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Registry No. [Cu(acac–2-amino-1-butanol)]$_4$, 64600-06-2; [Cu(acac–2-amino-1-phenylethanol)]$_4$, 64600-07-3; [Cu(acac–ethanolamine)]$_4$, 64600-08-4; [Cu(acac–ethanolamine)]$_4$·toluene, 64611-66-1.

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Contribution from the Istituto Chimico
"G. Ciamician" dell'Università, 40126 Bologna, Italy

Photochemistry of *trans*-Difluorobis(ethylenediamine)chromium(III)

M. F. MANFRIN,* D. SANDRINI, A. JURIS, and M. T. GANDOLFI

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The photochemical behavior of *trans*-Cr(en)$_2$F$_2^+$ in aqueous solutions (pH ~3) has been investigated. Regardless of the excitation wavelength (254, 365, 530 nm), the irradiation of the complex causes two photoreactions, i.e., the release of F$^-$ ions and the consumption of H$^+$ ions. The latter photoreaction is due to the detachment of one ethylenediamine end from the metal, followed by the protonation of the free amine group. For this photoreaction, which is predominant at each one of the irradiation wavelengths, spectrophotometric analyses have shown that at least a noticeable fraction of the product must have the two F$^-$ ions cis to one another. The quantum yields at 254, 365, and 530 nm are 0.15, 0.22, and 0.20 for ethylenediamine detachment and 0.030, 0.030, and 0.020 for F$^-$ release. The photochemical behavior of the complex is compared to that of analogous complexes and the role played by the various excited states in determining the photochemical behavior is discussed.

Introduction

The photochemistry of Cr(III) complexes continues to be a very important area of research since it offers unusual opportunities to investigate both the role played by the various excited states and the chemical mechanism of the observed photoreactions. The earlier work in this field has been summarized and discussed by several authors.[1-3] Most of the recent investigations have dealt with mixed-ligand Cr(III) complexes[4-17] with the aim of elucidating the directional nature of the ligand labilization, the wavelength dependence of the observed photoreactions, and the stereochemical course of the photoreactions. In the meantime numerous theoretical models have appeared[18-23] in an attempt to account for the experimental results and predict the photochemical behavior.

trans-Cr(en)$_2$F$_2^+$ is an important member within the family of the mixed-ligand Cr(III) complexes because of its spectroscopic properties.[24-26] Experiments carried out by Pyke and Linck[4] using 520-nm excitation have in fact indicated that the photochemical behavior of this complex is different from that of the other *trans*-Cr(en)$_2$X$_2^+$ complexes.[5,11,17] This paper reports a quantitative investigation of the photochemical behavior of *trans*-Cr(en)$_2$F$_2^+$ at three different excitation wavelengths.

Experimental Section

Materials. *trans*-Difluorobis(ethylenediamine)chromium(III) perchlorate, *trans*-[Cr(en)$_2$F$_2$]ClO$_4$, was prepared by the method of Vaughn et al.[27] and recrystallized three times from acidic water. Anal. Calcd for Cr(C$_2$H$_8$N$_2$)$_2$F$_2$ClO$_4$: C, 15.52; H, 5.21; Cl, 11.45; Cr, 16.79; F, 12.27; N, 18.09. Found:[28] C, 15.40; H, 5.18; Cl, 11.38; Cr, 17.03; F, 12.26; N, 17.99. The absorption spectrum of the complex was in excellent agreement with that reported in the literature.[29] All of the other chemicals used were of reagent grade.

Apparatus. Radiations of 254, 365, and 530 nm were obtained as previously described.[30] The intensity of the incident light, which was measured by means of ferric oxalate[31a] or reineckate[31b] actinometers, was of the order of 10^{-7} N$h\nu$/min at each one of the nominal wavelengths used. The fraction of absorbed light was calculated from the optical density of the irradiated solutions. The reaction cells were standard spectrophotometric cells (thickness, 1 cm; capacity, 3 mL) housed in a thermostated cell holder. The absorbance measurements and the recording of the spectra were performed with a Shimadzu QV-50 and a Perkin-Elmer 323 spectrophotometer. pH measurements were made by a Knick KpH 34 pH meter equipped with an Ingold Lot-type combined microelectrode. The same pH meter was used as a potentiometer for determining the concentration of F$^-$ ions by means of an Orion Model 96-09 combined fluoride electrode.

Procedure. A weighted amount of the complex was dissolved in a water solution containing 2×10^{-3} M HClO$_4$ and 1×10^{-4} M F$^-$ ions. The complex concentration was 5×10^{-2} M in all cases. The reaction cell was filled with a freshly prepared solution and then placed in the thermostated cell holder of the irradiation equipment. All the experiments were carried out at 10 °C unless otherwise noted. A sample of the same solution was maintained in the dark at the same temperature in order to provide control for the thermal reactions. No more than 10% of the reactant was decomposed, in order to avoid secondary photochemical reactions. A stream of purified nitrogen was used for stirring the irradiated solution. pH measurements were directly performed during irradiation. Potentiometric (F$^-$) and spectrophotometric measurements were performed after suitable irradiation periods.

