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Ligand Migration during Photoaquation of Bis(am(m)ine)(1,4,8,11-tetraazacyclotetradecane)chromium(III) Complexes

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The *cis*-(cyclam)(A-A)chromium(III) complexes (cyclam = 1,4,8,11-tetraazacyclotetradecane with A-A equal to ethylenediamine (en) and diammine were prepared and their photochemistry and doublet properties studied in acidic aqueous solution. The en complex is photoactive with a quantum yield at 436 nm of 0.091 ± 0.003, that is, just over half that for the diammine at 0.160 ± 0.009. In contrast, the room-temperature lifetimes of the doublet states are 8.4 ± 0.2 and 1.7 ± 0.1 μs, respectively, and their temperature dependencies correspond to activation energies for doublet depopulation of 41 and 37 kJ mol^{-1}, respectively. Chromatographic product analysis shows that the diammine complex photolyses to produce the *cis*-aquo ammine product. Similarly, the en complex gives only a single chromatographic product peak (under all conditions studied), suggesting the two complexes react by the same mechanism. By comparison of the photobehavior to that of other similar systems, it is argued that, after an initial Cr–N bond breaking, the entire ethylenediamine ligand migrates in the photochemical reaction. The photophysical results show that the excited-state reaction is slower for the en complex than for the diammine.

Introduction

The extensive research carried out on Cr(III) photoaquation mechanisms has established the patterns of ligand loss and provided unambiguous evidence that the photochemical pathway for substitution in strong field am(m)ine and acidoam(m)ine systems occurs with stereochemical change.[1-5] In one investigation, stereochemical change was shown also to occur during photoaquation in a room-temperature crystal.[6] Recently, there have been some studies[4,5,7-11] of the effect of stereochemical factors on the yields and pathways of photoaquation. As one example, it is known that several macrocyclic ligand complexes are photoinert, consistent with their inability to undergo irreversible ligand dissociation. However, the results reported show that the sar and diamsar ligands[7] have very different effects on the room-temperature doublet-state lifetime than does sepulchrate.[8] It seems that structural factors such as the trigonal twist angle of the ligand, which may influence doublet-state physical properties,[12] and steric factors influencing photoreaction rates, such as in the other work cited, may both have a role to play in determining emission lifetimes.

One interesting question that has not been much studied to date concerns the kinds of ligand rearrangement and migration possible during a photochemical reaction involving a bi- or multidentate ligand. In this work we use the complex $Cr(cyclam)en^{3+}$ to explore whether a bidentate ligand can migrate as a whole if necessary to photoaquation. We report here our findings.

Experimental Section

Materials. The complexes *cis*- and *trans*-$Cr(cyclam)(NH_3)_2^{3+}$ and $Cr(cyclam)en^{3+}$ were prepared via reaction of ammonia or diaminoethane with the dinitrato intermediates, as described in ref 5 and references therein, and converted to the perchlorates by reprecipitation with concentrated perchloric acid.

Anal. Found (calcd) for $[Cr(cyclam)(NH_3)_2](ClO_4)_2NO_3$: C, 22.29 (21.95); H, 5.39 (5.52); N, 17.75 (17.91); Cl, 13.09 (12.96). Found (calcd) for $[Cr(cyclam)(en)](ClO_4)_3$: C, 24.76 (23.60); H, 5.21 (5.28); N, 15.23 (13.76); Cl, 14.05 (17.41).

Their UV-vis spectral data have been included in Table I. The discrepancies in the analysis for the en complex and the small differences from the published molar absorptivities are in a direction consistent with the observation that the complexes tend to recrystallize as mixed nitrate/diperchlorate or nitrate/bis(hexafluorophosphate) salts.[5] The above data for the en complex are consistent with a 60/40 mixture of triperchlorate and diperchlorate nitrate. The UV-vis band maxima in Table I are in agreement with the published values, and an IR band at 1380 cm^{-1} in both complexes, less intense in the en case, confirmed the presence of the nitrate ion.

The cation purity was established as better than 98% by chromatographic analysis;[13] this would not of course recognize nonelutable species.

