites within a molecule and also reaction rates for Grignard addition to CO ligands trans to a substituent. Reaction rates of addition to cis carbonyl groups are governed by the steric requirements of L. The limitations inherent in applying a force constant/reactivity correlation are discussed.

We have previously suggested[2] that carbonyl stretching force constants may be used as indices to predict the active positions as well as relative reactivities of the carbonyl ligand in metal carbonyl and substituted metal carbonyl compounds. While high CO stretching force constants (or, as approximated by, ν_{CO}) correlate with a more positive carbon atom and therefore with nucleophilic attack at carbon,[2–5] low values of the CO stretching force constants (or ν_{CO})

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