Analytical Methods. The detachment of amine groups from the complex was followed by means of pH measurements. For each experiment, the pH changes resulting from irradiation were converted into changes in H$^+$ concentration by means of a ΔpH vs. Δ[H$^+$] calibration plot, obtained by adding known amounts of base to a portion of the same solution maintained in the dark. The concentration of F$^-$ ions present in the irradiated solutions was measured potentiometrically with the F$^-$ selective electrode. The potentiometric signals were converted into changes of the F$^-$ concentration using a Δmv vs. Δ[F$^-$] calibration plot obtained at the actual pH of the solution.

Results

Thermal Behavior. Before studying the photochemical behavior, the thermal reactivity of the complex was briefly

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Table I. Quantum Yields[a]

Irradiation λ,[b] nm	$Cr(en)(enH)(H_2O)F_2^{2+}$ (reaction 1)	$Cr(en)_2(H_2O)F^{2+}$ (reaction 2)
254 [$^4A_2g(b^4T_1g)$ + CT]	0.15 ± 0.02	0.030 ± 0.002
365 [$^4A_2g(a^4T_1g)$]	0.22 ± 0.02	0.030 ± 0.002
530 [$^4E_g(^4T_2g)$]	0.20 ± 0.02	0.020 ± 0.001

[a] Aqueous solutions, pH 3, 10 °C, average of at least four independent runs. [b] The predominantly populated excited state(s) is indicated in brackets.

examined under the same experimental conditions. The results obtained were as follows: (i) the pH of the solution increased with time; (ii) F^- ions were not released; (iii) spectral changes were observed with isosbestic points at 474, 386, and 352 nm; (iv) the rate constant for H^+ consumption was 1.5×10^{-6} s^{-1} at 10 °C and 1.2×10^{-5} s^{-1} at 25 °C, corresponding to an activation energy of ~23 kcal/mol. These results are in agreement with those previously reported by Pyke and Linck[32] and DeJovine et al.,[33] who assigned the observed reaction to the formation of $Cr(en)(enH)(H_2O)F_2^{2+}$, a monodentate ethylenediamine complex with the two fluorides trans to one another.

Photochemical Behavior. The photochemical behavior of the complex was qualitatively the same at each of the three excitation wavelengths used. For short irradiation periods the concentrations of H^+ and F^- changed linearly with the number of absorbed einsteins (after correction for the thermal H^+ consumption). No postphotochemical effect was observed. The quantum yields of H^+ consumption and F^- release are summarized in Table I. Differential spectrophotometric analyses of the irradiated vs. dark solutions showed that the photoreaction was accompanied by spectral changes which were clearly different from those obtained in the thermal reaction. Specifically, in the irradiated solutions isosbestic points were present at 467, 415, and 349 nm. The position of the isosbestic points was the same for experiments at 10 or 25 °C. The comparison of the spectrophotometric variations at different wavelengths[34] showed that secondary processes were not involved under our experimental conditions.

Discussion

Nature of the Photoreaction Products. Ligand field irradiation of mixed-ligand Cr(III) complexes may cause the release of the various ligands.[1-17] When one of the ligands is ethylenediamine, it has been established[4,5,8,35,36] that the primary photochemical step concerning this ligand is the detachment from the metal of one end of the molecule. In acid medium, fast protonation of the liberated ethylenediamine end takes place, whereas the complete detachment of the ligand from the metal only occurs by a slow thermal reaction. Thus, for our complex the following photochemical reactions are expected:[37]

$$\textit{trans}\text{-}Cr(en)_2F_2^+ \xrightarrow[H_3O^+]{h\nu} Cr(en)(enH)(H_2O)F_2^{2+} \tag{1}$$

$$\textit{trans}\text{-}Cr(en)_2F_2^+ \xrightarrow[H_2O]{h\nu} Cr(en)_2(H_2O)F^{2+} + F^- \tag{2}$$

The results obtained (Table I) show that both these photoreactions do occur and that reaction 1 is predominant at each one of the irradiation wavelengths.

The isomeric composition of the products of photoreactions 1 and 2 is difficult to establish for two reasons: (i) the products cannot be accumulated owing to the unavoidable presence of thermal and secondary photochemical reactions; (ii) the properties (e.g., absorption spectrum, ion exchange behavior, etc.) of the various isomeric species are often unknown. Point i is critical for reaction 2 which has a very low quantum yield, while point ii is particularly important for reaction 1 whose products may exist in four different isomeric forms, one with the two F^- ions in trans to one another and the three others with the F^- ions in a cis relative position. By means of ion-exchange chromatography Pyke and Linck[4] found that the main photoproduct (Φ = 0.46) of 520-nm irradiation was the same complex which is obtained in the thermal reaction,[32] i.e., the isomer with the two F^- ions trans to one another. They[4] also reported evidence for the formation of three unidentified minor products whose total quantum yield was ~0.15 and gave an upper limiting value of 0.08 for the quantum yield of reaction 2. Our results are in agreement with the formation of a $Cr(en)(enH)(H_2O)F_2^{2+}$ species as the main photoproduct, but, its quantum yield (0.20 at 530 nm) is much lower than that reported by Pyke and Linck.[4] Moreover, our spectroscopic measurements show that the spectral changes due to the photoreactions are noticeably different from those observed for the thermal reaction and cannot be absolutely interpreted by assuming the formation of *trans*-$Cr(en)(enH)(H_2O)F_2^{2+}$ in reaction 1. In this assumption, for example, the extinction coefficients of the product of reaction 2 should be 120 at 375 nm and 200 at 520 nm, which are by far higher than the reported[7] coefficients of the band maxima of *cis*- and *trans*-$Cr(en)_2(H_2O)F^{2+}$ in the same spectral regions. Therefore, we are forced to conclude that the product of photoreaction 1 exhibits an isomeric composition which is substantially different from that of the analogous thermal product. That is, in the photochemical reaction at least a noticeable fraction of the product must have the two F^- ions cis to one another. The importance of this conclusion lies in the fact that "in-plane" photolysis of *trans*-$Cr(en)_2X_2^+$ or *trans*-$Cr(en)_2XY^+$ complexes was so far considered to occur with retention of configuration,[11] in contrast with the complete stereochemical change which takes place on photosubstitution of the axial ligands.[17]