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Table I. Spectral, Photophysical, and Photochemical Results[a]

compd	UV–vis absorption: λ, nm	UV–vis absorption: ϵ, M^{-1} cm^{-1}	photoaquation: ϕ(18 °C)[b]	emission: τ(22 °C), μs	emission: $E_{act}(\tau)$, kJ mol^{-1} [c]
cis-[Cr(cyclam)$(NH_3)_2$]$(ClO_4)_2NO_3$	356 (366)	84 (80)	0.160 ± 0.009	1.7	−37.1 ± 0.4
	470 (468)	122 (115)	(0.2)	(1.7, 20 °C)	(−43.1 ± 0.8)
[Cr(cyclam(en)]$(ClO_4)_3$	357 (355)	102 (102)	0.091 ± 0.003	8.4	−41.2 ± 0.5
	467 (465)	142 (137)			

[a] Values in parentheses from ref 5. [b] Mean and σ of four independent measurements. [c] 50% v/v methanol/water solvent. For the diammine, the Arrhenius plot showed curvature in the lower temperature range (−25 to −15 °C) so the slope reported is for the fairly linear range −10 to +20 °C. The en data were linear and over the range 10–50 °C. σ's are given, but for diammine, values in the range 37–39 kJ mol^{-1} were obtained for different data subsets, showing the real uncertainty is larger than σ.

Since the anion purity was not important to the remainder of the project, we did not purify the complexes further, except for a sample of the en complex for which we will report the crystal structure elsewhere.

trans-[Cr(cyclam)$(NH_3)_2$]$(ClO_4)_3$ was also prepared from pure *trans*-dinitrato complex from a second route. *trans*-Dicyano complex was made in high yield[15] by direct reaction of the dichloro isomer mix from the first step of the synthesis with a 10-fold excess of sodium cyanide in dmso at 62 °C for 70 min. On heating of the latter complex to dryness with concentrated nitric acid, the *trans*-dinitrato complex is again obtained. The *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ complex was used only to determine its chromatographic retention time and as a precursor to the *trans*-aquo ammine complex similarly used as a chromatographic marker. Its UV–vis spectral band maxima (molar absorbance) values were 337 (45), 420 (33), and 445 nm (30) in reasonable agreement with the literature values[5] of 334 (50), 420 (36), and 445 nm (32).

The analogous aquo ammine complexes were prepared by hydroxide-catalyzed aquation of the diammines. The reaction was followed chromatographically and by UV–vis spectral changes. The monaquo species was formed completely in 30 s for the *trans* complex and in 4 min for the *cis* complex. The monoammines were isolated in rather impure form but were adequate for the exploration of their chromatographic behavior.

Several attempted routes to prepare the analogous 1,3-propanediamine complex failed. This diamine reacted with the dinitrato precursor to give a purple-red product, which could not be worked up to give useful products. Attempts to use a similar reaction starting with the bis(triflate), the dichloro, and the dibromo complexes were unsuccessful in a similar way.

Chromatographic Analysis. A Varian System 5000 liquid chromatograph with a 30-cm octadecylsilane RP column was employed, using an eluent consisting of 25 mM tetraethylammonium ion plus 25 mM butanesulfonate in 10% methanol/water at pH values of 5.0 and 6.5. This gave good separations of starting materials and products for all three complexes studied.

Identification and Determination of the Photoproducts. This was carried out by HPLC on solutions of known compounds and photolyzed and thermalyzed solutions of known compounds. This necessitated reliance on chromatographic retention times; these were found to be reproducible within a few percent, sufficient to be sure about peak sequences and identities, as shown later. Unfortunately, the quantities of material in these peaks are too small (about 50 nmol) for collection and analysis to be feasible at present.

Quantum Yield Determinations. Radiation at 436 nm (Balzers interference filter from a 1000-W mercury lamp) was passed through a 10-cm water filter to remove the infrared components. Efficiently stirred solutions in 1-cm rectangular cuvettes were thermostated at 18 °C during irradiation and the pH monitored continuously by an Ingold LOT combination electrode interfaced to a PDP-11 computer. By means of additions of standard acid from a 200-μL stepping motor buret, the pH of the solution was maintained constant with periodic recording of acid added. This permitted measurements of the rates of the thermal and photochemical reactions

$$Cr(cyclam)(en) + H_3O^+ \rightarrow Cr(cyclam)(enH)(H_2O)^{4+}$$

$$Cr(cyclam)(NH_3)_2^{3+} + H_3O^+ \rightarrow NH_4^+ + Cr(cyclam)(NH_3)(H_2O)^{3+}$$

both of which lead to proton uptake.