In our opinion, the disagreement between ours and Pyke and Linck's[4] results is likely to be due to the fact that under their experimental conditions (21 °C and chromatographic analysis of the irradiated solution) the thermal reaction was predominant over the photochemical reaction. Lack of complete correction for the thermal reaction (e.g., correction for the amount of the thermal products formed *during* the chromatographic analysis is not mentioned by Pyke and Linck[4]) can explain both the much higher quantum yield for reaction 1 and the similarity between the spectra of the thermal and photochemical products found by those authors.

Quantum Yields. The assignment of the absorption bands of our complex is known.[23-26] Accordingly, irradiation at 254 nm populates at about the same extent a charge transfer and the $^4A_{2g}(b^4T_{1g})$ ligand field state, while irradiation at 365 and 530 nm predominantly leads to the $^4A_{2g}(a^4T_{1g})$ and $^4E_g(^4T_{2g})$ excited states, respectively. The quantum yield for both photoreactions depends on the excitation wavelength (Table I). The quantum yield of F^- release shows a 50% increase in going from 530- to 365-nm irradiation. This suggests that the $^4A_{2g}(a^4T_{1g})$ excited state undergoes F^- release with a specific quantum yield, 0.01, the remaining 99% of the excited molecules presumably undergoing internal conversion to the lowest $^4E_g(^4T_{2g})$ state which releases F^- ions with quantum yield 0.02. This, however, does not mean that the $^4E_g(^4T_{2g})$ state is "more reactive" than the $^4A_{2g}(a^4T_{1g})$ state, which would be in contrast with that expected from a molecular orbital approach.[20,21,23] In fact as we have already pointed out,[10] the quantum yields are composite quantities whose values depend not only on the rate constant with which the excited state undergoes the observed reaction but also on the excited-state lifetime. In our complex, the $^4A_{2g}(a^4T_{1g})$ excited state has likely a much shorter lifetime than $^4Eg(^4T_{2g})$, which is the lowest quartet excited state.

The lower quantum yield for ethylenediamine detachment on 254-nm irradiation is presumably associated in some obscure way to the excitation of the CT band, as it happens for other complexes of this type.[8,10]

It is interesting to note that in-plane labilization (ethylenediamine detachment) is always larger than axial labilization (F^- release), contrary to what happens for other *trans*-Cr(en)$_2$X$_2^+$ [5,11,17] and *trans*-Cr(en)$_2$XY$^+$ [6,7,10] complexes. Considering the irradiation of the lowest quartet ligand field band (^4E_g($^4T_{2g}$) excited state), the quantum yield of the axial labilization decreases in the series Br > Cl > NCS > F, whereas the quantum yield of the in-plane labilization increases along the same series.[39] In particular, in going from *trans*-Cr(en)$_2$Br$_2^+$ [17] to *trans*-Cr(en)$_2$F$_2^+$ the Φ_X/Φ_{en} ratio varies more than three orders of magnitude. These results may be discussed in terms of σ-bonding effects,[4,7,11,15] π-bonding effects,[18–20] and relative populations of the d_{z^2} and $d_{x^2-y^2}$ orbitals in the lowest quartet excited state.[20,21,23] We think, however, that such discussions are of limited value because the quantum yields (i) are a function of the excited-state lifetime (which may well be different for the same excited state of different, even if similar, complexes) and (ii) for a number of Cr(III) complexes consist of a quenchable and unquenchable component,[40–46] which originate from different excited states and might depend on the nature of the axial ligand. Thus, the quantum yields cannot be taken as a relative measure of the "tendency" (i.e., the rate constant) of the same excited state of different complexes to undergo a certain reaction.

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Registry No. *trans*-Cr(en)$_2$F$_2^+$, 24407-74-7; *trans*-Cr(en)(enH)(H$_2$O)F$_2^{2+}$, 34398-37-3; *cis*-Cr(en)(enH)(H$_2$O)F$_2^{2+}$, 64091-08-3; Cr(en)$_2$(H$_2$O)F^{2+}, 64091-07-2.

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