The pHstat method has advantages over the ΔpH method used previously, the most important being that the pH remains constant throughout the quantum yield determination and can be set at a value that precludes errors or uncertainties arising from partial dissociation of photoproducts to the conjugate base form. In the conventional method this is an unknown contribution that varies with the final pH and can lead to errors in the method unless calibrated with tedious back-titrations to the starting pH.

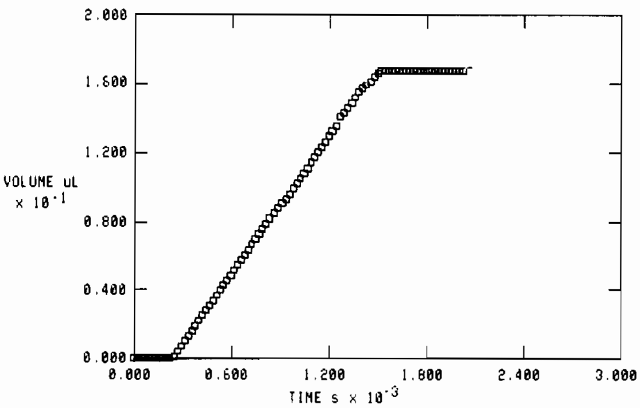

Figure 1. Measurement of proton uptake by the pHstat method, plotting volume of 0.1492 M $HClO_4$ added versus time in the thermal, photolysis, and postphotolysis thermal regimes. A 4.0 × 10^{-3} M solution of *cis*-Cr(cyclam)$(NH_3)_2^{3+}$ in 1.5 × 10^{-3} M $HClO_4$/0.1 M $KClO_4$ was irradiated at 436 nm from 250 to 1400 s. Note the linearity of the acid uptake during photolysis and the absence of any thermal proton uptake either by reactant or photoproducts.

The light intensity from the lamp was computer-monitored continuously by using the analogue output from an Alphametrics 1200 photometer and silicon photodetector. This signal was periodically calibrated in terms of the ferrioxalate actinometer so that the integrated computer reading during photolysis could be converted to integrated intensity falling on the front window of the photolysis cell. Irradiation was started and ended under computer control on instructions from the experimenter; this had the advantage that the start and end times were recorded by the computer with precision of a hundredth of a second, eliminating any uncertainty in short photolysis times, for example, in actinometry.

Test experiments and the results presented here show that the method has a reproducibility of better than 3%. A typical run is shown in Figure 1.

Results

The complexes are extremely inert thermally, and no thermal reactions of starting materials or products occurred during photolysis or subsequent analysis of the irradiated solutions. This can be seen in Figure 1. Table I shows our quantum yield, doublet lifetime, and activation energy measurements for the two compounds. They have quantum yields for proton uptake that are not too different, with the en compound the lower; the activation energies for the phosphorescence decay lifetimes are fairly similar, but the room temperature lifetime of the en compound is four times that of the diammine.

The chromatographic results for the *cis*-diammine complex are shown in Figure 2. There is a major photoproduct, marked P, together with a smaller peak, M, that elutes in a position that does not correspond to any of the expected products; we were unable to identify this material, but it amounts to only about 8% of the product. For the final chromatogram shown, the extent of decomposition of the starting material is about 20%, so M could be a secondary photolysis product. The main product has the same retention time as *cis*-Cr(cyclam)$(NH_3)(H_2O)^{3+}$ within the normal

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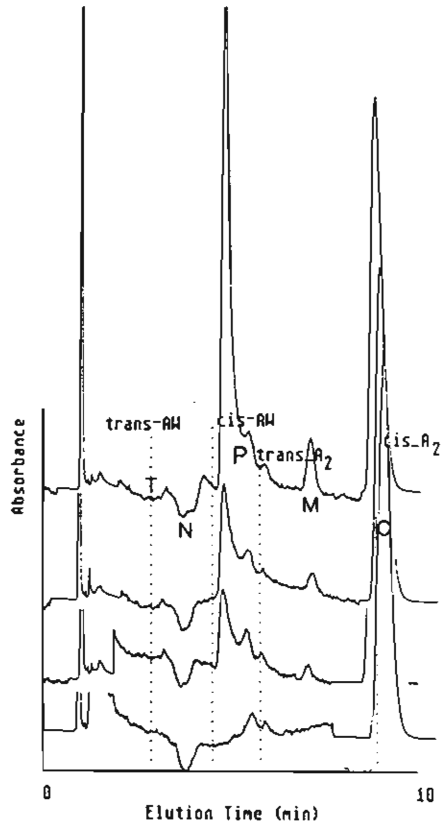

Figure 2. Chromatography of *cis*-Cr(cyclam)(NH$_3$)$_2$$^{3+}$ photoproducts with irradiation at 436 nm. The curves are displaced up for clarity in the sequence of irradiation times, 0, 453, 681, and 1500 s. Retention times for authentic samples are shown as the dotted lines. For further detail on peak identities, see Results.

variation we observe. Note the absence of any real chromatographic peak at position T, which is shown by the dotted calibration line to be the position for elution of *trans*-aquo ammine complex. The retention times are obviously variable, and there is possibly a small peak present at a slightly later time, superimposed on the leading edge of the negative peak, N, which is always present. (This arises from the absorption of the interacting sulfonate ion into the electrical double layer when the sample is loaded and retained.) If we assume this to be a genuine peak for the trans product, quantitative treatment for the maximum conversion chromatogram shown sets an upper limit of 4% on this product, assuming equal product molar absorptivities at the analysis wavelength of 240 nm.

For the en complex, only one photoproduct peak was found chromatographically, rather broad and eluting after the starting material as expected for a 4+ ion. Recognizing there is a possibility that this peak contains more than one component, the chromatography was repeated at a higher pH of 6.5, with still only one product peak. In the analogous Cr(tn)$_3$$^{3+}$ system,[11] the cis and trans 4+ photoproducts changed elution sequence completely over the pH range 3–5. This was because the cis isomer with its larger dipole moment elutes faster at low pH when both are 3+ ions, but with increase in pH, the more acidic trans isomer converts sooner than the cis isomer into the 2+ conjugate base, and the elution sequence reverses. The lack of change in the chromatogram for a change of 1.5 units in pH seen in this work gives some assurance against chance coincidence of retention times for two isomeric products. We conclude that it is unlikely that any significant trans product is formed in either photoaquation. No peak was seen in the position expected for Cr(cyclam)(H$_2$O)$_2$$^{3+}$.

Discussion

The nature of Cr(III) photostereochemistry is central to interpretation of our results. *trans*-diacido tetrakis(am(m)ine) complexes and acido pentakis(am(m)ines) photoaquate to *cis*-acido aquo products with isomeric purities approaching 100%,[1-3,16-18] demonstrating that photosubstitution occurs with stereochemical change. Particularly important is that *trans*-Cr(cyclam)Cl$_2$$^+$ has a photoaquation yield of 3 × 10^{-4} giving *trans*-aquo chloro product.[4] Note also the recently reported[5] photoinertness of *trans*-Cr(cyclam)(NH$_3$)$_2$$^{3+}$ and the photoactivity[4] of *trans*-Cr(2,3,2-tetraazaundecane)Cl$_2$$^+$, where one in-plane edge of the ligand permits the motion required to give cis product.

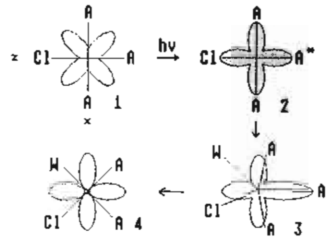

Figure 3. Vanquickenborne and Ceulemans theory of d^3 photostereochemistry, showing a pictorial representation for Cr(NH$_3$)$_5$Cl^{2+}. Excitation of ground-state 1 in the *xz* component of ^{4}E corresponds to a 45° rotation of charge (shown in the plane with axial ligands omitted), giving excited-state 2, in which all four in-plane ligands have been labilized. The weakest bond involves the ammonia ligand (A*) trans to chloride.[20] As entering water attacks a trans edge, the system evolves through a distorted pentagonal-bipyramidal transition-state 3 to the stereochemically changed product in its electronic ground-state 4. The process is "downhill" in energy throughout.[21] The ligand motions occur in the plane of excitation, constrained by the electron density of the occupied d$_{xy}$ and d$_{yz}$ orbitals.

Cumulatively, this evidence supports stereochemical change as a requirement of efficient Cr(III) photoaquation, with other routes having greatly reduced yields. Note that the process being described is not isomerization and also that stereochemical change (kinetic) may or may not result in different geometries for reactant and product.

Some results[19] reported to depart from this pattern involve complexes with weaker field ligands. The pattern described may therefore not be universal but certainly applies to the strong field ligand complexes used here.

It is also significant that the angular overlap model developed[3,20,21] by Vanquickenborne and Ceulemans (VC) predicts stereochemical change in d^3 systems because of symmetry restrictions on reaction of the quartet excited states, and evidence exists in support of this model over a simple edge displacement mechanism.[22] The VC model assumed a dissociative pathway, but we prefer an equivalent associative pathway, which is more in accord with observed apparent volumes of activation.[23] Figure 3 and its caption illustrate the process pictorially, and the predictions mesh well with the experimental evidence cited above.

For hexaammine complexes, only about 25% of the reaction occurs promptly via the quartet state either before or after some equilibration. The remainder is quenchable and occurs via the doublet state with its microsecond lifetime. However, a number of studies[24-26] have shown that the product yield distributions and stereochemistries are the same for the two pathways. The behaviour of the *cis*-cyclam diammine complex is complicated by

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(26) Recent work has shown[11] wavelength dependence of the cis/trans product ratio in Cr(tn)$_3$$^{3+}$ that suggests the quartet reaction is competitive with vibrational decay, complicating this simple model but not denying it.

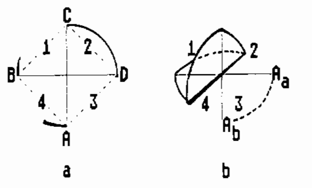

Figure 4. Photoreaction pathways for (a) $Cr(en)_3^{3+}$ (axial ligands omitted) and (b) *cis*-$Cr(cyclam)(A\text{-}A)^{3+}$ for A-A = $(NH_3)_2$ and en. See text for discussion.

the formation of a seven-coordinate intermediate of long lifetime,[27] but the photochemistry is otherwise normal.

The simplest, but much-debated[27-41] explanation of these similarities, and one consistent with doublet decay being a strongly coupled process,[42] is that doublet reaction occurs via reverse intersystem crossing and quartet reaction. The "quartet state" is rapidly reactive in room-temperature solutions and has not, so far, been an observable species. Its solution lifetime could be too short[43] for it to exist in a well-defined electronic state with a definite energy and configuration, vibrational, and rotational energy levels and, therefore, with the well-defined spectroscopy it shows in low-temperature solid matrices.[44]

It has been proposed[42,45] that reaction via the doublet occurs by "crossing to a ground-state intermediate". But in the VC model, the quartet excited state evolves smoothly from an excited-state to a ground-state product. There is no point on the continuum at which electronic "deactivation" occurs. For most systems studied to date, although not all,[22,46] the calculations made for the five-coordinate version of the transition state show it to be in the ground electronic state. The "ground-state intermediate" concept seems to be a partial restatement of the VC model but without its predictive and photostereochemical content.

Viewed in the above context, we think it valid to apply the VC model to both components of the photochemistry, the important feature being that the quartet and doublet pathways somehow arrive at some common point, such as the seven-coordinate transition state of Figure 3.

Genesis of the Problem. In the analysis of photostereochemical results such as obtained by Cimolino and Linck[24] for Λ-$[Cr(en)_3]^{3+}$ and our results[11] for $Cr(tn)_x(NH_3)_{6-2x}{}^{3+}$, $x = 1-3$, an uncertainty arises that is illustrated for $Cr(en)_3^{3+}$ in Figure 4a.

In any of the three excitation planes, there are two types of en ligand; one has both amine groups (C and D) in plane, while the other two have one amine end (A and B) on the orthogonal axis. For A and B, one trans edge (edge 2) is blocked by the in-plane en ligand but the other (edge 1 or 3, respectively) allows photoreaction. For example, trans attack of A at edge 1 and migration of the amine group B by rotation about its out of plane attachment leads easily to the cis product. Our study[47] of mixed ammine/en complexes, where en was found to be a significantly better leaving group than ammonia, shows this to be a facile process. Similarly, though tn was found[11] to be a much poorer leaving group than ammonia, the photostereochemistry observed was consistent with the above motions.

For the in-plane en ligand, amine D can be trans attacked at edge 4, giving rise to the trans product found experimentally[24] in 65% yield. Now the problem arises. Is it possible to displace D by trans attack at edge 1? It requires end D of en to detach and the entire en ligand to migrate so the amine group originally at C moves to site D. Should this motion be considered possible? The observation[5] that the *cis*-cyclam diammine complex was photoactive suggested a study of the en analogue would illuminate this question.

Application to *cis*-Cyclam Bis(am(m)ine) Complexes. By analogy, the *cis*-diammine isomer, Figure 4b, would photoaquate by trans attack of water at edges 2 and 4 for substitution of amine ligand nitrogens A_b and A_a, respectively. That only cis isomer is formed proves that attack (not necessarily trans) occurs only at these sites, since all other possible edges are blocked or would give trans product. Our observation of *cis*-aquo ammine photoproduct is silent on the question of stereochemical change, but also there is nothing about the photoreactions that suggests it does not occur and a model shows it to be sterically feasible.

In the analogous en complex, no evidence has been found for formation of the trans product, only the cis product, so there seems to be a good parallel between the behaviors of the two complexes. The quantum yield is lower than for the ammine analogue but only by a factor of 2. It is reasonable to see this as an reaction analogous to that of the diammine. Remember that in the trans-cyclam species, the stereoretentive pathway is negligible. We conclude that the photoreaction in the en complex occurs by migration of the whole en ligand.

Unfortunately, despite some effort, it was not possible to prepare the corresponding tn complex and explore the effect of ring size on this process.

Photophysics. Although the quantum yields of photoreaction for the two cis complexes differ by less than a factor of 2, at room temperature the doublet lifetime for the en complex is the greater by a factor of 4. The 10% difference in activation energy observed for the process depopulating the doublet state is in the right direction to lead to such a lifetime difference. The reasonable linearity of the Arrhenius plots in this temperature regime shows that a single process dominates doublet decay. Calculation of the *A* factors corresponding to the observed lifetimes and activation energies gives 2.7×10^{12} and 3.0×10^{12} s^{-1} for diammine and en, respectively. The close similarity of these *A* values suggests that the longer lifetime of the doublet state of the en complex reflects its higher activation energy for depopulation, which we believe corresponds to the energy gap for reverse intersystem crossing.

These differing lifetimes for the doublet states of the two complexes imply quite different rates of photoreaction. Waltz et al.[27] could not be definitive about the extent to which the diammine compound reacted via the doublet state but gave an estimate of $\geq 90\%$.

Assuming a similarly large fraction of reaction via the doublet state for the en analogue, the apparent rate constant for ammonia loss calculated[11] as if all the reaction were direct from the doublet is roughly 10 times ($0.16 \times 8.4/0.091 \times 1.7$) that of en. This is very different from the situation found for mixed en/NH_3 complexes, where en was the better leaving group. It suggests

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that the photoreaction is strongly inhibited in the en complex and that nonradiative decay to the ground state is a more effective competitor.

Part of this rate inhibition in the en complex could arise prior to reverse intersystem crossing because the larger energy barrier for the activated route allows more competitive doublet nonradiative decay. However, the extent to which such decay can be accommodated is restricted by the observed linearity of the Arrhenius plot. At the transition-state level, other possible reasons are easy to imagine. If the transition state is seven-coordinate, then it may be more sterically crowded and have higher strain energy for the en complex than for the diammine. Alternatively, it may be that the required migration of the whole en ligand is a difficult and slow process so that deactivation and/or recoordination have a greater opportunity to compete.

Finally, the diammine complex reacts[27] via a seven-coordinate species of microsecond lifetime. If the en complex behaves similarly, then its intermediate might be more likely to revert to starting material because of the bidentate nature of the leaving ligand.

Concluding Remarks. We have presented evidence that after photochemical Cr–N bond breaking has occurred, it is possible for the reacting bidentate ligand to migrate from one coordination site to another in an edge displacement reaction. Since our proof relies on the assumption of stereochemical change, in the future additional evidence will be sought. It is fairly straightforward to design experiments with appropriate stereochemical sign-posting to prove group migration incontrovertably. Unfortunately, it is difficult to identify systems in which the starting compound can be prepared and unambiguously characterized and its photochemistry explored with product identification including stereochemistry. The work has shown, however, that complex ligand motions are likely and that further study of such phenomena is tractable and worth pursuing.

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Electron Transfer in Mixed-Valence Biferrocenium Salts: Effect of Zero-Point Energy Difference and Pronounced Anion Dependence

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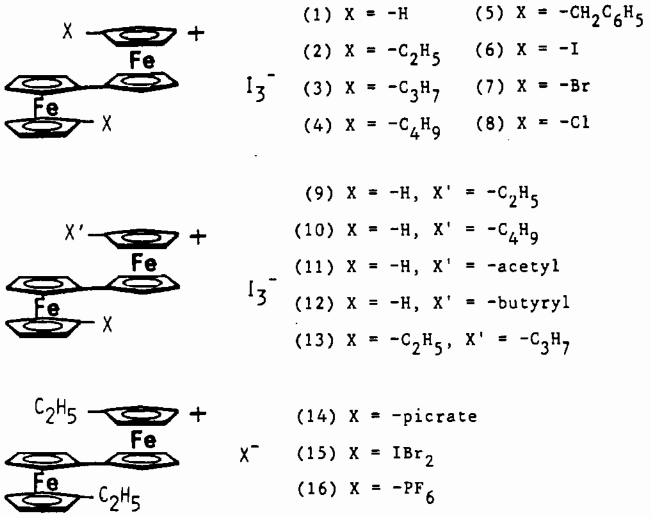
The effects of zero-point energy and counterion on the rate of intramolecular electron transfer in mixed-valence biferrocenium salts are investigated. All asymmetrically substituted biferrocenium triiodide salts, where the substituent is either 1′-ethyl (**9**), 1′-butyl (**10**), 1′-acetyl (**11**), 1′-butyryl (**12**), or 1′-ethyl 6′-propyl (**13**), are found to be localized on the Mössbauer, EPR, and IR time scales. In 300 K Mössbauer spectra they each show two doublets, one for Fe^{II} metallocene and the other for Fe^{III} metallocene (electron-transfer rates less than $\sim 10^7$ s^{-1}). The cation in each of compounds **9–13** is not symmetric; that is, the two irons are not in equivalent environments. This asymmetry induces a nonzero zero-point energy barrier for intramolecular electron transfer. The effects on the rate of electron transfer of replacing I_3^- by picrate (**14**), IBr_2^- (**15**), and PF_6^- (**16**) in **2** are also examined. Replacing I_3^- by picrate and IBr_2^- leads to a decrease in the rate of electron transfer. The Mössbauer spectrum taken at 300 K for **14** consists of two doublets. In other words, the electron-transfer rate of **14** is less than $\sim 10^7$ s^{-1}. In the case of **15**, the variable-temperature (100–275 K) Mössbauer spectra exhibit a localized electronic structure. The PF_6^- salt is converted from valence trapped at low temperatures to valence detrapped above 280 K. The difference in electron-transfer rates can be explained by the magnitude of the energy barrier of charge oscillation in anions and cation–anion interactions.

Introduction

Recently, there has been considerable progress made in understanding what factors control the rate of intramolecular electron transfer in the solid state for mixed-valence compounds.[1] In the case of binuclear mixed-valence biferrocenium cations,[2-13] it has been found that the nature of the solid-state environment about a mixed-valence cation can have a dramatic impact on the rate of intramolecular electron transfer. When there is an onset of

Chart I



I_3^-
(1) X = -H
(2) X = $-C_2H_5$
(3) X = $-C_3H_7$
(4) X = $-C_4H_9$
(5) X = $-CH_2C_6H_5$
(6) X = -I
(7) X = -Br
(8) X = -Cl

I_3^-
(9) X = -H, X' = $-C_2H_5$
(10) X = -H, X' = $-C_4H_9$
(11) X = -H, X' = -acetyl
(12) X = -H, X' = -butyryl
(13) X = $-C_2H_5$, X' = $-C_3H_7$

X^-
(14) X = -picrate
(15) X = IBr_2
(16) X = $-PF_6$

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